TOPICAL REVIEW

Spectroscopy and dynamics in helium nanodroplets

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Abstract

This article provides a review of recent work in the field of helium nanodroplet spectroscopy with an emphasis on the dynamical aspects of the interactions between molecules in helium as well as their interaction with this unique quantum solvent. Emphasis is placed on experimental methods and studies introducing recent new approaches, in particular including time-resolved techniques. Corresponding theoretical results on the energetics and dynamics of helium droplets are also discussed.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Understanding the properties of matter starting from the interplay of atoms and molecules has been achieved to a great deal by the study of small or model systems containing only a few atoms. A detailed view on geometric as well as electronic properties has been brought forward largely through the application of spectroscopic tools. These tools are continuously being improved, in particular with the aid of the availability of sophisticated new laser systems, setting new milestones in terms of repetition rate, power and the time and frequency structure of ultrashort pulses. On the other hand, the path from small model systems to complex functional structures is arduous to climb. In recent years, it has became clear that one approach towards the understanding of complex structures of atoms and molecules is to start with well-defined structures and well-defined distributions of populated states. This calls for spectroscopic studies at very low temperatures and now a new field emerged dealing with cold molecules or ultra-cold chemistry. In this regard, spectroscopic experiments involving helium droplet beams (HElium NanoDroplet Isolation (HENDI)) proved, since their introduction in 1992 \cite{1}, to be a versatile method that provides temperatures below 1 K and offers the possibility of studying well-defined and complex structures of atoms and molecules. Moreover, the quantum nature and in particular the superfluid properties of the droplets allow one to investigate these quantum properties in a size-limited aggregate on the nanometre scale. Today the field of helium
droplets is well established and several review articles have appeared during the last decade highlighting a variety of experimental as well as theoretical aspects [2–14]. In this review, we will not attempt a comprehensive overview of the entire field because many experimental as well as theoretical approaches have already been reviewed, summarized and pointed out. Besides, the field has grown to the point that a truly comprehensive review would now need to be a monograph instead of a review article. We focus particularly on dynamical aspects of the droplets and recent advances triggered, e.g., by up-to-date femtosecond techniques on the experimental side and on the theoretical side by significant progress in the understanding of the dynamics and energetic properties. We emphasize material that was not available when the several reviews were written that appeared in the special issue of the Journal of Chemical Physics [5–9] in late 2001.

The paper is organized as follows: we start with experimental aspects in the first part. In particular, we summarize the conditions and parameters relevant for the formation and doping of $^4$He as well as $^3$He droplet beams having certain size distribution. We expect this information to be useful for a broad readership to get a feeling for apparatus designs as well as feasibility considerations. In the next part, the properties of helium droplets are reviewed, in particular focusing on energy, momenta and excitation considerations which mainly determine the dynamics of, e.g., cooling and energy dissipation processes. The last part reviews recent work in the field, particularly addressing dynamical processes.

Much of the present knowledge about helium nanodroplets results from the work of Roger Miller and his students at University of North Carolina, Chapel Hill. We deeply regret the untimely passing away of Roger Miller. Without his ideas and scientific activities, the field of helium droplets would be far less advanced than it presently is. He was a colleague of unusual warmth, openness, and enthusiasm, and arguably the most accomplished spectroscopist of his generation. In order to admire his work we dedicate this review to him.

2. Experimental aspects

2.1. Production of helium nanodroplets and source design

The formation of helium droplets in the size range starting from a few helium atoms up to aggregates having centimetres in diameter has been achieved by a variety of techniques. This review focuses on nanodroplets in the size range of a couple of hundreds to about a million helium atoms which are produced as a beam in a supersonic expansion. In the following, other approaches are shortly summarized.

Macroscopic drops having diameters from 1 $\mu$m up to 2 cm have been formed from capillaries or as ‘mist’ from the boiling liquid. These drops were levitated in magnetic [15] or laser dipolar [16] traps. Because of the much smaller surface to volume ratio compared to nanodroplets and thus limited rate of evaporative cooling, these large drops have temperatures in the Kelvin range. Kim and co-workers [17, 18] generated fog of superfluid helium by placing an ultrasonic transducer beneath the surface of the helium liquid, generating drops of the order of 100 $\mu$m in size. However, trapped large drops have not yet been utilized for the isolation of molecules and spectroscopic studies. Ghazarian and co-workers formed droplets in a pulsed helium expansion operated in the vapour above liquid helium [19]. Pick-up of neutral and charged copper atoms as well as electrons was achieved from a laser plasma generated on a rotating disc at cryogenic temperatures. In these experiments, the droplets are most likely not formed in the supersonic expansion; the authors assign postexpansion condensation in the chamber filled with helium at pressures of the order of 10 mbar to be responsible for the agglomeration of atoms to form droplets. Sizes are not given but likely to be larger compared
Figure 1. Schematic view of a helium droplet machine used for spectroscopic studies. Depicted are the different vacuum chambers for formation, doping and detection (PI: photo-ionization detection, LIF: laser-induced fluorescence, BD: beam depletion by means of Langmuir–Taylor surface ionization [23]) of the droplet beam. Typical distances and required pumping speeds are included.

to the nanodroplets discussed in this review. Charged droplets having sizes in the micrometre range have also been generated by electro-spray methods [20]. Furthermore, the possibility of extraction of charged droplets from a liquid surface was discovered many years ago [21]. Grisenti and Toennies have produced a jet of micron size droplets by break up of a superfluid liquid jet expanding into vacuum [22].

So far, all the experiments on the use of helium nanodroplets to spectroscopically study attached species at milli-Kelvin temperatures utilize supersonic expansion to form a droplet beam freely travelling under high or ultra high vacuum conditions. One has to establish nozzle temperatures $T_0$ below 40 K and stagnation pressures $P_0$ in the range of a few to 10 MPa (100 bar) for the helium to condense to clusters or droplets. Mean droplet sizes $\bar{N}$ of about 5000 He atoms per droplet, which is the standard size for spectroscopic measurements, are formed under conditions of $P_0 = 5$ MPa and $T_0 = 20$ K, when using a nozzle of 5 $\mu$m in diameter (cf figure 2). With reasonably achievable pumping speeds in the source vacuum chamber ($<10000\ \text{l s}^{-1}$), the nozzle pinhole openings have to be 20 $\mu$m or less to get a decent flux of droplets. Aperture discs for electron microscopes, commercially available in high quality, are commonly used. A typical design of a helium droplet machine is depicted in figure 1. In most of the cases, the source chamber has an oil diffusion pump attached, providing high pumping speed. We use unbaffled pumps 40 cm in diameter specified with 8000 l s$^{-1}$. However, in some cases, we also utilized turbo pumps providing 2000–3000 l s$^{-1}$ with small nozzles. Droplet fluxes were still on the same order of magnitude when compared to a set-up having a large diffusion pump.

The process of helium droplet formation is well understood and discussed elsewhere [12, 27, 28]. Starting at nozzle conditions $P_0$, $T_0$, the droplets cool along an adiabatic line in the phase diagram (isentropic expansion). The mean droplet size is determined by $P_0$, $T_0$ and the nozzle diameter. Depending on whether one passes the critical point at the high- or the low-temperature side, the droplets are formed by aggregating from the gas (subcritical expansion) or by dispersing the liquid (supercritical expansion), respectively. These two
regimes of expansion parameters (nozzle conditions) are clearly identified in the resulting size distributions (cf figure 2): supercritical expansion forms large droplets ($\bar{N} \gtrsim 3 \times 10^4$), whereas a subcritical expansion is suited to generate droplets having $\bar{N} \lesssim 3 \times 10^4$. Pushing nozzle temperatures below $\approx 4$ K leads to very large droplets ($\bar{N} \approx 10^{10}$) with velocity as low as 15 m s$^{-1}$ [22]. In this case, Rayleigh instabilities break up the liquid helium flow. The beam of droplets so produced had a divergence of only $\approx 1$ mrad and thus had extremely high flux.

Absolute sizes have been measured by means of deflection in scattering experiments [24, 29, 30] or attachment of electrons and deflection in electric fields [31]. The reason why most of the spectroscopic experiments have been performed in the size range around 5000 helium atoms can be seen in figure 3 where the droplets flux in terms of typical fluorescence signal is plotted versus nozzle temperature. Decreasing the nozzle temperature increases the droplet size. The maximum signal corresponds to the just mentioned size of about 5000 helium atoms per droplet. Note the substantial lower achievable intensity in the supercritical regime which starts for $^4$He droplets below 12 K under the conditions used in figure 3.

As a rule of thumb, the divergency of the skimmed droplet beam is determined by the geometry of skimmer opening and distance. We measured almost Gaussian profiles. The beam is already several millimetres in diameter at a distance of 20 cm (e.g., skimmer: 0.4 mm in diameter, nozzle skimmer distance: 16 mm).

All the characteristics and properties mentioned so far refer to the formation of continuous droplet beams. A pulsed nozzle operated at high pressure and cryogenic temperatures was successful used by the group of Vilesov [32]. Compared to a continuous beam, orders of magnitudes higher droplet flux during the pulse have been achieved. Pulse lengths have been determined to 30–100 $\mu$s. Apparently, this technique ideally combines with other inherent pulsed detection techniques, in particular when short pulse lasers or time-of-flight techniques are involved. However, due to shot-to-shot fluctuations, these pulsed beam sources so far are less attractive if one is using a beam depletion detection method.
2.2. Doping of droplets

After having passed a skimmer, doping of the droplets is commonly achieved by inelastic collision within a scattering cell, termed as the pick-up technique [33, 34]. The collision energies (velocities) involved in this process are large compared to relevant energies of the superfluid (Landau critical velocity). Thus, frictionless transport is not an issue and dopants are efficiently trapped within the droplets. Pick-up cross sections have been determined to be of the order of 50–90% of the total integral geometrical cross section of the droplets [35]. In terms of dissipation of translational energy, this means that time scales for cooling have to be less than ≈100 ps. Of course, to trap a solute, its translational energy must fall below the solvation energy in that time, not reach equilibrium with the droplet. Typical lengths of the scattering cells are a few centimetres. The required partial pressure of molecules in the cell has to be of the order of about $10^{-2}$ Pa, providing a maximum of singly doped droplets of $N = 5000$. Depending on the material of interest, different techniques are suitable to provide the required vapour pressure inside the scattering cell. Gases or high vapour pressure liquids and solids samples are directly introduced through room temperature capillaries. Higher temperatures are often used to establish the required vapour pressure from bulk material inside a heated cell. Temperatures exceeding 1500 K have been used in order to evaporate metals [36]. Thermal radiation from the cell or heating is not a problem for the droplet beam because dipole active transitions in helium require 20 eV of photon energy. In the same way, high-temperature assemblies have been employed to dope radicals by means of pyrolysis [37]. In this case, an effusive continuous beam of radicals efficiently dopes the helium droplets.

One of us (FS) introduced laser evaporation as an alternative way to produce doped helium droplets [38]. The material is ablated from a rotating and translating rod by a pulsed YAG or excimer laser. The laser plasma is produced several millimetres below the beam near to

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This time corresponds to passing a droplet having 100 Å diameter at a velocity of 1000 m s$^{-1}$. 

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Figure 3. Formation of helium nanodroplets when cooling down the droplet source [26]. The graph compares absolute intensities of $^3$He (red) and $^4$He droplets (black), measured as a fluorescence absorption signal of sodium-doped droplets.
the nozzle, which means doping takes place within the helium source vacuum chamber. This location appears to be essential; apparently the high divergent flux of helium atoms emerging from the nozzle opening is necessary to thermalize the large translational energies of the atoms from the laser plasma. Metals like, e.g., vanadium, which are hard to evaporate thermally (required temperatures more than 1800 K), have been successfully loaded into the droplets in this way. The peak flux of singly doped droplets proved to be as high as doping from an oven. Since high-intensity nanosecond laser pulses are required in order to produce the plasma, only a fraction of the continuous droplet beam can be doped. Typically, the doped fraction arrives at the detector spanning about 100 µs. Since a significant part of the laser plasma consists of charged particles, ions can also be attached to helium droplets. For Mg, one finds that the probability of finding positively charged droplets steeply increases with increasing droplet size [38]. The time-of-flight mass distributions of these ion-doped droplets revealed surprisingly large charged droplet distributions which suggest that the presence of charged particles enhances the condensation of droplets. The absolute fluxes of doped droplets passing a typical detection area of 1 mm² at a distance of 50 cm are on the order of 10¹⁰ s⁻¹ corresponding to a number density of 10⁸ cm⁻³. Combination of laser evaporation with a pulsed helium nozzle should substantially further increase the flux.

