Helium droplets: a chemistry perspective

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Helium droplets provide an exotic and unique environment for the study of physical and chemical phenomena. Properties of these droplets include a low temperature (0.37 K), their superfluidity, and the ability to easily add a wide variety of atoms and molecules. This *tutorial review* provides a concise account of the basic principles of helium droplets, including how to form, dope, and interrogate these objects. There then follows a series of selected applications grouped under particular themes, with strong bias towards topics likely to be of particular interest to chemists.

1. Introduction

There are several reasons why scientists are motivated to study atoms and molecules at very low temperatures. One incentive is that quantum mechanical effects are more pronounced as the temperature begins to approach absolute zero. This can be seen from the de Broglie equation, which links the wavelength of a single particle, λ , to its linear momentum, p , through the expression $\lambda = h/p$, where h is Planck's constant. For a collection of gaseous particles the average momentum of the particles will decrease as the system is cooled and the average wavelength will

therefore increase. When the wavelength of each particle becomes comparable to the nominal size of the particle we move into a regime where fascinating quantum mechanical phenomena can occur, such as Bose–Einstein condensation and superfluidity.

Chemists are more typically focused on molecules and important benefits accrue from studying molecules at low temperatures. By reducing the temperature fewer and fewer quantum states have significant occupation probabilities. This is commonly exploited in spectroscopy, since it reduces spectral congestion and can either sharpen lines (in low resolution experiments) and/or simplify the spectral assignment process. In addition, working at low temperature makes it possible to form chemical species that would have, at best, only a fleeting existence at room temperature. It is through such low temperature experiments that exquisitely detailed information on free radicals, molecular

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ions, and weakly bound clusters of molecules have been collected in recent decades.

Simple refrigeration, where the vessel containing the desired molecules is cooled to a temperature of a few K or less, is generally unsuitable for producing cold molecules. Suppose, for example, that the aim is to cool N_2 to 10 K in order to record spectra of individual molecules in the gaseous state at this temperature. If the N_2 gas is inside a sealed container, which in turn is placed inside some appropriate refrigeration device, the gas will condense into a liquid at ~ 77 K and will solidify at ~ 63 K. Thus the original aim of maintaining a gaseous system at 10 K is defeated by condensation, a problem that would be encountered for any type of molecule.

The solution to the condensation problem has been known for many decades: cool the molecules in a seeded free jet (supersonic) expansion. This involves mixing the desired molecules with an excess of inert carrier gas, such as helium or argon, and expanding the mixture under pressure into a vacuum through a pinhole aperture. The system cools by isentropic expansion, which converts random translational energy into directed flow *via* two-body collisions. In this way it is possible to achieve a translational temperature, as defined by the *distribution* of particle velocities, of <1 K. However, the combined effect of decreasing translational temperature and decreasing particle density as the gas recedes from the pinhole largely eliminates the three-body collisions necessary for condensation. Additional cooling of the internal degrees of freedom of the molecules, particularly the rotational motion, occurs through the exchange of rotational and kinetic energy *via* two-body collisions, but the finite number of collisions means that this is always incomplete and so a higher ‘temperature’ for the rotational degrees of freedom is the norm, although rotational temperatures of a few K or even lower are attainable.

An alternative means of cooling molecules was demonstrated in the early 1990s. It had long been known by that time that large clusters of helium, which we refer to from here onwards as helium droplets (HeDs) because of their liquid behaviour (see below), could be made by pre-cooling the gas to low temperature and then expanding into a vacuum to complete the cooling process. However, it wasn't until the early 1990s that studies of atomic and molecular dopants in and on HeDs began. In particular, once spectroscopic techniques were developed to detect dopant molecules inside HeDs,^{1,2} powerful techniques were born to probe both the droplet itself and the dopants inside or on the surface of the droplet. Many properties were quickly established including the very low temperature of the HeDs (0.37 K)³ and the unimpeded rotation of dopant molecules, which has been taken as evidence of superfluidity in the doped droplets.⁴ There are some distinct advantages of using HeDs to study molecules when compared to supersonic gas expansions, some of which will be rehearsed below. At this point we can simply note that HeDs provide a gas-like environment within which molecules can be trapped and cooled to a very low temperature. This distinguishes HeDs from other rare gas matrices, such as low-temperature argon matrices, which are solid and provide a rigid cage within which molecules are fixed in location and usually cannot even rotate.

Several reviews on HeDs and their applications already exist (see, for example, ref. 5–10), but this review aims to extract topics

of particular relevance to chemists. The ‘tutorial’ nature of this review means that the material will be presented in what will hopefully be an accessible and concise form. After brief descriptions of the properties of HeDs along with some experimental details, we turn to consider a number of areas of molecular science where HeDs offer new insight or provide new capabilities. In keeping with the format of tutorial reviews, the aim is not to provide an extensive survey of the literature, but is instead more selective in its coverage while still hoping to convey some of the excitement of past work and the scope for future discoveries.

2. Properties of helium droplets

^4He is the most abundant isotope of helium. The exceptionally weak interactions between helium atoms mean that low temperatures are required to liquefy this element. ^4He has a critical temperature of 5.2 K and thus cannot be liquefied at temperatures above this even with a large excess pressure.¹¹ At atmospheric pressure the boiling point of ^4He is 4.21 K, but a truly remarkable observation is that ^4He does not solidify at atmospheric pressure even at a temperature of absolute zero. This property derives from a combination of the low mass of atomic helium and the exceptionally weak attractive forces between helium atoms, which means that the zero point vibrational energies within the condensed phase are comparable to the very weak interatomic binding energies, thus preventing individual atoms from being pinned to a particular lattice site (except at high pressure). Liquid helium is often referred to as a quantum fluid because its properties are strongly influenced by the large amplitude zero point vibrational motion, a quantum mechanical phenomenon.

Bulk liquid ^4He shows another remarkable property: a change in phase at 2.18 K.¹¹ Above 2.18 K helium behaves like most other liquids and this phase is sometimes referred to as the ‘normal’ fluid phase, or the He I phase. However, below 2.18 K the liquid becomes a superfluid, designated as He II, which confers some astounding properties including a viscosity approaching zero and a thermal conductivity approaching infinity. We will not delve into the physics of superfluids in this article. Suffice it to say that the ability to form the superfluid phase derives from the bosonic nature of ^4He particles (they have zero net spin) and at a sufficiently low temperature the system can be described by a single macroscopic wavefunction in which individual particle identities are lost. This, in essence, is the superfluid phase.

The temperature of bulk liquid helium can be continuously adjusted up or down using refrigeration techniques. However, imagine instead that a small droplet of liquid helium is introduced into a vacuum. At least initially the droplet will not be in thermal equilibrium with its surroundings. As already mentioned above, the He–He binding energy is exceptionally weak: in the bulk phase this is 5 cm^{-1} and we will assume that the same applies to HeDs.¹² If the HeD is initially formed with excess energy, it can easily be removed by evaporating helium atoms. This is a rapid process because the energy removed per helium atom is small and, at least in the superfluid phase, the thermal conductivity of helium is exceptionally high. Evaporation will continue until the energy content of the droplet is insufficient to evaporate any further helium atoms. Experiment has shown that the steady-state temperature reached

is close to 0.37 K and thus a newly formed ^4He droplet will automatically cool to a temperature which puts it well into the superfluid phase. If the properties of the bulk scale are assumed to be transposed to the nanoscale, a liquid HeD would be expected to have an exceptionally high thermal conductivity and an exceptionally low viscosity. Thus, if a molecule is placed inside this environment, it should cool rapidly to 0.37 K and yet can translate and rotate more freely than would be the case in a normal liquid. As will be seen later, there is abundant evidence for exactly this behaviour.

A brief mention of the other isotope of helium, ^3He , is appropriate. Liquids of this isotope only become superfluid at temperatures below 0.003 K. This stark difference between ^4He and ^3He arises because the latter is a fermion (half integer net spin), whereas superfluid formation requires bosons (integer net spin). The reason why liquid ^3He is able to form a superfluid at all is that ^3He atoms are able to pair up to form bosons, but this is only possible at exceptionally low temperatures. Droplets of ^3He have been formed and these are expected to reach a steady-state temperature of 0.15 K after evaporative loss of helium atoms, which is lower than for ^4He droplets because of the higher zero point vibrational energy in liquid ^3He , which reduces the He–He binding energy to 1.9 cm^{-1} . Thus ^3He droplets are not superfluid and this makes them far less useful as hosts for the study of the rotation of molecules when compared to ^4He droplets. A very important practical issue is that ^3He has a natural abundance $\sim 10^6$ times lower than ^4He , which makes it far more expensive than ^4He . Consequently, from here onwards our focus will be entirely on ^4He droplets.

3. Experimental techniques

3.1 Making helium droplets

For many applications the preferred size of HeDs numbers a few thousand He atoms. Assuming spherical droplets with the same density as bulk liquid helium, these droplets will have a diameter on the order of a few nm.⁵ Consequently, these droplets are often referred to as nanodroplets. This size regime

Fig. 2 Illustration of the range of helium droplet sizes for two different sets of sub-critical expansion conditions, with the trace in blue corresponding to a larger mean droplet size than the trace in red. Conversion of the distribution shown in red to the one shown in blue can be achieved by lowering the nozzle temperature and/or by raising the helium stagnation pressure.

is accessed by pre-cooling gaseous helium, typically to temperatures between 10 and 20 K and pressures of several tens of bars, and then expanding into vacuum to continue the cooling process. Condensation occurs early in the expansion process and then further cooling of the droplets proceeds by evaporative loss of helium atoms until the steady-state temperature of 0.37 K is reached, as illustrated in a simplified fashion in Fig. 1. Given that droplet formation is a statistical process, a beam of monodisperse HeDs is not expected. In fact for HeDs formed from gas condensation the droplet size distribution is expected to be a log-normal distribution, as illustrated in Fig. 2, and evidence based on scattering measurements supports this assumption.¹³ It is common to use the mean size, $\langle N \rangle$, where N is the number of helium atoms, as a measure of the droplet size. $\langle N \rangle$ can be altered by adjusting source conditions, most notably the helium stagnation pressure and the temperature of the nozzle. As the temperature is reduced and/or the pressure is increased $\langle N \rangle$ increases.