At elevated pick-up pressure, the droplets successively collect more than a single atom or molecule. If one neglects the change in the droplet capture cross section with number of atoms or molecules previously trapped, the probability of picking up \( k \) species is expected to follow a Poisson distribution

\[
P_k = \frac{\bar{k}^k}{k!} e^{-\bar{k}}
\]

where \( k \) is the number of atoms or molecules picked up and \( \bar{k} \) is the mean number of \( k \), which is proportional to pick-up cell pressure. This pressure dependence has been verified for many molecules [35, 39, 40]. If we neglect the speed of the solutes relative to that of the droplet beam, we can approximate \( \bar{k} = \sigma \rho L \) where \( \rho \) is the number density of the solutes in the pick-up cell, \( L \) is the cell length and \( \sigma \) is the capture cross section (which is \( \approx 0.15 \times N^{2/3} \) nm² if one assumes the geometric cross section of the droplet). Because of the high mobility in the superfluid and the limited size of the confining droplet, the individually collected atoms or molecules aggregate to form complexes or clusters [35]. When assuming \( \sigma \) and \( L \) to be constant, these Poissonian curves can directly be measured by varying the pick-up pressure. Such measurements are a powerful tool to allow assignment of a spectroscopic feature to a certain oligomer sizes. We applied this procedure successfully for clusters up to \( k \approx 10 \). Even the onset of the intensity distribution allows an unambiguous assignment when recording intensities of a complete series of cluster sizes \( k \). The high-pressure tails in the distributions often significantly deviate from the Poisson functional form. In particular, the assumption of a constant pick-up cross section \( \sigma \) no longer holds at high pressure. This is presumed to be due to the dissipation of the collisional, internal and complexation energies leading to the evaporation of helium atoms from the droplet and a subsequent shrinkage. In the case of dopants which are only weakly bound to the droplets, desorption can drastically change the cluster size distributions as discussed, e.g., in [41]. Finally, the cross section \( \sigma \) scales as \( N^{2/3} \). This means the optimal pick-up density for doping a specific number of dopants depends on the chosen mean He droplet size. For different metals (alkali and alkaline earth metals) the spectroscopic measurements done in our group (fs) and the group of Meiwes-Broer in Rostock showed that one can agglomerate these atoms in a helium droplet without forming clusters unless they are laser excited. A conclusive mechanism for such a behaviour is still lacking.

Due to the statistical character of the pick-up process, experiments with a single cluster size cannot be performed without further mass selection. The ensemble of droplets is always
Figure 4. Measured magnesium cluster size distributions agglomerated in helium droplets. Data taken from [42]. Distributions are shown for two different densities of the Mg vapour in the pick-up cell, set by different cell temperatures of 520 K (red triangles) and 555 K (black circles), respectively. The fitted log-normal functions (solid lines) have maxima at cluster sizes of $k = 227 \pm 43$ and widths of 0.4 (0.46).

loaded with a distribution of sizes. Since for small clusters the abundance of individual cluster sizes can be extracted from the measured Poisson distributions, one can experimentally verify cluster distributions also for larger clusters. As an example, in figure 4 the size distribution of magnesium clusters is shown, using photo-ionization and time-of-flight mass separation. Hence, if spectroscopic features of different cluster sizes overlap, some ambiguity in the determination of individual spectra cannot be avoided unless alternative means of cluster size separation, such as dispersed emission, is used. Limitations in the number of picked-up constituents are determined by the energy needed to dissipate collisional and binding energies on one hand, and the energy ‘capacity’ of the droplet on the other hand. Evaporation of one helium atoms dissipates $5 \text{ cm}^{-1}$ of energy [43]. Droplets of size 5000 provide around 3 eV energy for cooling capacity. Large droplets have been employed to form metal clusters (e.g., Mg$_N$, Ag$_N$) containing several thousands of atoms [44–46].

A unique strength in the formation of complexes and clusters in helium nanodroplets lies in the ability to mix constituents arbitrarily and in a well-defined order just by placing pick-up assemblies in series along the droplet beam. In this way, specifically designed complexes containing a certain number of atoms and molecules can be synthesized and studied. Just to name a few, studies have been performed on Mg$_{1–3}$HCN [47, 48], Ne–, Kr–, Ar–HF [49], tetracene–Ar [50], HCN with H$_2$, HD and D$_2$ [51, 52], Ag$_N$ with Ne$_N$, Ar$_N$, Kr$_N$, Xe$_N$ ($N = 1–135$) [53], NaCs and LiCs [54], HF–(H$_2$)$_N$ [55], OCS–(H$_2$)$_N$ ($N = 1–17$) [56–58].

In general, the attached species are embedded inside the droplets forming compressed helium solvation shells as discussed below. So far, only alkali atoms [59, 60] and molecules [61, 62], and partly alkaline earth atoms [63–66] are located on the surface because of their bubble-like solvation structures. Ancilotto, Lerner and Cole have presented a simple and successful model for predicting the location of an atom or molecule bound to helium [67].

2.3. $^3\text{He}$ droplet beams

The study of $^3\text{He}$ droplets adds in many experiments interesting aspects because of the normal fluid property of these droplets compared to its superfluid $^4\text{He}$ counterpart. The lower chemical
potential results in higher rates of desorbing atoms; thus the terminal temperature of $^3$He nanodroplets in the evaporative cooling process amounts 150 mK [68] which is considerably lower compared to 380 mK for $^4$He droplets. Since small $^3$He droplets appear not to be stable for sizes $\lesssim 30$ [69–71], aggregation is hindered because droplets cannot be grown from small clusters adding one by one to an atom. In contrast, cluster formation requires highly multiple collisions. As shown in figure 3, at comparable nozzle size and stagnation pressure, the formation of $^3$He droplets sets in at lower nozzle temperatures than for $^4$He droplets. Note however, that the absolute intensities are quite comparable. Determined droplet sizes are included in figure 2 as open symbols. Surprisingly, there is some kind of plateau region around $\bar{N} \approx 5000$; smaller sizes are missing. In the regime of subcritical expansion, size distributions have been determined to be log normal for both $^4$He [29] and $^3$He droplets [24]. Mixed $^3$He–$^4$He droplets have also been formed by pick up of $^4$He by previously formed $^3$He droplets. In these, the helium largely phase separates with the $^4$He located near the centre of the droplets. The temperature of such mixed droplets is determined by the evaporative cooling of the outer $^3$He layer.

2.4. Spectroscopic tools

Most spectroscopic tools and detection techniques that have been developed or used in molecular beam studies are in principle applicable in combination with doped helium nanodroplet beams. A large variety have already been applied and are described in previous review articles [6, 12, 72]. The most commonly used have been laser-induced fluorescence (LIF) and depletion spectroscopy. LIF is applicable and provides the greatest sensitivity, when atoms or molecules with high quantum yield for optical emission are excited. When using continuous wave laser sources with sufficient intensity to approximately saturate the electronic transitions, photon detection rates as high as $10^8$ s$^{-1}$ have been observed in our experiments. When using pulsed lasers, the time averaged emission rate is reduced due to the small fraction of the beam that can be pumped, $\approx 10^{-4}$ when using a 10 Hz laser. Because of the need for very high stray light rejection (>10$^{12}$), careful baffling is needed and multiple passing of the excitation light over the molecular beam is not practical. One can use wavelength selection of the emission with a filter and (for pulsed excitation) time gating to reduce the scattered light, which almost always dominates the noise. Measurement of the wavelength dispersed LIF often provides insight into the dynamics following absorption. Time-correlated photon counting provides a way to study sub-nanosecond dynamics. Resonant multiphoton absorption and ionization has been used to great effect as discussed below. Time-resolved pump–probe spectroscopy using femtosecond pulsed lasers has proved to a powerful tool for rapid dynamics. While most studies have used laser excitation sources, two groups have exploited synchrotron radiation in the deep UV, which has allowed the study of the electronic excitation bands of the helium itself [73–76].

When exciting ro-vibrational excitations in the IR or for many electronic excitations as well, little or no fluorescence can be detected. In these cases, most of the energy optically deposited in the droplet is ultimately lost by the evaporation of helium atoms. As mentioned earlier, a loss of about one helium atom per 5 cm$^{-1}$ of deposited energy is expected based upon the helium evaporation energy [77], though no quantitative experimental measurement of this helium loss rate is yet available. The helium evaporation has been detected by the depletion of the on axis molecular beam, using either a bolometer [78] or a mass spectrometer [79]. The two detection methods were directly compared on the same machine in the lab of Roger Miller and the bolometer was found to provide greater sensitivity [80]. The bolometer-detected beam noise in a 1 Hz bandwidth is equivalent to about one part in 200 000 depletion of the beam.
close to the expected shot noise in the flux of droplets. The excitation laser is typically passed many times over the molecular beam using a pair of parallel, flat mirrors, so that with kHz pulsed lasers a high duty cycle can be achieved. Because of their low bandwidth (≈250 Hz), bolometer detectors cannot be effectively used with gated detection, for which mass spectrometer detection is advantageous. Depletion spectroscopy is more demanding of power in the excitation source; ideally one wants to use sufficient optical intensity to have high probability of at least one excitation per doped droplet.

For vibrational transitions in the IR, the typical linewidth in helium is ≈0.5 GHz. If we assume a vibrational transition dipole moment of 0.1 Debye and a transition wave number of 3000 cm$^{-1}$, then the peak absorption cross section will be ≈2 × 10$^{-16}$ cm$^2$ and the excitation rate will be ≈4 × 10$^3$ I s$^{-1}$ where I is the optical intensity in W cm$^{-2}$. If 10 cm of the beam is illuminated by the laser, this implies that the saturation intensity will be of the order of 1 W cm$^{-2}$, and the saturation fluence is on the order of 250 µJ cm$^{-2}$. The situation in droplets is more complex, especially with cw excitation, due to the fact that linewidth is often inhomogeneously broadened and that there is spectral diffusion between states and relaxation during the ≈250 µs that the molecules are being pumped [82–84].

3. Energy, angular momenta and excitations in helium droplets

3.1. Helium droplet excitations

The excitations of helium nanodroplets play an important role in the thermodynamics and much of the real-time dynamics that occurs in pure and doped droplets. As Landau pointed out long ago [90], the excitation spectrum of bulk helium is responsible for its superfluid properties and it is natural to assume that the excitations of droplets are key to understanding superfluidity (or even if that term has any real meaning) on a nanometre scale. The interaction of molecules with the helium excitations allows molecules to be cooled inside the droplets and the rate of such cooling is important in many chemical applications of HENDI. Even after the molecule and droplet reach equilibrium, the molecule–droplet excitation interactions determine time scales for fluctuations and relaxations, and thus determine, among other things, the homogeneous width of spectral lines.

Unfortunately, despite their importance, we have yet to develop experimental methods to directly probe the excitation energies of helium nanodroplets, with the exception of electronic excitations in the deep UV (<60 nm) [73]. In bulk helium, the low-energy excitations are mostly known from x-ray and neutron diffraction experiments, but such measurements have
not been done on droplets and are perhaps unlikely given the relatively small helium droplet density presently available. Thus, much of what we know comes from theory, and in particular the liquid drop model [77], which allows one to make connections between the droplets and the well-known case of bulk helium [91].

The liquid drop model (LDM) [77] treats a helium nanodroplet as a sphere with the same density as bulk helium, \( \rho = 21.8 \text{ nm}^{-3} \). This implies a droplet of \( N \) helium atoms has a radius, \( R(N) = 0.222N^{1/3} \text{ nm} \). It is known from quantum Monte Carlo (QMC) calculations of various types [92, 93] that the ground and thermally averaged density profile of pure droplets is close to that assumed in the LDM, except that the outer boundary is diffuse, with a 10–90% width of \( \approx 0.6 \text{ nm} \). The elementary excitations of such a sphere can be classified as two types, ripplons and phonons. Ripplons are quantized capillary wave excitations. They imply no change in density of the droplet but a change in shape. As such, their restoring force constant is proportional to the surface tension, \( \sigma \), which in the LDM is treated as equal to the bulk value 0.363 mJ m\(^{-2}\). These are characterized by an angular momentum quantum number, \( L \geq 2 \). A ripplon with angular momentum \( L \) is a \( 2L+1 \) degenerate harmonic oscillator. The excitation energy of this oscillator in the LDM is given by

\[
\sqrt{\frac{4\pi\sigma L(L-1)(L+2)}{m_{\text{He}}R(N)^3}} = 3.77N^{-1/2}\sqrt{L(L-1)(L+2)} \ \text{K}
\]

For large \( L \), this goes over to the \( k^2/\rho \) excitation curve known for capillary waves on a flat surface [94]. While ripplons have no density change, except for the surface, there is a hydrodynamic flow field that scales as \( (r/R(N))^L \) and thus becomes increasingly surface localized for higher \( L \) [94]. Ripplons are the lowest energy excitations of a nanodroplet and dominate its thermodynamics below 1 K [77, 95].