With a continuously operating helium droplet source of the above type the typical aperture diameter for the nozzle is 5–10 μm , although larger apertures can be used if pumps of very large speed are available. To help prevent blockage of the aperture by condensation of impurities, helium with at least 99.9999% purity is highly desirable. Pulsed HeD sources have

Fig. 1 Simplified illustration of a helium droplet nozzle and pickup source. A mass spectrometer is located downstream of the pickup source which can be used for beam diagnostics, as well as for recording depletion spectra (see Sections 3.3 and 3.4).

also been produced and offer the advantage of requiring a reduced pumping capacity when compared to continuous sources.^{14–16} Pulsed sources can also operate successfully with lower purity helium gas than continuous sources because the apertures for the former are much larger than the latter.

Two other droplet formation regimes can be exploited, both of which operate at lower source temperatures than the gas condensation (subcritical expansion) scheme described above. In the supercritical regime the droplets are formed from liquid helium behind the nozzle, which then undergoes fragmentation into droplets as it passes through the pinhole,¹⁷ resulting in an exponentially varying distribution of droplet sizes.¹⁸ At even lower source temperatures near to or below the bulk superfluid phase transition temperature, 2.18 K, the liquid helium can be driven out at pressure to form a microjet, which subsequently fractures into droplets with diameters similar to the size of the nozzle aperture. Huge and nearly monodisperse droplets, with on the order of 10^{10} helium atoms and therefore diameters on the micron scale, can be formed in this way.¹⁹

3.2 Adding dopants

Dopants are added to HeDs by collisions with gas/vapour downstream of the nozzle, a so-called *pickup* process. The normal arrangement is to select the central portion of the HeD expansion using a skimmer and then one or more dopants are added in a subsequent vacuum chamber (see Fig. 1). The pickup process is statistical, and so the acquisition of a specific number of dopant atoms/molecules is not possible even in the hypothetical case of a monodisperse source of HeDs. The pickup probability is governed by Poisson statistics, with the probability that k atoms/molecules will be picked up being given by

$$P_k = \frac{(\rho\sigma l)^k}{k!} \exp(-\rho\sigma l) \quad (1)$$

where ρ = number density of the pickup gas/vapour, σ is the cross sectional area of the HeDs (which is given by $15.5\langle N \rangle^{2/3} \text{ \AA}^2$ for ^4He assuming a uniform density close to bulk liquid helium⁵), and l is the length of the pickup zone. Eqn (1) shows how the pickup process scales with the easily adjustable experimental parameters, namely the partial pressure of the dopant in the pickup zone and the size of the HeDs. The partial pressure for optimum pickup of a single dopant atom or molecule is typically on the order of 10^{-6} mbar, but of course the precise value will depend on the sizes of the HeDs and the length of the pickup zone.

There are several assumptions implicit in eqn (1), including a fixed droplet size and also that the droplet size does not change as dopants are added. We have already seen in the previous section that the first of these assumptions is flawed. The assumption of an unchanged droplet size after dopant pickup is also flawed. If a molecule is added to a HeD it will eventually transfer both rotational and vibrational energy into the droplet, as well as kinetic energy from the collision. For a small molecule with a high vibrational frequency the mean vibrational energy per molecule will be small at room temperature but the mean rotational energy should be close to the classical limit of $3kT/2$, or $\sim 310 \text{ cm}^{-1}$. This energy will be dissipated relatively quickly by

Fig. 3 Graph showing how the probability of picking up k dopant atoms/molecules varies with pick-up pressure for a fixed mean helium droplet size. The distributions are derived from Poisson statistics, as per eqn (1).

helium atom evaporation, eliminating some 60 helium atoms from the droplet on average. Likewise, the kinetic energy from the collision will also be dissipated rapidly. The energy added will scale with the number of molecules, but there will be additional energy released as the molecules bind together. If the molecules undergo van der Waals binding the additional energy released will be small but if stronger bonds are formed between constituent particles this could lead to evaporation of a sizeable proportion of the surrounding helium, or in an extreme case the entire droplet.

Given the aforementioned flaws, it might seem that eqn (1) would be of little value. However, providing the HeDs are sufficiently large such that dopant addition does not create a large change in droplet size, eqn (1) turns out to be a useful guide in assigning a specific spectroscopic signal to a particular sized cluster or complex. To do this, the signal needs to be monitored as a function of dopant partial pressure and the response can be compared with eqn (1) to find the value of k that yields the best fit. An illustration of the Poisson curves for different values of k is shown in Fig. 3.

Dopants that are gaseous or derived from volatile liquids are easy to add to HeDs. For less volatile species an oven can be used to heat the sample to a sufficiently high vapour pressure. This has, for example, been used successfully to add metal atoms to HeDs.²⁰ Notice that the relatively high temperature required for metal evaporation does not lead to any destruction of the HeDs through radiative heating since HeDs are transparent to radiation spanning from the microwave through to well into the vacuum ultraviolet region of the electromagnetic spectrum. Laser ablation has also been used to add metal atoms to HeDs but in that case care must be taken to avoid the highly energetic ablation plasma from coming into contact with the HeD beam.²¹

To close this section we ponder why there is such interest in adding dopants to HeDs when one might just as well try adding them to bulk liquid helium. The principal reason derives from the poor solvation characteristics of liquid helium, which makes it difficult to inject and retain dopants inside bulk liquid helium since they will rapidly coagulate at the walls of the vessel. By way of contrast HeDs are wall-free nanoscale helium cryostats and so this problem is completely avoided: the dopants have nowhere else to go.

3.3 Mass spectrometry of doped helium droplets

How can you ascertain that you have successfully formed HeDs? The simplest diagnostic is to record a mass spectrum. Since HeDs are a collection of loosely bound helium atoms, the threshold ionization energy for a HeD will be similar to that of a single helium atom, 24.59 eV. Thus electron impact at the energy typically used in mass spectrometers, 70 eV, is far above the ionization threshold and leads to the formation of He^+ and He_n^+ cluster ions in the gas phase when applied to HeDs. Fig. 4 shows part of typical mass spectrum derived from nominally pure HeDs. The detection of a series of He_n^+ ions is a clear indicator of HeD formation,^{22,23} since only He^+ will be observed if gaseous helium is present in the absence of HeDs.

When a dopant is located inside a HeD electron impact ionization can ultimately lead to the positive charge residing on either a helium cluster ion, as is the case for pure HeDs, or on the dopant. Providing dopant addition does not significantly change the HeD size, the initial ionization event is unchanged, namely removal of an electron from a helium atom somewhere in the droplet and most likely near the surface: the probability of direct electron impact ionization of the dopant is statistically small, especially if it is deep within the HeD. However, once a He^+ ion is formed the charge can resonantly hop between adjacent helium atoms until the hopping chain is terminated either by the irreversible formation of He_2^+ , leading ultimately to the ejection of He_n^+ ions into the gas phase, or by the formation and ejection of dopant cations. The available evidence suggests that the positive charge can hop between up to 10 helium atoms and if the dopant has not been reached by this point the charge localizes and forms He_2^+ .^{24–26} If the charge reaches the dopant this is an irreversible process because all molecules have ionization energies well below that of helium, creating a huge energy barrier for the reverse process.

As discussed in a later example, photoionization can also be used to ionize dopants in HeDs. Recent studies have shown that it is also possible to use low energy electron impact of doped HeDs to form and eject *anions* of dopant molecules and their clusters.²⁷

Fig. 4 Part of a mass spectrum obtained from undoped helium droplets. This mass spectrum was recorded using a time-of-flight mass spectrometer equipped with a 100 eV electron beam for ionization. The dominant features are due to He_n^+ cluster ions.

3.4 Spectroscopic detection of molecules in helium droplets

The most widely used means of recording spectra of molecules in HeDs is depletion spectroscopy. Since helium is transparent to all but very short wavelength radiation, as mentioned in Section 3.2, only the dopant can absorb the light from traditional laboratory laser sources. If absorption takes place, energy is added to the doped droplet and may ultimately appear as heat in the droplet, leading to the evaporation of helium atoms. For example, if a photon is used to excite a C–H stretching vibration in a molecule at 2900 cm^{-1} , this will ultimately lead to the evaporation of 580 helium atoms from the surrounding droplet, assuming each takes away only the minimum possible energy, 5 cm^{-1} (see Section 2). If a means is found to measure the shrinkage in droplet size, this could in turn be used to register successful light absorption by the dopant.

In the earliest spectroscopic experiments on doped HeDs the reduction in HeD size after dopant light absorption was detected using a bolometer, which is a sensitive heat measuring device. As the droplet shrinks the energy delivered into the bolometer by the impinging droplet beam is reduced, and thus a so-called *depletion* spectrum can be acquired by scanning the wavelength of the light source (a laser) while measuring the bolometer output.¹ An illustrative experimental arrangement for this type of experiment is shown in Fig. 5. An alternative means of registering droplet shrinkage was demonstrated by the Göttingen group of Toennies and co-workers, who used a mass spectrometer instead of a bolometer for detection (see Fig. 1).² The ion signal following electron impact ionization is proportional to the size of the HeD, since the ionization cross section is related to the geometrical cross section of the droplet, and this can therefore be used to register evaporative loss of helium atoms. Whether using a bolometer or a mass spectrometer, the preference in a depletion spectroscopy experiment is for relatively small droplets on the order of 2000–5000 helium atoms to ensure that depletion produces a large fractional change in the droplet size, which therefore makes it easier to detect the depletion event. Furthermore, working with smaller HeDs also delivers a higher instantaneous number density of droplets, which in turn leads to a higher number density of doped HeDs, thus boosting the potential spectroscopic signal.