The other elementary excitations are phonons. In the LDM, these are the compressional normal modes of a sphere and are characterized by a radial quantum number, \( n \), and an angular momentum quantum number, \( L \). Phonons have amplitudes described by a spherical Bessel function, \( j_L(k_{n,L}r) \); the values of \( k_{n,L} = r_{n,L}/R(N) \) where \( r_{n,L} \) is the \( n \)th root of \( j_L \) [94]. In the LDM, the excitation energy of a phonon with wave number \( k \) is assumed to be the same as that of a bulk helium excitation of the same wave number; the complete empirical curve was given by Donnelly and Barenghi [91]. This excitation curve has a maximum of 13.76 K at \( k = 11 \text{ nm}^{-1} \) (the maxon) followed by a minimum at \( \Delta = 8.87 \text{ K} \) at \( k = 18.5 \text{ nm}^{-1} \). Phonons with wave number near the minimum of the curve are called rotons. The nature of these excitations have been discussed in [96]. For \( k > 21 \text{ nm}^{-1} \), the excitation energy rapidly approaches \( 2\Delta \) due to hybridization with two phonon states. For \( k \) significantly below the maxon, the excitation curve is approximately linear with a slope given by the speed of sound in helium, \( u = 236 \text{ m s}^{-1} \). The lowest energy phonon is the symmetric breathing mode (\( n = 1, L = 0 \)) which has an excitation energy 25.5\( N^{-1/3} \) K [77]. Given the terminal temperature reached by evaporative cooling of droplets [79], even the lowest phonon is largely unpopulated for droplets with \( N < 10^5 \). Ripplons dominate the nanodroplet thermodynamic properties for temperatures below 1 K, but the larger number of phonon excitation states cause them to dominate the thermodynamics at higher temperatures. At such temperatures, however, the interactions between excitations are known to become significant in the bulk. It is likely that the phonon contribution to the thermodynamic functions of the droplets at such high temperatures should be calculated from the empirical bulk values [91]. In doped helium droplets, it is known that the solute will strongly modulate the helium density in the first solvation shell and often in the second [97, 98]. In addition, the spherical symmetry will be lost for molecular solutes or even atomic solutes not in S atomic states. The phonon spectrum in the presence of solutes, even spherical, is largely unknown, but peaks observed in the phonon wing of many electronic spectra have often been assigned to phonons localized in
the solvation structure around a solute [99], and thus expected to be weakly dependent upon droplet size. The energy of the lowest phonon of each symmetry has been estimated using the POISTE method [100], which monitors the rate of decay of carefully selected trial functions under imaginary time propagation [101]. Energies are extracted using a maximum entropy-stabilized inverse Laplace transform. A more general method that calculates the normal modes using time-dependent, density functional theory is under development [102] and will give the entire phonon spectrum, but with the limitations of present density functionals which are unreliable for external potentials with very attractive interactions. Krotscheck and co-workers have used variational Monte Carlo methods [103] and quantum many-body methods known as HNC/EC [104], random phase approximation and correlated basis function methods [11] to study the lowest excitations of each angular momentum in pure and doped droplets.

Another type of ‘excitation’ that should be considered is quantum evaporation [105]. In bulk helium, it is known that when a phonon/roton with excitation energy greater than the atom binding energy (7.2 K) strikes a vacuum interface, coherent emission of an atom occurs. There is also a low-energy phonon produced, with the angles of the atom and phonon such that the momentum parallel to the surface is conserved in the process. In the LDM, the helium binding energy is reduced by a 11.23N⁻¹/³ K due to a surface energy correction [106]. The conservation of parallel momentum is replaced by the conservation of angular momentum, which will produce a centrifugal barrier for the departing atom which will raise the threshold by ≈1.23L(L + 1)N⁻²/³ K [107]. The time scale for quantum evaporation can be estimated by the time it takes a phonon to transverse from the centre to edge of a droplet (≈10 ps using the speed of sound) and this will lead to a lifetime broadening of the phonons of ≈1 K. This will largely ‘wash out’ the discrete excitation spectrum of the droplets and thus provide a true continuum into which relaxation can take place. Given the low phonon density of states in nanodroplets, some broadening mechanism is needed to rationalize the relatively smooth, narrow lineshapes of ro-vibrational transitions of molecules solvated in helium.

A vortex or vortex ring is a qualitatively different type of excitation that is possible in nanodroplets [108, 109], but as of yet there is no evidence for their presence [110]. A vortex is a topological defect with a quantum of helium circulation around the defect. The simplest such excitation is a straight line vortex going down the middle of a droplet (north pole to south pole). Such a vortex has one unit of angular momentum per helium atom, and each atom at a distance of r from the vortex has a velocity of ħ/mr. In bulk helium, a hollow core model is quite successful at predicting the energetics and velocity of quantized vortices [111]. Applied to helium droplets, such a model predicts an energy of a vortex in a helium nanodroplet of a few hundred K for droplets of interest in experiments. Extensive density functional theory (DFT) calculations have been made of the straight vortex in pure and doped droplets and the energetics are close to those predicted by the simple hollow core model [109]. The vortex angular momentum is predicted to distort the droplet from spherical symmetry, but only slightly [109, 110]. This energy of a vortex is so much higher than the droplet temperature that it was suggested that vortices would rapidly decay in nanodroplets. However, such droplets are by far the lowest energy states of high angular momentum and there do not appear to be any open channels by which such vortices could decay, conserving both energy and total angular momentum, which is of course required [110]. Furthermore, there are a whole family of curved vortex solutions that have a vortex rotating around the droplet [108]. Both the energy and angular momentum of such solutions drop as the distance of closest approach of the vortex from the axis is increased. To date, only hollow core model calculations have been done on such solutions due to their lower symmetry [108, 110]. It is predicted that vortex solutions will be the lowest energy states of a droplet for the total angular momentum of 131 (846) ħ for droplets with N = 10³(10⁴) [110]. These values of
the total angular momentum are quite a bit higher than the rms value expected for a droplet treated at a canonical ensemble at $= 0.38$ K (8.5 (38.7) $\hbar$ for $N = 10^3(10^4)$). However, recent statistical evaporative cooling calculations that include angular momentum conservation have found that a substantial fraction of the initial angular momentum deposited upon pick-up of a solute atom or molecule (typically several thousand $\hbar$) is trapped in the droplets after the helium evaporation is finished. Thus, the doped droplets studied in experiments should have sufficient angular momentum to produce vortex solutions. In a doped droplet with a vortex, the impurity is expected to bind to the vortex [112] (as is known to occur in the bulk) and could be expected to align strongly with the vortex axis (though no quantitative calculation has yet been made). Such a pinned solute molecule would not be expected to display the gas phase like ro-vibrational structure that is almost always observed in helium droplets. It has been predicted that the presence of a vortex will cause Ca atoms to move from surface to bulk binding to a helium droplet [113]. The lack of observation of droplets with trapped vortices is one of the most significant unresolved puzzles in the field.

For doped helium nanodroplets, another form of excitation is the translational motion of the solute. The minimum energy position of a solvated atom or molecule (with the exception of alkalies and some alkaline earths atoms and their molecules) is in the centre of a droplet [67, 114]. If one assumes that the helium solvation structure moves with the solute, then one can calculate the effective confinement potential of the solute in terms of the long-range He-solute $C_n$ constants [114] and a buoyancy correction [115] due to the number of helium atoms displaced by the solute. This leads to a 3D, approximately harmonic trap with vibrational frequencies typically below 1 GHz. The translation motion of the solute results in a dense set of many populated ‘particle in a box’ states [114, 116]. The direct excitation of these modes upon optical absorption is not expected since the predicted Doppler broadening is much narrower than the frequency of the oscillator, leading to strong motional narrowing [114]. Stated in another way, since the absorbers are confined in a droplet much smaller than the excitation wavelength, there expected Doppler broadening is Dicke-narrowed [117] away. However, there are at least three mechanisms that can lead to changes in the solute translational energy upon optical excitation. One is that the potential of interaction of the solute with the helium solvent changes upon electronic and/or vibrational excitation [114]. Change in the helium solvation structure leads to a ‘phonon wing’ in the spectrum that is typically observed upon electronic excitation [118, 119]. A change in the long range interaction coefficients (particularly the $C_6$) will result in a difference in the effective trapping potential between the two solute states in the transition. This will result in nonzero Frank–Condon factors for transitions that change the translational state and thus fine structure on the absorption lines. Another mechanism to ‘light up’ the translational motion states is coupling to the rotation of the molecule [114]. A molecule at the very centre of a droplet will experience an isotropic potential. However, when it is displaced from the centre, the dependence of the $C_6$ on the orientation of the helium relative to the molecule axis results in an anisotropic potential that increases in magnitude rapidly as the solute is displaced further from the centre. There is another coupling that arises from the fact that the effective translational mass of the solute is a function of its orientation and that this leads to a hydrodynamic coupling of the orientation of the molecule with its instantaneous momentum [114]. Both mechanisms lead to a mixing of different translational states with molecular rotor states (especially those that differ only in the angular momentum projection quantum number and thus are degenerate without considering this interaction). This translational state mixing leads to splitting of what would otherwise be expected to be single solute ro-vibrational transitions. Since these translational energy changes depend strongly on the size of the droplet, and almost all experiments done to date
sample a broad droplet size distribution, the expected fine structure on solute transitions will likely be washed out, contributing to the line broadening of the transition.

3.2. Evaporative cooling and the temperature of helium nanodroplets

In most HENDI experiments, droplets are doped by the pick-up technique pioneered by Scoles and co-workers [33]. The pick-up process will deposit substantial kinetic energy and angular momentum into the droplets, in both cases approximately proportional to the mass of the picked-up species. In addition, any thermal internal energy of the dopant, the solvation energy of the dopant in helium and any binding energy (in the case of cluster formation) will contribute to the deposited energy. If we assume the droplets statistically distribute this energy, the temperature of the droplets will raise to several K, typically above the \( \lambda \) transition of bulk helium. Following this temperature jump, the droplets will rapidly cool by helium evaporation [77, 107].

Treatment of the many-body evaporation by real-time quantum dynamics is clearly a very difficult problem. Statistical rate treatments of evaporation are certainly feasible and one can hope reasonably accurate, once the droplets have cooled sufficiently that the evaporation rate is slow compared to the rate for equilibration between the excitations of the droplet. Unfortunately, we have no estimate for what that rate is! The statistical rate equations only require knowledge of the density of states as a function of energy and the threshold energy for evaporation [120]. Brink and Stringari [77] made such a calculation, using the LDM to calculate the density of states. They predicted that for the evaporation time appropriate for HENDI experiments, the terminal temperature should be \( \sim 0.3 \) K. Later IR HENDI experiments, starting with Hartmann et al [79], demonstrated that the rotational populations of solvated molecules are well described by Boltzmann distributions with temperatures in the range \( 0.37 \pm 0.02 \) K. This result was interpreted as strongly supporting the statistical evaporation model and also the natural interpretation that the rotational populations of the solvated molecule were in equilibrium with the droplet excitations resulting in the equal temperature.

Based upon the surface energy contribution to the evaporation energy, one would expect that smaller droplets would cool to a lower temperature. This is not the case, however, because, at a minimum, the spread of droplet internal energy at least matches the evaporation energy of the last helium atom, and this corresponds to a larger spread of droplet temperature in a smaller droplet, which of course has a lower heat capacity. Attempts to experimentally test the predicted dependence of final temperature on mean droplet size are frustrated by the fact that the individual ro-vibrational transitions broaden and become strongly asymmetric in shape for smaller droplet sizes, which makes the determination of the temperature from the spectrum less precise [80].