Fig. 5 Arrangement used for depletion spectroscopy of a doped helium droplet beam. In this apparatus a bolometer is used to register any decrease in the helium droplet size following laser light absorption. Also shown in this image is a pair of electrodes, which can be used to apply a strong electric field for the determination of the dipole moments of molecules in the helium droplets. In contrast to the apparatus shown in Fig. 1, here the laser beam enters perpendicular to the helium droplet beam but the electrodes serve also as a multi-pass cell to maximise the optical path length. Image taken from ref. 45 and reproduced by permission of the PCCP Owner Societies.

The depletion method has proved particularly successful for recording vibrational spectra, since energy from excited vibrations and from simultaneous excitation of rotational degrees of freedom is efficiently coupled into the helium matrix in most cases. The requirement here is that at least some of the absorbed energy is transferred to the helium on the timescale of the experiment, which is typically a few ms and is determined by the time taken for the HeD beam to travel from the pick-up cell to the bolometer or mass spectrometer. In contrast to vibrational spectra, electronic excitation results in excited states which are often much slower to release their excess energy into the helium matrix, or instead of releasing the energy as heat they release it in the form of fluorescence. Thus the depletion methodology has proved to be more restrictive for recording electronic spectra and laser-induced fluorescence is often used as an alternative.²⁸ Electronic spectra of molecules in HeDs have also been successfully recorded using resonance-enhanced multiphoton ionization (REMPI) spectroscopy.^{29,30}

To close this section, we note that the depletion method has also been used to obtain pure rotational spectra of doped HeDs by exciting with microwave radiation.³¹ This is a remarkable observation given that individual microwave photons fall well short of delivering sufficient energy to remove even a single helium atom. However, with a sufficiently intense microwave source coupled with fast rotational relaxation, such that the same molecule can be excited and de-excited multiple times, sufficient helium atoms can be removed to see a measurable depletion effect, as first shown in the case of HCCCN in HeDs.³¹ This work provided new limits on the rate of rotational relaxation in HeDs, which certainly occurs in $<10\text{ }\mu\text{s}$ for HCCCN and most likely occurs on the ps timescale for this and many other molecules.

4. Illustrative applications

4.1 Where does the dopant reside?

For many applications of HeDs it is important to know whether the dopant is inside the droplet or on the surface. We expect the location to be driven by energetics and an interior location will be preferred if the energy lowering induced by solvation of the dopant by helium atoms exceeds the energy required to create the host cavity within the helium. A simple relationship has been derived by Ancilotto *et al.* which can be used to predict the likely location and this takes the form³²

$$\lambda = \frac{\rho \epsilon r_{\min}}{2^{1/6} \sigma} \quad (2)$$

where σ and ρ are the surface tension and density of liquid helium (note that these are different definitions of ρ and σ from those used in eqn (1)) and $r_{\min}$ and ϵ are the standard Lennard-Jones parameters defining the pair potential energy between the dopant and the solvent. The prediction for helium as the solvent is that dopants for which the Ancilotto parameter, λ , exceeds 1.9 will be solvated in the interior of the HeD while those with $\lambda < 1.9$ will be on the surface of the droplet.

It has been established that all alkali metal atoms reside on the surface of HeDs. The first conclusive evidence for this came

from spectroscopic studies, which showed electronic spectra with band positions which were very similar to those of the atoms in the gas phase.³³ By way of contrast a much larger spectral shift was expected for alkali atoms located in the interior of HeDs. The surface location derives from the exceptionally weak attractive interaction between alkali atoms and helium, which is caused by the diffuse nature of the valence *s* electron and is predicted by the Ancilotto parameter, which is substantially below 1.9 for all alkali atoms. The Ancilotto parameter is more ambiguous for the alkaline earth metal atoms, with values close to 1.9 for Ca, Sr and Ba while Mg shows a value of 2.6. All of the available evidence strongly points towards a surface location for Ca, Sr and Ba but Mg has been a more controversial case and it is only recently, with the assistance of calculations, that a reliable picture seems to be emerging.³⁴ The Mg-He attractive interaction is very weak but just sufficient for an interior location. However, the borderline nature of the Mg-He binding results in strongly delocalized Mg atoms throughout the droplets.