Most of the literature on helium droplets have, sometime tacitly, assumed that the droplets are described by a canonical distribution at a final temperature near 0.38 K. We cite, as examples, the predictions of spectral structure by one of the present authors [114] and the wide use of path integral Monte Carlo calculations [98, 121] which provide an average over a canonical distribution (i.e., Boltzmann weighting) of states. However, it is clear that individual droplets, after evaporation has stopped or slowed to a negligible rate, have a constant energy, \( E \), not constant temperature, i.e. are more properly described as a microcanonical ensemble. Of course, it is possible for individual droplets to have definite energy and for the ensemble of droplets probed in an experiment to follow a canonical distribution. However, the evaporative cooling calculations predict that for droplet in the size range studied in most experiments, the spread of final energies for a given droplet size is determined by the evaporation energy, not
the energy fluctuations of a canonical ensemble. Perhaps more importantly, an isolated droplet must also conserve total angular momentum, $J$, and thus should be described by an ensemble that has both $E$ and $J$ as good quantum numbers [107].

The evaporative cooling calculations of Brink and Stringari ignored angular momentum constraints. It is straightforward to include these in the evaporative cooling using a formalism analogous to phase space theory in the treatment of unimolecular dissociation [120]. Such calculations require knowledge of the density of states as a function of both $E$ and $J$. This density of states has been calculated and fit to simple analytic functions for both ripplons and phonons (in the limit that they can be treated with a linear dispersion relation) [95]. Perhaps not surprisingly, the density of states as a function of $J$ for fixed $E$ turns out to be very accurately described by a Boltzmann distribution for a spherical top, but with an effective temperature that has nothing to do with the droplet temperature. The droplet temperature, defined in terms of the derivative of the log of the density of states with respect to energy at fixed total $J$, is a strong function of $J$ for fixed total $E$. Monte Carlo statistical evaporative cooling calculations have been performed, conserving total angular momentum, and the result was somewhat surprising [95]. The final states are spread over a broad range of $E$ and $J$, but are clustered in a narrow band around a line of constant temperature in the $E$, $J$ plane. This final temperature is essentially identical to that predicted by the earlier Brink and Stringari calculations. However, the spread of $E$ and $J$ is more than an order of magnitude higher than predicted for a canonical distribution at the same temperature. For fixed $E$, the fraction of the initial angular momentum that is trapped in the droplet increases with increasing $J$. Also, the initial alignment of the angular momentum (which for pick-up is primarily perpendicular to the droplet velocity vector) is largely conserved. Statistical theory predicts that this alignment is partially transferred to the angular momentum of a solvated rotor. Experiments had demonstrated a lab frame alignment of tetracene, in qualitative agreement with these predictions [122]. The statistical theory predicts that the evaporated helium atoms are anisotropic in the frame moving with the droplet and measurement of that distribution could provide a quantitative test of the statistical evaporation model.

The recent evaporative cooling results [95] imply that the assumption of a canonical distribution of internal states of the droplet and solute is likely a very poor approximation. This calls into question the accuracy of using the path integral Monte Carlo for modelling helium droplets. It also predicts that the distribution of centre of mass states of the solute is likely much broader than previously predicted. This may explain, at least in part, the failure of theory to predict the inhomogeneous line broadening that is commonly observed in IR spectra of doped helium droplets [114]. An interesting consequence is that the high angular momentum introduces a bias into the populations of a rotor such that the temperature extracted from a fit to those populations in shifted higher than the temperature of the entire droplet–solute system, treated as a statistical ensemble [123]. In order to account for the strongly nonthermal effects that arise from the trapped angular momentum, a realistic knowledge of the terminal distribution is needed. While statistical models can predict this, at present we have no way to assess if these predictions are at all reliable. Getting the final temperature correct only provides support that statistical theory is correct for the evaporation of the last few helium atoms, which we would have expected to begin with. Clearly, there is a important need for experiments that can measure the distribution of the droplet excitations. At the end of evaporative cooling, most of the trapped angular momentum is predicted to be in the lowest ripplon mode, creating a quadrupole distortion of the droplets. It is at least in principle possible that excitation in this mode could be probed with Raman spectroscopy (though signal estimates are not encouraging!) or by atom scattering experiments, particularly by atoms held, e.g., in a magneto optical trap.
4. Superfluidity and molecular rotation in nanodroplets

Superfluidity in helium has continued to fascinate since its discovery in the 1930s. The phenomenological two fluid model is of great value in interpreting experiments [124]. In this model, helium below the $\lambda$ point is treated as a mixture of normal and superfluid liquids. Landau developed the theory of the normal fluid component as a gas of quasiparticle excitations [90]. He also gave an experimental definition of the normal fluid fraction in terms of the ratio of the observed to classical moment of inertia for infinitesimal rotation of the sample, a definition used by Andronikashvili in his classic experiment with a torsional oscillator [125]. Ceperley developed a path integral Monte Carlo (PIMC) estimator that calculates this inertial response of a sample in a simulation cell [126]. This involves calculating the projected areas of Feynman loops that include He exchange. Superfluidity as defined by Landau is a macroscopic concept; Feynman explicitly warns against giving it a microscopic interpretation [127]. Yet, the appeal to interpret behaviour of helium nanodroplets in terms of a superfluid has been irresistible. Nanodroplets provide a way to study superfluidity on a nanometre length scale, but as is common with other bulk thermodynamic quantities, ambiguities arise when applied on the atomic scale.

Sindzingre, Klein and Ceperley [128] provided the first calculations of the normal and superfluid fractions of a helium cluster. They found clusters as small as 64 He displayed clear evidence for superfluidity based upon the inertial response, and clusters of 128 atoms displayed a remnant of the $\lambda$ transition. Similar calculations were then done on a 39-atom helium cluster doped with SF$_6$ [98]. The observation that molecules often have substantially reduced rotational constants when observed in helium nanodroplets was interpreted as a ‘microscopic Andronikashvili experiment’ [129], with the increase in the moment of inertia assigned to a helium normal fluid that rotates with the molecule. In order to calculate such a predicted moment of inertia, one needs the spatial dependence of the normal fluid density, which is not provided by Ceperley’s original method. Kwon and Whaley [130] introduced a PIMC estimator of a local normal fluid density based upon a separation of the number of short and long exchange paths. Assuming that this ‘normal fluid’ rotated rigidly with the molecule (what they referred to as adiabatic following), they calculated the helium contribution to the effective moment of inertia of SF$_6$ in helium and found good agreement with the experimentally determined value [130]. This group published several papers using this approach [131–133].

This definition of local normal fluid has been questioned by Draeger and Ceperley [134]. The derived local density, when integrated, does not reproduce the inertial properties calculated with the Ceperley PIMC estimator, i.e. it does not give the proper global normal fluid fraction. It is a scalar quantity, while the inertial response and thus normal fluid fraction of an inhomogeneous quantum fluid is a second rank tensor as is the Ceperley PIMC estimator. Draeger and Ceperley introduced new definitions of local normal and superfluid densities that have the proper symmetry and integrate to the correct global densities. They used the normal fluid estimator to calculate the moments of inertia for rotation of (HCN)$_n$ clusters in helium [134] by assuming that this normal fluid rotates with the molecule. One interesting conclusion of their work is that there is a normal fluid fraction for rotation around the symmetry axis that reflects thermal excitations in the first solvation layer present even at 0.38 K. Such excitations carry angular momentum and result in the prediction of a Q branch in the spectrum. Such Q branches have been seen in the spectrum observed by the Miller group [135] and their relative intensities are in at least qualitative agreement with the predictions of the normal fluid fractions calculated [136]. The Draeger/Ceperley estimator is not unique. One could add to the definition a second rank tensor that will integrate to zero and still recover the proper global superfluid estimator. Recently, Kwon and Whaley [137] have introduced such a
Another approach to the calculation of the effective rotational constants of molecules in helium is to calculate the hydrodynamic flow of helium needed to maintain a static helium solvation structure in the rotating form of the molecule [138, 139]. This treatment assumes adiabatic following of the helium density structure that rotates rigidly with the molecule (but not the helium atoms themselves). This assumption, combined with the equation of continuity, gives a differential equation for the helium velocity. It is further assumed that the helium flow is irrotational, which Lord Kelvin showed was the minimum kinetic energy solution to the equation of continuity for a given time-dependent density [94]. This implies that the local helium velocity can be written as minus the gradient of a scalar function known as the velocity potential. This definition of adiabatic following of the quantum hydrodynamic model is distinct from that introduced independently by Kwon and Whaley [130] and is based upon an assumption that the frequency for molecular rotation is low compared to the excitations of the helium. The normal fluid response calculations are based upon infinitesimal rotation and thus are also dependent upon an assumption of a separation of time scale. The helium density structure was estimated using helium density functional theory [140], though this approximation was not essential. Good agreement was found for the rotational constants of a number of heavy molecules (especially considering the considerable uncertainty of the He– molecule interaction potentials), but not for light molecules HCN and HCCH. The latter were attributed to a breakdown of adiabatic following, which was later demonstrated experimentally [141] and theoretically [142] in the case of HCN.

A similar hydrodynamic calculation for the hydrodynamic mass of alkali cations in helium was found to be in essentially quantitative agreement [143] with high level QMC calculations [144]. Kwon et al [131] reported that the hydrodynamic model dramatically underestimates the effective moment of inertia of SF₆ in helium. Lehmann and Callegari [145] agreed with this conclusion if one used previously reported PIMC densities as input to the calculation, but found that if diffusion Monte Carlo (DMC) densities (calculated with the same potential!) were used, the hydrodynamic calculations were in quantitative agreement with experiment. They argue that since the hydrodynamic model is a zero-temperature theory, the ground-state helium density (which are calculated with DMC) should be used instead of the thermally averaged density (which is what is calculated by PIMC).

For light rotors ($B > 0.5 \text{ cm}^{-1}$), adiabatic following breaks down and one must explicitly account for molecule rotation in any quantum simulation. Viel and Whaley [142] used the POITSE method to estimate the energy of excited rotational states of HCN. The Whaley group has continued the development of this method and has applied it to a number of systems [146–148]. More accurate is the use of imaginary time orientational correlation functions to extract the excited rotational states which were introduced by Moroni et al [149–153]. This has allowed for essentially exact calculation of the rotational excitation energies of molecules in small to modest size helium clusters and has been found to be in essentially quantitative agreement with recent experiments (discussed below). Blinov and Roy [154, 155] have introduced similar calculations using PIMC instead of DMC to calculate the orientational correlation functions. The Whaley group is also using similar methods [156, 157] in addition to several others that they have pioneered.

Zillich and Whaley have developed the DMC/CBF method for treating the interaction of molecular rotation excitation with the phonons and rotons of helium and applied it to the case of HCN [158] and C₂H₂ [156], an important yet challenging problem. This model treats the phonons of the droplet as if they are continuous and have the same form as for bulk helium and then decomposes the density anisotropy that rotates with the molecule in terms of these
phonon modes. In this model, off-resonant interactions shift the rotational excitation energy. The interaction of the rotor with the rotons is predicted to lead to absorption intensity for the rotons. The observation of such absorption would provide an important further test of the DMC/CBF model.

The use of density functional theory for treating helium has been very active and is beyond what we can realistically cover in this review. The groups of F Ancilotto, M Barranco, F Dalfovo, J Eloranta, E S Hernandez and L Szybiryz have been particularly active. A great part of this work has been reviewed in [14].

5. Review of recent work

5.1. Femtosecond dynamics

Dynamical processes are directly accessible applying femtosecond real-time spectroscopy. The first explicitly time-resolved studies in helium droplets used the technique of time-correlated photon counting, which allowed the detection of time-resolved changes in emission with $\approx 100$ ps time resolution. This proved sufficient to detect radiative and quenching rates and the exciplex formation rates in cases of a sufficiently high barrier. Ultrafast laser pump/probe experiments allow probing time scales from tens of femtoseconds up to hundreds of picoseconds. These methods allow the nuclear motion of the probed atoms and molecules and changes in solvation structure to be addressed. In connection with the experiments in helium droplets this is of peculiar interest because of the quantum nature at these low temperature and effects related to, e.g., the delocalization of atoms or the superfluid properties, which outstandingly alter the dynamics of a fluid. In collaboration with C-P Schulz (Max-Born-Institute Berlin), one of our groups (FS) has performed over several years femtosecond pump–probe experiments of doped helium nanodroplets. It was demonstrated that even with the dilute target of a doped droplet beam, dynamical studies can be successfully realized. A variety of problems have been tackled which are summarized in the following.