The binding energies of alkali atoms to the surface of HeDs are weak, requiring only $\sim 10\text{ cm}^{-1}$ to desorb the atoms.³⁵ This has important consequences for clusters of alkali atoms, which tend to desorb if a metal-metal bond is formed when more than one alkali atom is picked up by a HeD. For this reason alkali dimers are observed on the surface of HeDs only in their triplet states, since the singlet states form strong chemical bonds which release $>0.5\text{ eV}$ of energy and this forces them to selectively desorb from the droplet surface. Similar findings apply to trimers and tetramers, which therefore also form high spin states on HeDs, but there has been some debate about whether or not even larger alkali metal clusters can form in high spin states on HeD surfaces.^{35,36} In fact it has recently been shown using mass spectrometry that once alkali clusters reach a sufficiently large size they switch from a surface location to an interior location. For Na_n clusters this occurs at $n = 21$ while for K_n clusters the switch to interior solvation occurs for $n > 80$.^{37,38}

When an alkali or alkaline earth atom is combined with other dopants interesting behaviour can be seen. Fig. 6 compares the infrared spectrum of HCN-Mg with that of HCN-Na in the C-H stretching region: these complexes were formed by sequential pickup of HCN and the metal atoms by HeDs.³⁹ The HCN-Mg spectrum is rotationally resolved and shows structure which is characteristic of a linear complex. The effective rotational constant deduced from the data analysis is substantially lower than would be expected for the free HCN-Mg complex, which is a common observation for molecules and their complexes when solvated inside HeDs.⁵ A simplistic interpretation is that a proportion of the helium in the immediate proximity rotates with the complex, creating a larger effective moment of inertia and thus a smaller rotational constant. The precise effect of the helium varies from molecule to molecule. For the lightest rotors very little reduction in rotational constant is seen, presumably because these molecules rotate too quickly for the helium to follow. However, for most molecules the reduction in rotational constants is by a factor of 2–4. Inspection of the rotational structure for HCN-Na shows a completely collapsed rotational structure and a rotational contour analysis gives a rotational constant some 55 times smaller than

Fig. 6 Comparison of IR spectra of Mg-NCH and Na-NCH in the C-H stretching region, showing their dramatically different rotational profiles when placed in helium droplets with an estimated mean size of 7200 helium atoms. The effective rotational constants for these two complexes deduced from the rotational structure are shown on the right hand side. Also shown is the ratio of a calculated rotational constant (obtained from MP2 *ab initio* calculations) for the free molecule to the value measured in the helium droplets. In the case of Mg-NCH the reduction in rotational constant in helium compared to the gas phase is 2.4, which is similar to observations made for many other molecules. However, the reduction for Na-NCH is two orders of magnitude larger and is explained in the main text. Reprinted with permission from ref. 35. Copyright 2007 American Chemical Society.

that of HCN-Mg, a very surprising observation given that similar rotational constants are expected for these two complexes in the gas phase. The inertial following of the surrounding layer of helium cannot explain such a huge decline, and so it has been proposed that the Na atom resides at the surface of the droplet while the HCN is located inside. Thus rotation of the complex effectively corresponds to the rotation of the entire helium droplet about an inertial axis through the centre of the droplet and thus the rotational constant is really a measure of the moment of inertia of the droplet rather than the HCN-Na complex. Variation of the source expansion conditions shows that the rotational constant scales with the mean size of the HeD, providing strong evidence for this model.

Although some metal atoms and their clusters reside on the surface of the helium, steps can be taken to draw these species inside the droplet. A nice illustration of this was provided by Lugovoj *et al.*, who explored the chemiluminescent $\text{Ba} + \text{N}_2\text{O} \rightarrow \text{BaO}^* + \text{N}_2$ reaction, where BaO^* represents electronically and vibrationally excited BaO.⁴⁰ The Ba atoms and N_2O were added in sequence using separate pick-up chambers and a fibre-optic light collector and spectrograph were attached to the N_2O pick-up chamber to record the spectrum of any emitted light. From earlier comments we would expect that Ba will reside on the surface of a HeD and the chemiluminescence spectrum supports this, showing a very broad emission feature characteristic of rotationally hot BaO^* ejected from the surface of the HeD when N_2O is added. In other words, the BaO molecules responsible for this broad emission are formed on the droplet surface and are rapidly ejected into the gas phase without any significant cooling. However, there are also some sharp vibrational bands superimposed upon the broad emission feature which are attributable to electronically excited

but rotationally cold BaO. The assumption here is that the cold molecules derive from BaO molecules which recoil *into* the droplet and then undergo rapid cooling and emission from within the HeD. This is confirmed by altering the experiment to add xenon gas in the first pick-up cell and then Ba and N_2O in subsequent pick-up cells. In this case the broad emission feature disappeared entirely and only the sharp vibrational structure remained. The addition of a cluster of polarisable Xe atoms is thought to provide a sufficiently strong attractive force to drag the Ba atom inside the droplet, prior to the addition of N_2O . Formation of BaO^* therefore takes place by reaction between Ba and N_2O within the droplet and rapid cooling of the BaO^* can then occur prior to fluorescence, removing the hot component entirely.