5.1.1. Wave packet propagation of alkali dimers. The goal of studying the geometric and electronic structure of molecules at low-temperature conditions relies on the weak and isotropic interaction with the helium environment. Results and their interpretation may significantly degrade if one is not able to quantify the perturbation of the surrounding matrix. For that reason, the vibrational motion of molecules attached to helium droplet has to be compared to gas-phase experiments. Vibrations of alkali dimers attached to helium nanodroplets were followed in real time applying femtosecond pump–probe techniques. Depending on parameters such as the excitation wavelength or photon intensity, wave packet propagation in potassium dimers has been observed in the electronically excited states $A^1 \Sigma_u^+$ and $2^1 \Pi_g$, as well as in the singlet ground state $X^1 \Sigma_g^+$ [159], see for example figure 5. The oscillation of the mass-selected photo-ionization intensity directly images the wave packet motion revealing vibrational frequencies as well as its time dependence. A Fourier analysis of the time spectra comprises the assignment to the excited vibrational states. Furthermore, the phase of the oscillations gives information on transition probabilities and the location of the probe window, i.e. the distance at the internuclear coordinate which amplifies the probe step and is required for detecting dynamics. When compared to the free dimer, the formation of a ground state $(X^1 \Sigma_g^+)$ wave packet from a Raman process was found to be strongly enhanced in the droplet environment. At photon energies around 12 500 cm$^{-1}$ this process even dominates the pump–probe signal. Since the vibrational motion in the ground state was found to be unaltered when compared to the gas-phase $K_2$, the difference in the transition probabilities must originate from the perturbed
Figure 5. Wave packet propagation of potassium dimers attached to helium nanodroplets. Pump and probe pulses at 12 000 cm$^{-1}$ were used. The offset present in the original measured trace was subtracted to centre the oscillation around the origin. The oscillation essentially represents the vibrational motion in the $\text{A}^1\Sigma_u^+$ state.

Figure 6. Spectrogram of the pump–probe oscillation shown in figure 5. The main intensity around 66 cm$^{-1}$ corresponds to a wave packet in the $\text{A}^1\Sigma_u^+$ state of potassium dimers attached to helium nanodroplets. The inset contains the same data, but normalized for each delay time in order to illustrate the shift of the vibrations during desorption of the dimer from the helium droplet.

electronically excited states. Indeed, the wave packet propagation in the electronically excited $\text{A}^1\Sigma_u^+$ state clearly discovers a reduced vibrational wave number by about 1 cm$^{-1}$. The influence of the helium matrix leads to a wider vibrational level spacing in that part of the excited-state potential. Time-resolved Fourier analysis (spectrogram technique [160]) allows one to follow the vibrational energies approaching gas-phase values during desorption of the excited potassium dimer from the helium droplet. In figure 6, a corresponding spectrogram
is presented. The inset clearly illustrates the shift to higher frequencies upon desorption. Furthermore, the decrease in the amplitude of the oscillation is worth noting. It is either associated with decoherence effects upon desorption or in changes of the Franck–Condon detection window. In this regard, desorption times upon electronic excitation have been determined for the first time. The experiments give a desorption time of K\textsubscript{2} excited into the electronic A state of ≈3 ps. The analysis of excited wave packets in higher electronic states of K\textsubscript{2} reveals an even faster desorption behaviour [159].

Exploiting the advantage of a preferential formation of weakly bound alkali dimers and clusters [161], for the first time wave packet propagation of triplet dimer states has been observed. Experiments on sodium dimers attached to helium droplets allowed the observation of vibrational wave packets in the 1\textsuperscript{3}Σ\textsuperscript{1}\textsubscript{u}(a) as well as 1\textsuperscript{3}Σ\textsuperscript{1}\textsubscript{g}(c) states [162] which confirm former measurements performed in the frequency domain and support the theoretical calculations on the dimer interaction potentials.

5.1.2. Fragmentation dynamics of alkali clusters. The fragmentation dynamics of alkali clusters (K\textsubscript{n}, 3 < n < 11) has been studied in order to directly measure the energy dissipation and cooling process of helium droplets [164]. These experiments were performed using small potassium clusters because their electronic excitation and subsequent fragmentation have been investigated in a variety of experimental studies. The pump–probe experiments of alkali-cluster-doped helium droplets allow one to follow the abundance of selected cluster sizes in real time. In this case the probe step determines the yield of mass-selected ions from a non-resonant photo-ionization process. Figure 7 plots such a recorded ion yield as a function of delay time. Following a fragmentation model introduced by Kühling \textit{et al} [163], a fragmentation time of 5.8 ps is determined in this case. In the gas-phase, potassium as well as sodium show values which are around ≈1 ps [165]. The longer fragmentation times determined in connection with helium droplets are interpreted in terms of a competing channel where the energy of the laser-heated alkali cluster is dissipated into the helium droplet prior
to fragmentation. Figure 8 shows a striking droplet size effect of the measured fragmentation dynamics. The larger droplets cool the energy much more efficiently, resulting in even longer fragmentation times. The energy to be dissipated depends on the photon energy, cluster size, etc. and will be discussed thoroughly in [164]. Roughly speaking, excess energy of the order of 1 eV is transferred to the helium droplet in less than a picosecond to comply with the observed effects. Assuming that this energy (thousands of K) cannot reside in internal degrees of freedom of the droplet and is ad hoc evaporatively cooled, this means that of the order of 2000 helium atoms per picosecond leave the droplet. Experiments on NO$_2$ excited well above the gas-phase dissociation threshold but with no evidence of dissociation in helium also suggest vibrational relaxation cooling with similar ultrafast rates [166, 167].

5.1.3. Surface dynamics. In the same line of experiments, recent results demonstrate that alkali atoms can be utilized as probes for surface excitations of helium droplets [168, 169]. Inducing a spatial expansion of the alkali valence electron orbital upon laser excitation, the helium environment rearranges. Several time-dependent features are identified in pump–probe experiments. Assignment to specific surface modes of the droplets could so far not be achieved. As expected, strong droplet size effects are present. The expansion of the dimple structure takes place at picosecond time scales. In these experiments, normal fluid $^3$He droplets have been directly compared to superfluid $^4$He counterparts. Surprisingly, $^3$He droplets show a comparable behaviour and quite similar effects.

5.1.4. Exciplex formation. The experiments of alkali atoms on the surface of helium droplets revealed a variety of aspects on dynamical processes triggered by laser excitations. In several studies, the formation of alkali–helium exciplexes upon excitation of atomic transitions explained the observed features in wavelength dispersed, laser-induced fluorescence spectra [59, 60, 170–172]. Figure 9 illustrates the formation process. The alkali excited in the p-state
will strongly bind a He atom if it approaches the nodal plane of the p orbital. Hence, an excited alkali–helium molecule is formed upon $p \leftarrow s$ laser excitation, bound by a couple of hundreds of cm$^{-1}$, depending on the corresponding alkali. Since the binding energy of the exciplex to the droplet surface is weak, the binding energy release leads to desorption. Eventually, the complex dissociates when radiatively decaying into the electronic ground state, typically after nanoseconds. To date, this process has been experimentally confirmed for Na, K, Rb and Cs. Besides diatomic exciplexes one also observes larger molecules ($M^*\text{He}_n$, $M =$ metal, $n > 1$) as known from studies in bulk helium [173, 174]. From the beginning, the dynamics of this process appeared to be an interesting example of photo-induced molecule formation. The first experiment giving information on the dynamics of the formation process was carried out in Princeton, applying time-correlated photon counting [175, 176]. The evolution of the fluorescence of Na*He as well as K*He was monitored. A substantial difference in formation rates was observed following excitation of the two different spin–orbit component of the excited $^2P$ alkali state. Modelling the data based on a tunnelling process into the molecular alkali–helium well, the contributions of the extraction energy of helium atoms from the droplet and spin–orbit coupling effects were discussed. Predicted exciplex formation times of the heavier alkalies were derived from the model. Since the measured formation times of 50 ps (K*He) approached the resolution of the applied experimental technique, the use of femtosecond pump–probe techniques became evident. Indeed, the formation times could be determined for K*He as well as Rb*He employing mass-resolved multiphoton ionization in a pump–probe arrangement [170, 177]. These experiments included a direct comparison of $^4\text{He}$ and $^3\text{He}$ droplets. Figure 10 shows the real-time spectra monitoring the yield of Rb*4He and Rb*3He. Formation times are determined to be 8.5 ps and 11.6 ps, respectively. For
both isotopes the exciplex formation occurs very much in the same way, although we are
dealing with very different fluids, on one hand a Bose–Einstein condensed ⁴He superfluid
liquid, and, on the other hand the ³He Fermi normal fluid. The longer formation time of the
³He exciplex is a very surprising result and does not agree with the predictions of the just
mentioned tunnelling model. Different vibrational relaxation times are suggested to account
for the difference, which still has to be confirmed in a quantitative theoretical model.

In the same exciplex formation process, quantum interference structures have been
observed [168, 178]. Recent experiments having attosecond time resolution in recording
interference fringes demonstrate that quantum interference structures are suitable to get
detailed information on the vibrational structure of the exciplex molecules. Moreover, the
interaction potential can even be monitored during the formation of the metastable molecules.
The interference oscillations survive the bond formation process and provide a new tool to
determine the energy of vibrational states with a resolution of the order of \( \approx 1 \text{ cm}^{-1} \) [178].

5.2. Fragmentation of dopants

Employing intense femtosecond laser pulses, femtosecond ionization of magnesium clusters
has been studied by high-resolution mass spectrometry in the group of Meiwes-Broer [45].
Decomposition of the Mg clusters dominates the process. The charging of the fragments is
significantly governed by the interaction with the helium droplet. Pump–probe experiments
on the MgHe⁺⁺ snowball formation clearly show dynamics up to 50 ps.

Fragmentation dynamics upon ionization of neon clusters (Neₙ, \( n < 14 \)) embedded
in helium nanodroplets have been theoretically investigated by Halberstadt and co-workers
[179]. Here, a molecular dynamics with quantum transitions (MDQT) approach has been
used; the helium environment is modelled in terms of friction forces. Besides fitting the
friction coefficient of helium droplets which surprisingly comes out rather high compared to
superfluid helium, fragmentation branching ratios are calculated which are compared with
experimental studies on electron impact ionization of neon-doped droplets [180]. Here, the
helium environment significantly stabilizes larger fragments. The calculations give a detailed view on the short-time evolution of the proportion of the species involved in the dissociation process.

5.3. Photo-dissociation in helium droplets

The first photo-dissociation experiments using helium droplet isolation were performed on K triplet dimers and on Na and K triplet trimers, using both the methods of wavelength-resolved emission and time-correlated photon counting. This work revealed that excitation of K\textsubscript{2} to a largely repulsive $^3\Pi_g$ state leads to both the expected atomic K emission and also to emission from molecules in the $^1\Pi_u$ state, demonstrating that intersystem crossing in excited alkali states can compete even with direct dissociation [181]. In the case of the quartet trimers, the rate of predissociation following electronic excitation, due to curve crossing by a repulsive single surface, has been measured as a function of vibrational energy in the excited state [182]. This dependence suggests that the crossing occurs slightly above the minimum in the excited state. The atomic and dimer emission to higher energy than the excitation wavelength is allowed due to the formation of the stronger singlet dimer bond upon dissociation of the weakly bound quartet trimer. The presence of dimer emission from the $^1\Pi_u$ state but not the lower energy $^1\Sigma_u$ state points to dissociation on a state that is antisymmetric with respect to the molecular plane of the trimer.