Away from the alkali and alkaline earth atoms and their clusters and complexes the expectation is that all molecules, at least in their ground electronic states, will reside inside HeDs. Even the diatomic free radical, NO, has been shown to be solvated by the helium.⁴¹ For all larger molecules, including free radicals, the multiple interatomic van der Waals interactions with helium will bring about Ancilotto parameters well above the threshold value of 1.9 for droplet submersion.

4.2 Solute-solvent complexes

Bulk solutions are complex environments from which it is difficult to extract the behaviour of individual molecules. Consequently, there has been considerable interest in developing a 'bottom up' approach to solvation whereby complexes of a solute with one or more solvent molecules are used to model solute-solvent interactions. While such 'microsolvation' complexes can never fully reproduce the interactions in bulk solutions, they can potentially provide information about solvent shell formation and incipient charge transfer between solute and solvent. This information can in turn be used to parameterise computer models of solutions.

There have been many spectroscopic studies of solute-solvent complexes in the gas phase, particularly using free jet expansions. The low number density of complexes in this environment necessitates indirect detection techniques, such as REMPI or photodissociation spectroscopy. However, such techniques can have severe limitations. Photodissociation spectroscopy, for example, can be hampered by high solvent binding energies and/or by long dissociation timescales, which results in many complexes being unobservable *via* this route. Equally, a spectroscopic technique such as REMPI or LIF requires the user to undertake a lengthy search for an accessible electronic excited state, which in addition must also possess favourable properties to allow successful REMPI or LIF spectra to be recorded: such cases are relatively rare and, furthermore, favourable cases can become unfavourable cases with the addition or removal of a single solvent molecule.

Helium droplets offer an alternative environment for studying solute-solvent complexes with the important advantage of allowing an essentially universal spectroscopic technique, depletion spectroscopy, to be used. Furthermore, these complexes are guaranteed to be cooled to the droplet temperature, 0.37 K. In principle it is possible to follow the spectroscopy from the smallest complex, where just a single solvent molecule is in contact with the solvent

molecule, through to complexes with dozens or even hundreds of solvent molecules. Of course there is a serious limitation too; the lack of mass selectivity, which means that spectra become highly congested if a multitude of different sized complexes contribute. Nevertheless, the use of HeDs has considerable potential for providing new information on solute–solvent interactions.

One application has been to explore how molecules behave when mixed with unconventional solvents, such as rare gas atoms or small molecules such as H_2 .^{42,43} The main purpose of these studies, particularly in the case of H_2 as the solvent, is to use the solute as a spectroscopic probe of the solvent behaviour, rather than as a practical means to explore specific solute–solvent interactions. For example, when using two pickup cells, one to add Ne or Ar and the other to add tetracene, the LIF spectrum of the tetracene chromophore was found to depend on the order in which the dopants were added.⁴³ This suggests that the rare gas forms a rigid solid in the HeD, so if tetracene is added first the Ne or Ar packs around the tetracene to ‘solvate’ it, whereas if tetracene is added second it simply sits on the surface of a neon or argon ice particle. On the other hand, the spectroscopy when H_2 was used as solvent was found to be independent of the order of pickup, suggesting that the $(\text{H}_2)_n$ solvent is fluxional under the conditions inside the HeDs.

The most important solvent in chemistry is water. The interaction of a small number of water molecules with chemically important solutes, such as acids and salts, would seem a natural target for HeD applications. In the past few years there have been several spectroscopic studies of $\text{HCl}(\text{H}_2\text{O})_n$ complexes in HeDs.^{44–47} In very small $\text{HCl}(\text{H}_2\text{O})_n$ complexes the HCl is expected to retain its covalent character, but once a sufficient number of water molecules are added the HCl should undergo ionic dissociation. *Ab initio* calculations suggest that this transition occurs at $n = 4$, giving the $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n\text{Cl}^-$ complex. The identification of this solvated ion pair was recently claimed in an infrared study of $\text{HCl}(\text{H}_2\text{O})_n$ in HeDs by Gutberlet *et al.*⁴⁶ but a subsequent investigation by Flynn *et al.* suggests a misassignment, with the spectrum responsible being due to a cyclic $(\text{HCl})_2(\text{H}_2\text{O})_2$ complex.⁴⁷ Consequently, the identification of a fully dissociated acid in the smallest water cluster awaits discovery.

Similar experiments on salt–water complexes in HeDs are possible, although these have so far not been attempted. However, IR spectra of HCN–salt complexes in HeDs, where the salt = LiF, LiCl, NaF or NaCl, have been reported.⁴⁸ The N-bound isomers were found for each of these complexes by recording spectra in the C–H stretching region and from the resolved rotational structures these complexes were shown to be linear. To date these are the only studies of salt–solvent complexes in HeDs, but our expectation is that many more will follow.