A novel experimental strategy to directly probe the translational dynamics of neutral species embedded in helium nanodroplets has been pursued by Drabbels and co-workers [183, 184]. They created fragments from a photo-dissociation process with well-defined velocity distributions inside a helium nanodroplet. The comparison of the fragments’ initial and final (after having left the droplet) velocity distribution provides detailed insight into the translational dynamics and the interaction with the helium environment. The three-dimensional speed and angular distributions of various departing reaction products are measured using a velocity map imaging set-up. Photo-fragments are non-resonantly ionized by femtosecond laser pulses, delayed 20 ns after triggering the photolysis. The 266 nm A-band photo-dissociation of CH\textsubscript{3} I and CF\textsubscript{3} I has been investigated inside \textsuperscript{4}He droplets having sizes from 2000 to 20 000. For all the examined sizes, some of the photo-fragments escape from the helium droplets, though sometimes with a small helium cluster around them. Compared to classical solid clusters where already a few solvation shells around the parent molecule lead to complete caging [185–187], the helium droplets reveal extraordinary dynamical properties. The measured velocities are found to be considerably shifted to lower speeds with respect to the photo-dissociation of gas-phase photo-dissociated molecules. Based on the observed speed distributions and anisotropy parameters, it is concluded that the CF\textsubscript{3} fragments escape via a direct mechanism, only partially transferring their excess kinetic energy to the droplet. Iodine atoms, despite their lower initial kinetic energy, escape with lower fractional loss of kinetic energy. Accompanying Monte Carlo simulations suggest that mainly binary classical collision with the helium atoms can account for the findings. Since recoil energies are quite high, no quantum nature in terms of superfluidity and Landau’s critical velocity had to be introduced to model the findings. The low-energy fragments show an isotropic angular distribution. With increasing recoil energy and product mass, the reaction product angular distribution become similar to the free molecule. As expected, larger mean droplet sizes result in higher kinetic energy losses and more isotropic angular distributions of the departing products. As an example, in figure 11 the angular as well as velocity distributions of the CF\textsubscript{3} fragments dissociating CF\textsubscript{3} I are shown. The molecules were dissociated using pulses from the 266 nm fourth harmonic of a Nd:YAG laser. The fragments were ionized in a non-state-selective way
employing femtosecond 800 nm laser pulses delayed 18 ns with respect to the dissociation. Results obtained with different cluster sizes are compared.

5.4. Photo-electrons of pure and doped helium droplets

Many detection schemes include ionization processes of the embedded atoms and molecules. The outcome and interpretation of results is often linked to the dynamics and the fate of the produced charged particles. It is therefore instructive to study the produced electrons by means of photo-electron spectroscopy. The first task in that direction indicated that the kinetic energy distributions of electrons is dominated by slow electrons having average energies less than 0.6 meV, when photon energies of about 24 eV are used for ionization of the droplets [76]. A corresponding strong interaction or ‘thermalization’ of electrons produced inside the droplet would therefore limit the usefulness of photo-electron spectroscopic techniques for the study of embedded species. Fortunately the results introduced in the following confirm that this is not as a universal behaviour following intra-droplet ionization.

The first photo-electron spectrum of an embedded neutral species was presented by Tiggesbäumker and co-workers [188]. Mass-selected Ag₅ clusters were resonantly (R2PI)
ionized by 3.96 eV photons. The ionization threshold was found to be in good agreement with available theoretical calculations and previous gas-phase experiments. In contrast to the experiments on the pure droplets, the ionization threshold is not significantly altered by the helium environment. This is perhaps surprising given that the conduction band for electrons in bulk helium is almost 1 eV above vacuum, which would appear to imply that the ionization threshold in helium should be raised by nearly this amount. In this regard, the nanometre dimensions of the helium droplets are crucial in the process ablating the electron and not forming a solvated bubble state. Interestingly, the results show that prior to the absorption of the second photon the system relaxes to a metastable state, most likely by vibrational relaxation. Depending on the photon energy up to 80 meV of energy are to be dissipated into the helium droplet on a time scale much less than a nanosecond. A quite similar result was found when studying the silver trimer [189]. Again, excess excitation energy relaxes into a long living state, the lifetime of which was determined to be $5.7 \pm 0.6$ ns. The ionization potential was found to be in accordance with gas-phase experiments; hence direct escape of the electrons from the droplet without significant interaction appears to be the major channel.

Drabbels and co-workers recently studied photo-electron spectra of aniline attached to helium nanodroplets [190]. Although the spectra resemble closely that of the gas phase, a droplet size-dependent shift was observed, lowering the ionization threshold upon solvation in the droplets. This shift, which is of the order of 800 cm$^{-1}$, is assigned to polarization effects and can be readily estimated from the dielectric constant and the cluster radius. In terms of resolution the photo-electron peaks are asymmetrically broadened, showing a tail extending 100–300 cm$^{-1}$ towards lower kinetic energy. By analysing the lineshape, droplet size-dependent contributions could be extracted. The results give a linear increase with the droplet radius by $9.8 \pm 0.8$ cm$^{-1}$ Å$^{-1}$. In conclusion, the line broadenings due to the surrounding helium droplets are comparable to achievable width given by a common apparatus function and are not a severe limitation in applying photo-electron spectroscopy in helium nanodroplets.

5.5. Theory of electrons attached to helium droplets

The already mentioned experimental studies involve ionization processes. In particular, in the case of photo-electron spectroscopy the interaction of the emitted electrons with the droplet importantly impacts the results of the experiments. Jortner and Rosenblit provided a thorough theoretical study of the energetics and dynamics of electron bubbles in $^4$He and $^3$He droplets [13]. The energetic stability is determined by comparing the results to the energy of the quasi-free electron state $V_0$ with the total energy of the electron bubble in the ground state $E_i$. The latter includes contributions of the electronic and reorganization energy. At a cluster size of 6500, $V_0$ was obtained to be reduced only by less than 10% compared to the bulk value of $V_0 = 1.06$ eV. Decreasing the droplet size rises the total energy $E_i$ of the balloon-like structure continuously. The minimal droplet size for which an electron bubble is energetically stable was determined to about $N = 5200$. For such droplets having a radius of 39 Å, the radius of the electron bubble is 13.5 Å. An interesting result to point out here is the role of superfluidity. The energetic structure proved to be insensitive to the properties of the superfluid, being nearly identical for $^4$He below or above the lambda point as well as $^3$He droplets. Also the calculated formation time $\tau_f$ of 9 ps of an equilibrium electron bubble configuration is only weakly affected by superfluidity: dissipating effects in normal fluid droplets increase $\tau_f$ by 15%.

On the other hand, the dynamic stability, given by tunnelling of the electron into the vacuum, is strongly affected by the superfluid phase. In normal fluid helium, the motion in the confining potential of the droplet is highly dissipative and therefore the electron bubble
rests in the centre of the droplet [191]. In contrast to that, the nondissipative motion in a superfluid droplet is predicted to decrease the tunnelling lifetime by 20 orders of magnitudes. Apparently, \( \tau_f \) strongly increases with droplet size. Finally, defining a dynamic lifetime by \( \tau_f \) being longer than the time scale of an experiment (10^{-6} \text{ s}), one obtains a minimal droplet size for dynamic stability of \( \approx 6200 \). The theoretical picture and the numerical results nicely go along with measurements on attached electrons to helium droplets and experimentally determined lifetimes [192, 193].

Rosenbilt and Jortner have also analysed the binding of a free electron to the outer surface of helium droplets. Above a bulk helium surface, such an electron is weakly bound by polarization forces. However, due to curvature of the surface in droplets, the binding energy is expected to be depressed and a minimum droplet size for a bound electron state is predicted to be \( 3 \times 10^5 \) helium atoms [194]. Such a threshold is not expected if the droplet contained a positive charge. The hypothetical Rydberg-type state of an electron circulating around a positively charged droplet, but prevented from neutralization by the helium electron repulsion, was first discussed by Golov and Sekatskii [195, 196] and later named ‘Scolium’.

5.6. High-resolution electronic spectroscopy

High-resolution electronic spectroscopy of doped helium nanodroplets can serve as a powerful tool not only for obtaining structural information but also to study dynamics in photo-chemical processes. In particular, charge transfer or proton transfer in complex systems can be targeted. Often such processes take place in the femtosecond time regime and real-time pump–probe techniques have been applied in ambient environments [197–200]. Since lifetime effects in this domain significantly contribute to line broadenings, frequency domain spectroscopy can be applied as an alternative approach having advantages, e.g., in terms of sensitivity. Limitations lie in the achievable spectral resolution and the assignment of spectral features. In complex systems, this can only be accomplished in a homogeneous cold ensemble of molecules. Moreover, the efficient cooling mechanism present in helium nanodroplets allows not only to state selectively laser-excited molecules but also to observe emission spectra of well-defined states because vibrational excitations are cooled prior to the radiation decay. The benefit of high spectral resolution in absorption spectra of complex molecules has been demonstrated in a number of experiments [7, 201–203]. In some molecules, the first vibrationally resolved electronic spectra have been recorded [202, 204]. This line of work has been extended to high-resolution fluorescence emission spectroscopy by Slenczka and co-workers [205–207]. Molecules such as tetracene, pentacene, perylene and phthalocyanines have been studied. The results clearly demonstrate discrete and long-lived states of the solvation structure of the surrounding helium matrix. Explicitly, the emission spectra show contributions from different progressions. Since vibrational modes of localized helium atoms are not expected to exist in superfluid helium, the experiments confirm the existence of a solid-like (snowball) solvation shell [206, 207]. Depending on the molecule, different helium layer configurations have been assigned and relaxation probabilities were derived. QMC calculations have found two different helium solvation structures for 150 He atoms around phthalocyanine [208]. For pentacene, e.g., the authors found only a single configuration of the helium layer, independently of the electronic state. More generally, multiple sharp lines are often observed for each vibronic transition of polyatomic molecules [50, 99, 177], along with a broad absorption feature to the blue of the lowest energy sharp transition. The broad peak has been assigned as a ‘phonon wing’ involving excitation of bulk such as phonons and rotons in the droplet [119]. The additional sharp lines have been assigned in some cases as excitations of helium vibrations localized in the solvation shell [203, 209] or as zero phonon lines (pure molecular excitations)
of alternative helium structures. The intensity of the zero phonon line is proportional to the squared overlap of the ground-state helium wavefunction solvated around the ground- and the excited-state molecule, respectively, and thus is expected to decrease extremely rapidly with increasing solvent reorganization. Hole burning experiments as well as dispersed emission as described above can be used to assign peaks to different solvation structures (as was first done in the spectrum of tetracene [210, 211]), but this requires the structures to have a lifetime longer than the excitation laser pulses. It is worth noting that the localized vibrations and different isomers can be viewed as points on a continuum. As helium density in the first solvent shell increases, one or more helium mode become ‘soft’ and move down in excitation energy below the roton energy (where it belongs based upon its wavelength). As the density further increases, the ‘soft’ mode can become an unstable mode with multiple minima. The latter can be viewed as a result of freezing of the highly compacted first solvation shell due to strong He–He repulsion.

Generally, the resolution of electronic spectra has not been sufficiently high to allow the resolution of rotational structure. An exception is glyoxal [212] for which a surprisingly large change in rotational constants upon electronic excitation was observed and attributed to be primarily due to changes in helium solvation structure. The zero phonon spectrum of phthalocyanine was studied with 1 MHz resolution and found not to have any evidence of rotational structure [213]. This work determined that the experimental width of the zero phonon line was dominated by the inhomogeneous size distribution of the droplets, even for the largest droplets that could be formed. The asymptotic shift with droplet size is expected to be proportional to the droplet helium number and the change in helium-molecule $C_6$ coefficient. The latter is typically much larger for electronic than vibrational excitation, thus making droplet size inhomogeneous effects more important in electronic than vibrational spectroscopy [214].

HENDI has also been used to study the electronic spectroscopy of complexes formed inside the helium droplets. Additional rare gas atoms such as Ar are often used [50], since it is common to have jet spectra of such complexes to compare to. Recent examples include the study of tetracene with H$_2$, D$_2$ (ortho and para forms) and HD [215]. They discovered multiple isomers of each complex, some of which were not observed in free jet spectroscopy of the same complexes. It was recently observed that the beam depletion spectrum of perylene when complexed with O$_2$ was much stronger than expected based upon the Poisson distribution and this was attributed to increased quenching and thus greater heat release per excitation [216]. This suggests that comparison of LIF and depletion spectra could be used to determine quantum yields for emission in helium. A recent study reported the UV spectrum of benzene and the benzene dimer in helium [217]. The monomer was found to have a larger blue shift (30 cm$^{-1}$). In a more recent measurements on five substituted benzene molecules, it was found that their blue shifts (and that of benzene) were highly correlated with calculated changes in the electron density on the aromatic ring [218]. Curtis et al [219] found a $\approx$1 cm$^{-1}$ blue shift for the benzene transitions when they are observed using two photon ionization detection compared to detection by LIF or beam depletion [217]. It is likely that this reflects the REMPI detection being sensitive to the detection of smaller droplets for which the electron has a higher probability of escaping. The benzene dimer was found to have the same spectroscopic structure as previously found in the gas phase, but compressed [217]. Remarkably, helium solvation was found to substantially inhibit excimer formation upon $S_1$ excitation, a process that occurs in a few picoseconds for the isolated dimer in the gas phase. Krasnokutski et al [220] have reported the spectrum of anthracene in helium, thus completing the observation of the series of 1–5 fused benzene rings in a line. Huang et al [100] have done QMC calculations of the interaction of helium (up to 24 atoms) with these ‘nanosurfaces’ and find strong localization
of helium in the first solvent layer above and below the rings. Pendular state spectroscopy has been observed for 9-cyanoanthracene in helium using fields up to 200 kV cm$^{-1}$, achieving what the authors report to be the highest degree of alignment yet obtained [221]. It is likely that such spectra could provide measurements of the moments of inertia of such large molecules in helium since the pendular frequencies will depend upon these moments.

One of our groups (FS) introduced the possibility of studying charge transfer and lifetime effects in doped helium nanodroplets when probing, e.g., 3,4,9,10-perylenetetracarboxylic-dianhydrid (PTCDA) complexes [40, 204]. Only the high selectivity of molecular transitions attained in helium droplets allows for a detailed analysis on excitonic transitions and a determination of their lifetimes. Evaluating the spectral widths, a dephasing time of about 10 fs was deduced. Analysis of lineshapes in 3-hydroxyflavon has been performed by Slenczka and co-workers [222]. They determined the proton back transfer of tautomers of 3-hydroxyflavon into its normal form in 250 fs. Furthermore, the influence of a polar solvent environment by adding water molecules was probed. Note that these experiments have full control on the size of the additional water complexes.

5.7. Optically selected mass spectroscopy in helium nanodroplets

There is a long history to the study of electron impact ionization of helium nanodroplets, of which we cite only some of the most recent [223, 224]. The Miller group introduced a new approach that dramatically cleans up many of the ambiguities of previous work, by looking only at the modulation in the mass spectrum induced when an IR transition of a particular species is pumped [225]. This allowed, for the first time, reliable absolute branching ratios between different mass (ion products) to be determined, from droplets with a known composition. The work refined the ion hopping probability and demonstrated that there is a long-range steering, such that the He cation ion preferentially approaches the negative parts of the molecule, leading to regio-selective ionization. Fragmentation after ionization was studied for HCN [226] and the large organic molecule, triphenyl-methanol [227].

5.8. IR–IR double resonance

The high power available from OPOs has been exploited by the Miller group to use IR–IR double resonance to study dynamical behaviour in helium nanodroplets. The C–H stretching spectrum of cyanacetylene (HCCCN) was studied as a test case [228]. A high power 3 $\mu$m OPO was used as a pump and a lower power F-centre laser was used as a tuneable probe of the spectrum, $\approx$175 $\mu$s after the pump, sufficient time to allow evaporative cooling to effectively finish. As expected, a saturation hole in the probe absorption was induced by the pump. However, this was narrower than the one photon transition and an increase in absorption (a 'hill') was observed slightly higher in wave number. The interpretation is that the cluster size distribution makes a significant contribution to the width of the single resonance spectrum and that there is a blue shift of the absorption spectrum due to the evaporation of $\approx$660 helium atoms induced by the pump laser absorption. It should also be recognized that the total angular momentum will be conserved in the droplets and that the initial absorption will lead to a reduction in the angular momentum trapped in the droplets following initial pick-up, so that the change in the droplet spectrum may not reflect only the change in mean size.

In a subsequent study, Miller and co-workers used double resonance to study the IR-induced isomerization between the linear HCN–HF and the bent HF–HCN complexes [229]. Both complexes are formed upon joint pick up of HCN and HF [230], and in each isomer both the C–H and F–H stretching modes were observed. Excitation of the lower energy HCN–HF
complex resulted in branching probabilities of 58% to produce HCN–HF absorption in a smaller droplet and 29% to produce absorption of the higher energy HF–HCN isomer. The results are interpreted to result from photo-dissociation of the complex after IR absorption (which is commonly observed for isolated complexes) followed by recombination, much as in the initial formation process of the complex following pick-up. The ≈13% loss of intensity was attributed to droplets lost from the detector due to the increased transverse momentum of the droplets produced by the evaporative cooling. In particular, no evidence was found for an IR-induced absorption of the isolated HCN or HF molecules in the droplets, which implies that the ejection of one of the monomers due to the translational energy imparted upon photo-dissociation is at most a minor channel. Pumping the vibrations of the higher energy HF–HCN isomer, in contrast, lead to quantitative transfer of the population to the lower energy HCN–HF isomer. Two mechanisms were proposed to explain this result. One is that for this complex, vibrational energy redistribution (IVR) is sufficiently fast that photo-dissociation does not take place. Instead, one creates a vibrationally hot molecule with energy well above the isomerization barrier, and that this cools sufficiently slowly that the system anneals to the lowest minimum structure. The alternative is that photo-dissociation does take place but produces a vibrationally excited product that does not relax until after recombination. The subsequent vibrational relaxation of the complex then leads to annealing. Time-resolved pump–probe spectroscopy, with sufficient time resolution to ‘catch’ the absorption spectrum of the fragments before geminal recombination, is clearly needed to resolve this ambiguity in the mechanism.

5.9. Complex formation in helium droplets

Helium nanodroplet spectroscopy has been used to study complexes since the first IR spectral study by Goyal et al [1]. Here, we will restrict discussion to work that have appeared since the entire field was reviewed in the special issue on helium nanodroplets that appeared in the Journal of Chemical Physics in late 2001.

The study of weakly bound complexes formed in supersonic expansions is a well-established method that has provided great insight into noncovalent interactions between molecules. Likewise, the study of the IR spectra of complexes trapped in cryogenic matrices, particularly Ar and Ne, is also a well-established technique. The study of complexes in helium offers several features that compliment these other methods. For one, the long-range ‘steering’ of molecules when formed in helium can lead to the selective production of structures that are not formed significantly in jets or classical matrices. The cooling provided by the helium allows the quenching of complexes in higher energy structures that are separated by even modest barriers from the global minimum structure. The most dramatic example of this is the formation of long, polar complexes of HCN and HCCCN [86, 231]. A more recent example is the exclusive formation of an ‘open’ polar form of formic acid dimer [232]. Such barriers are particularly important when preformed hydrogen-bonded rings must be broken up to reach the minimum energy structure for the next larger complex. In a study of the growth of HF polymers in helium, it was found that a cyclic tetramer is formed (which requires insertion into the cyclic trimer), but that the fifth HF is not able to enter the ring and thus leads to a polar pentamer [233]. The formation of cyclic water complexes has also been studied [234, 235]. For the complex of HF and HCN, both hydrogen-bonded complexes are formed in helium [230] while only the lower energy HCN–HF complex is observed in jet spectroscopy. In contrast to that, for complexes between HCCCH and HF only the ‘T’-shaped isomer is observed in helium despite a predicted minimum in the HCCCH–FH structure [233]. It is presumed that the latter is shallow enough that the system can tunnel out of this minimum even if initially
populated. It has been demonstrated that helium can trap and allow the study of ‘entrance channel complexes’ (Cl, Br, I)–HF [236].

Helium nanodroplets are particularly suited for the study of molecules bound to small metal clusters grown inside the droplet. The Miller group has published several papers reporting the IR spectra of HCN [47, 48, 237], HCCCN [238] and HCCH [239] complexed with Mg atoms and small clusters. Strongly nonadditive shifts in the IR fundamental transition of the molecules are suggestive to changes in the bonding of the Mg clusters, particularly upon going from Mg$_3$ to Mg$_4$ [237].

The Toennies–Vilesov group published an important series of papers on the IR spectra of OCS complexed with different numbers of hydrogen and its isotopomers [56, 58, 240, 241]. A controversial finding of this work is certain para-$\text{H}_2$ clusters become superfluid between the temperatures of 0.37 K (found in $^4\text{He}$ droplets) and 0.15 K (found in mixed $^3\text{He}/^4\text{He}$ droplets). The principal observation supporting this interpretation is the loss of Q branches in the spectrum of these complexes when upon cooling. Paesani et al [148, 242] have performed theoretical calculations that provide support for this interpretation. One of us (KL) and others have argued that this observation is consistent with a set of pH$_2$ rings that can internally rotate (cyclic exchange) and the expected spin statistical weights of the internal rotation levels [6]. A later paper from Toennies and Vilesov [58] reached substantially the same conclusion. It is a semantic question whether such 1D rotations should be considered as ‘superfluid’.

The Miller group has studied HCN [51, 52, 55, 243] and HF [244] complexed with ortho and para $\text{H}_2$ and D$_2$, and with HD, including mixed clusters. Perhaps the most important result of this work is the study of HCN–(HD)$_n$ complexes, where Q branches were found to disappear for $n = 12$ and 13 and reappear for $n = 14$ [52]. This was interpreted as due to the formation of cages with nearly isotropic potentials for HCN rotation for the $n = 12$ and 13 cases. Since HD is a composite fermion, it is clear that the disappearance of Q branches in the IR spectrum cannot be viewed as conclusive experimental evidence for the formation of superfluid solvation shells, no matter how liberally one wants to interpret that phase.

5.10. IR spectra of isolated molecules

The bulk of more recent IR studies of isolated molecules have focused on probing the interactions between the molecule and the helium solvent and the dynamics that are produced. Several studies have explored enhanced line broadening in IR spectra that reflect rapid, solvent-induced relaxation, often facilitated by intramolecular anharmonic resonances. Madeja et al studied the spectrum of h(2)- and d(1)-formic acid in the spectral region of the O–H and C–H stretching vibrations, as well as several combination bands that gain intensity through Fermi and Coriolis resonances [245]. Lindsay and Miller studied the C–H stretching fundamental spectrum of ethylene [246], while Scheele et al studied the first C–H stretching overtone region of the same molecule [247]. This work again demonstrated extreme variation in broadening between different vibrational bands. Slipchenko and Vilesov have re-examined the 3 $\mu$m spectrum of NH$_3$ [248], greatly extending a previous, lower resolution study [249]. This work demonstrated that the rotational constants ($B$ and $C$) are reduced by only 5% compared to the gas-phase values and that the inversion splitting is within 6% of the gas-phase value. The latter is perhaps surprising in that one would expect a significant change in helium solvation upon inversion, thereby increasing the tunnelling mass.

The Havenith group has studied the fundamental IR spectra of both NO [250] and CO [251] in helium. In the case of NO, they found that the rotational spacing between the lowest two levels was 76% of the corresponding gas phase value, demonstrating that this
molecule is in the ‘intermediate following’ limit, as had previously been experimentally demonstrated for HCN and DCN [141]. For the Q(0.5) 2Π1/2 transition (between the lowest rotational levels of each vibrational state), the transitions are quite narrow and laser limited (∼150 MHz FWHM), and they were able to resolve both the Λ doubling and hyperfine splittings. The hyperfine interaction constant is unchanged in helium, demonstrating the small effect of the helium on the electronic density of the NO molecule. The Λ doubling constant is increased by 55% compared to the gas phase. This is the opposite effect from that expected, based upon the change in B value and also the expected increase in the Rydberg-type excited states. These authors point out that 90% of the Λ doubling arises from mixing of excited 2Σ valence states, which are expected to be only weakly shifted in helium. The authors suggest that the confinement of the unpaired electron by the helium may increase the matrix element ⟨Σ|L_y|Π⟩ (which appears in the expression for the Λ doubling splitting). They offer as an additional possible source for the increased Λ doubling helium density fluctuations in the helium droplet that slightly perturb the rotational symmetry around the NO axis. For a rigid NO in a 2Π state, the helium density should undergo Jahn–Teller distortion leading to a difference in helium density in the nodal plane of the Π orbital compared to that perpendicular to it, i.e. leading to the anisotropy of helium density that the authors predict. For the Q(1.5) transition, the fine and Λ doubling splittings are unresolved, and the transition is Lorentzian with a FWHM of 1.05 GHz, which suggests that the upper rotational state relaxes with a population lifetime of 152 ps. This is a relatively fast decay (for helium). Rotational relaxation J′ = 1.5 → 0.5 will liberate 4.965 cm\(^{-1}\) of energy, well below the energy required to produce a roton (∼6 cm\(^{-1}\) in bulk helium). The authors attribute this broadening as due to coupling of the NO rotation to droplet phonons. As discussed above and also by the authors in their CO paper (see below), one must assume that the phonons are themselves coupled to some much higher density of states in order to rationalize the observed smooth Lorentzian lineshape.

In the IR spectrum of CO, only the R(0) line could be observed due to the low temperature of the droplets relative to the rotational spacing. However, by observing the same transition in four isotopic species (\(^{12}\)C\(^{16}\)O, \(^{13}\)C\(^{16}\)O \(^{12}\)C\(^{18}\)O and \(^{13}\)C\(^{18}\)O) and exploiting the different reduced mass dependence for the respective constants, the shifts for both the vibrational frequency and rotational constant (more properly the J = 0–1 spacing) were deduced. The rotational constant of \(^{12}\)C\(^{16}\)O is 62.9% of the gas-phase value, confirming that CO is also an intermediate following molecule. The authors point out that this reduction is larger (in per cent) than that of HCN (79%), despite the fact that the gas phase rotational constant of CO (1.922 cm\(^{-1}\)) is larger than that of HCN (1.478 cm\(^{-1}\)). This is attributed as due to a significantly higher anisotropy of the interaction potential of CO with He compared to that of HCN with He. Quantum Monte Carlo calculations on clusters CO–He\(_N\) (\(N = 1–30\)) by Cazzato et al [151], rotational excitation energies combined with vibrational shift calculations by Paesani and Gianturco [252] are in excellent agreement with IR experiments on such cluster sizes [253]. These calculations found that the rotational excitation energy was almost constant after the completion of the first helium solvation shell (\(N = 14\), and by extrapolation predicted a nanodroplet B value, 78% of the gas phase value, considerably larger than what was found [251]. von Haefen et al interpret this extra reduction as due to interaction of the CO rotation with long wavelength phonons in the droplet which are not present in the small clusters. This is supported by calculations using the CBF/DMC method [158]. These calculations predict a nanodroplet CO rotational excitation, 69% of the gas-phase value (compared with 63% inferred from the experiment).

For all four isotopic species of CO, the R(0) transitions exhibit Lorentzian lineshapes with FWHM of 1.02 GHz, almost identical to that observed for the NO Q(1.5) transition. In the CO
case, the energy released upon rotational relaxation is only 2.2 cm$^{-1}$, well below the energy of both roton formation and quantum evaporation (4.4 cm$^{-1}$ for droplets of 2600 helium atoms). The CBF/DMC calculations (which treat the phonons as continuous instead of discrete as they are in nanodroplets) predict a homogeneous width of 0.54 GHz, approximately one-half the observed value. The authors discuss the fact that the phonons alone cannot provide the needed quasi-continuum to produce a homogeneously broadened line of 1 GHz width. They report that if one includes all the states generated by coupling of droplet phonons and centre of mass motion states [114] for the CO, this produces a density of about ten states per linewidth of the CO transition. They assign the line broadening as arising from inelastic relaxation of the excited $J = 1$ level of CO into $J = 0$ levels of CO with production of excitation in mixed phonon/centre of mass motion states. No mechanism was proposed for the coupling that would produce such simultaneous excitation of phonons and translational motion. We would like to note that such a coupling is of higher order and thus likely weaker than the direct coupling of the rotor to the phonons. The centre of mass motion potential is nearly harmonic and thus strong propensity rules for its change in quantum numbers are expected. We would also like to point out that elastic orientational relaxation (changes in the $M$ quantum number) will also lead to line broadening in the IR spectrum and this is most effective for low $J$ states [254]. The ripplon states excited in the droplets (and the translational motion states) have a high degeneracy in the harmonic limit and these could couple to the angular momentum of the molecule (as was explicitly calculated for HCN in [114]). Time-resolved pump/probe experiments with polarized light could provide unambiguous determination of the relative contributions of elastic, inelastic and pure dephasing contributions to the homogeneous broadening in the spectrum of CO and other molecules.

Nauta and Miller reported the spectra of diacetylene and cyclopropane [255]. In both cases, the rotational constants are the factor of \( \approx 3 \) smaller than the corresponding gas-phase values expected for heavy rotors. The asymmetric C–H stretch of diacetylene shows a small vibrational origin redshift (\(-0.304\) cm$^{-1} \)) in contrast to the small blue shift (\(+0.13\) cm$^{-1} \)) observed for the corresponding band of acetylene. Rotational independent line broadening with FWHM of 1.6 GHz is observed\(^4\) which is attributed to vibrational relaxation. For the observed $\nu_8$ C–H stretching mode of cyclopropane, the fundamental wave number is blue shifted by \(+4.069\) cm$^{-1} \), rather a large vibrational shift. Küpper et al obtained the $3 \mu m \nu_1$ spectrum of propargyl radical, formed from a pyrolysis source [37]. The authors provided the first experimental determination of the dipole moment (\(-0.15\) Debye) of this important free radical species. Stiles et al [256] carefully studied the Stark effect to determine the effective dipole moments in helium of HCN (2.949(6) compared to 3.017 46 Debye in gas phase), HCCCN (3.58(8) compared to 3.731 72 Debye for gas phase). For the first time this work demonstrates the perturbation that helium spectroscopy introduces into the determination of dipole moments. The authors found that these small shifts in the effective dipole moments could be accounted for by helium polarization, using an elliptical cavity model with realistic parameters.

The Vilesov group has used an OPO and H$_2$ crystal Raman shifting of the OPO to re-examine the IR spectra of several simple molecules, including H$_2$O, NH$_3$ and CO$_2$. In the case of H$_2$O [257], they have found that all the monomer transitions can be assigned (three from the $\nu_3$ band and two from the $\nu_1$ band) start from the lowest ortho and para rotational levels. Transitions previously assigned to higher lying rotational levels of H$_2$O (which would imply incomplete rotational relaxation) were established to be water dimer transitions. From

\(^4\) Note that there is a typographic error in the unit of the linewidth reported in table 1 of this paper, as inspection of the simulated spectrum presented in figure 1 makes it obvious. The unit should read cm$^{-1}$, not MHz.
the limited number of transitions, only one combination difference could formed (between the 2_{02} and 0_{00} levels in the ν_3 excited state) and this differs by only 0.5% from the corresponding gas-phase value, indicative of the tiny effect helium has on the rotational constants of H_2O. The three transitions to levels that are symmetry allowed to undergo rotational relaxation have FWHMs between 2.3 and 3.0 cm\(^{-1}\), which implies lifetimes of 2 ps. The two transitions that go to the lowest ortho or para rotational level in the excited vibrational state have nearly laser-limited linewidths of 0.34 cm\(^{-1}\). Saturation measurements indicate that the excited state vibrational relaxation lifetime is at least 7 ns, the length of the excitation pulse.

Slipchenko and Vilesov [248] observed the 3 μm spectrum of NH_3 and observed a total of ten transitions in the ν_1, ν_3, 2ν_4(l = 0) and 2ν_4(l = 2) vibrational bands. They also reassigned an earlier spectrum observed in the ν_2 umbrella fundamental. Like for H_2O, transitions only come from the lowest rotational level for the ortho and para species, though the upper tunnelling level of the J = K = 1 level is weakly populated. All transitions are close to the gas-phase values, and fits (which require some constraints given the few transitions observable) predict B and C rotational constants \approx 95% of the gas-phase values, as expected for such a light rotor (B = 9.96 cm\(^{-1}\)). The sum of the tunnelling splitting of the ground and excited ν_1 state was found to be 1.67(5) compared to a gas-phase value of 1.78 cm\(^{-1}\), indicating a small perturbation on the inversion frequency, especially compared to the previous analysis of the ν_2 spectrum. Again, as in the case of H_2O, transitions to levels that have symmetry-allowed rotational relaxation channels are broadened, indicating lifetimes of 1–7 ps, while transitions to levels with only vibrationally inelastic decay channels have nearly laser-limited widths of 0.33 cm\(^{-1}\) FWHM. This includes the sQ(1,1) level which could relax via relaxation by transition to the lower tunnelling inversion level (a \rightarrow s) in the excited state.

Hoshina et al. [258] recently reported observation of a ‘phonon wing’ in the R(0) absorption of CO_2 in the fundamental band [258]. All previous IR spectra were assigned to pure excitation of the solute molecule, but observations of phonon wings are quite common in electronic spectra in helium. The strength of the phonon wing reflects changes in the helium solvation structure upon excitation, which are expected to be much larger upon electronic than vibrational excitation. The large cross section of the CO_2 fundamental band combined with the high peak power of the pulsed laser source used allowed the broad, phonon wing to be brought up in intensity by the saturation of the pure molecular excitation (zero phonon line). These authors further reported that the fractional intensity in the phonon sideband can be predicted using a ‘toy model’ of a rigid, planar ring of helium atoms coupled to the rotation of the molecule [259]. This suggests that in this case the phonon wing does not arise from the changes in helium solvation structure upon vibrational excitation, but rather due the rotational excitation of the molecule and its coupling to helium rotation of the first solvent shell. A prediction of this model for the phonon sideband is that the relative strength should be very weakly dependent upon the degree of vibrational excitation and also that the phonon sideband should be predictably stronger for the R(1) transition, which could be observed in the C^{18}O_2 isotopic species.

5.11. Small helium clusters

While outside the formal scope of this review, we would like to close by briefly reporting on important recent work on helium clusters smaller than those we have considered until now.

Toennies and co-workers have continued to study small 4He and mixed 3He/4He clusters using transmission diffraction gratings to spatially resolve clusters by mass as they introduced in [260]. Recently, they reported enhanced production of 4He clusters with certain ‘magic number’ sizes (N = 10–11, 14, 22, 26–27 and 44 atoms) [261]. This was quite surprising as
the best DMC calculations [262] indicate that no enhanced stable clusters should exist based upon their ground-state energy. However, the magic number clusters are predicted to have reduced free energy due to the creation of additional stable ripplon modes as the clusters grow [261].

Particularly germane to the subject of this review is a series of papers reporting the IR (McKellar group) and microwave spectra (Jäger group) of simple molecules with growing numbers of helium atoms. These include OCS [263–265], NNO [266], CO$_2$ [267, 268], and CO [253, 269]. They have been able to follow how the spectra evolve as helium atoms increasingly solvate the molecules, following the spectra up to $N = 19$ for the cases of CO and NNO. For the cases besides CO, the first helium atoms strongly bind to the side of the linear molecules and a fairly rigid ring builds up. The moments of inertia are close to the classical values and rise with increasing number of helium atoms. However, once this ring is saturated, the additional helium atoms become more loosely bound, primarily on the ends of the molecules. This opens up the possibility of quantum exchange and leads to a decrease in the moment of inertia as more helium atoms are added. In detail, the rotational constants have a complex and highly structured evolution with the number of helium atoms which provides a window into the changing rotational dynamics. It is clear that the convergence to the nanodroplet limit is quite slow with a lot of road to be yet explored. Particularly insightful have been a series of DMC calculations that have extracted the excitation energies by fits to the imaginary time correlation function for the rotor orientation [146–153]. These have been in quantitative agreement with the experiments, nearly reproducing every detail of the changes of rotational constant with $N$.

6. Conclusions

As we hope this review makes clear that the field of helium nanodroplet spectroscopy is advancing rapidly, and much has been learned in the past years. The field is mature in the sense that many of the basic spectroscopic properties of molecules solvated in helium can now be predicted. The location and binding of a given solute at the surface or in the bulk of the droplets is well conceived as well as the temperature determination and cooling mechanisms. We have a good understanding of the size of helium perturbations to the spectroscopic constants of the molecule, though we still lack generally predictive theories. We have learned how to exploit the unique properties of helium droplets to make novel chemical species and probe them in new ways. However, our understanding of the dynamical coupling of the solute to the helium remains limited. Ultrafast pump–probe experiments have provided the first direct view into the reorganization of the helium solvent following photo-excitation. Moreover, several recent pump–probe experiments done with ns and even cw lasers have also provided windows into the dynamics of molecules in helium on time scales longer than accessible with ultrashort pulses. The feasibility to study complex dynamical processes is demonstrated in the mentioned experiments, but much more can and needs to be done. In particular, we look forward towards the development of time-resolved state-to-state measurements that will reveal the detailed flow of molecules through state space as they relax in this quantum solvent.

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