4.3 Entrance and exit channel complexes

The unique combination of rapid cooling and a very low ultimate temperature, while maintaining a fluid environment, makes it possible to bring atoms and/or molecules together in HeDs and trap them in very shallow potential energy wells. Among the many interesting systems one might study with this capability are pre-reaction and post-reaction complexes, *i.e.* complexes corresponding to minima in the entrance and exit channels, respectively, on a

reaction potential energy surface. Such complexes are important to characterise because the corresponding potential energy wells can have both qualitative and quantitative effects on reaction rates and product branching ratios. Pre- and post-reaction complexes are often studied using supersonic gas expansions, but while this approach is suitable for some complexes it is less effective when the barrier for subsequent reaction or dissociation is very low. The problem here derives from forming the complex by combining the constituents at a relatively high initial temperature, usually room temperature, which can initiate reaction of pre-reaction complexes or dissociation of post-reaction complexes before cooling has significantly progressed. In contrast, HeDs cool reactants to 0.37 K *prior* to them coming into contact to form a complex. In this way, much more weakly bound and intrinsically more reactive complexes can be formed by helium droplet methodology than are possible with supersonic gas expansions.

A good illustration of this is the observation of the entrance channel complexes for the $\text{X} + \text{HF} \rightarrow \text{HX} + \text{F}$ reaction, where $\text{X} = \text{Cl}$, Br or I . Prior to helium droplet studies information on these X–HF complexes had been extracted only indirectly from anion photoelectron studies or under the low resolution conditions available from IR spectra in solid rare gas matrices. By forming these complexes in HeDs, spectra can be recorded to definitively establish the equilibrium structures. A particular challenge in such experiments is to deliver halogen atoms for pickup by the HeDs. Merritt *et al.* used pyrolysis of the molecular halogens at temperatures >1000 K to achieve dissociation into halogen atoms and with a sufficiently high temperature unit dissociation efficiency could be achieved.⁴⁹ The experiment employed two pickup cells in series, the first of which contained an oven for generating the halogen atoms. The HF was added to the HeDs in the second pickup cell and the partial pressure of HF was chosen so that pickup of a single HF molecule was the most probable event.

Fig. 7 shows two low resolution survey scans in the H–F stretching region for the Br_2 –HF system, the lower one for the oven turned off and the upper one with the oven turned on and therefore generating Br atoms. In addition to seeing signal from the same complexes formed without pyrolysis, a new band appears at 3867 cm^{-1} in the upper spectrum which was assigned to the Br–HF complex. With free rotation possible in helium droplets, rotational structure could be recorded and this is shown in Fig. 8. The rotationally-resolved spectrum shows the simple P, Q and R branch features characteristic of the spectrum of a linear molecule, thus providing the first firm evidence for the structure of the Br–HF complex. Linear complexes were also found for Cl–HF and I–HF. Unfortunately, the increased moments of inertia caused by the surrounding helium, as described in Section 4.1, means that the rotational constants cannot be used to extract quantitative structural information.

As well as entrance channel complexes, exit channel complexes have also been studied in HeDs. Two examples are CH_3 –HF,⁵⁰ which is the exit channel intermediate in the $\text{F} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{HF}$ reaction, and CH_3 – H_2O ,⁵¹ which is the exit channel intermediate in the $\text{OH} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{H}_2\text{O}$ reaction. In both cases the CH_3 radical was made by pyrolysis of either azomethane (CH_3NNCH_3) or di-tertbutyl peroxide ($(\text{CH}_3)_3\text{COOC}(\text{CH}_3)_3$) and vibrational

Fig. 7 Infrared spectra recorded in the H-F stretching region with (A) the oven switched on and operated at 1200 K and (B) the oven switched off. The former spectrum shows a new peak due to the Br-HF complex in addition to peaks arising from (HF)₂ and Br₂-HF, which are also seen with the oven switched off. Image taken from ref. 45 and reproduced by permission of the PCCP Owner Societies.

Fig. 8 Rotationally-resolved scan of the Br-HF band (upper trace) and a simulation (lower trace) assuming a linear molecule in a $^2\Pi_{3/2}$ state. Image taken from ref. 45 and reproduced by permission of the PCCP Owner Societies.

spectra with partly resolved rotational structure were used to establish the geometries of the complexes.

One exciting way to extend this work would be to look at the photo-induced conversion of an entrance channel complex into an exit channel complex inside HeDs. This will be possible for those reactions where vibrational excitation of the entrance channel complex lifts the system over the barrier to reaction, and thus should be a source of information which will be highly sensitive to the details of the reaction potential energy surface. The viability of photo-inducing chemical changes in helium droplets has already been demonstrated in molecular complexes, as shown by the photoisomerism of HCN-HCCH complexes.⁵² These complexes were found to show two equilibrium structures in helium droplets, one bent and the other linear. Conversion between these isomers

was achieved by excitation in the C-H stretching region and the efficiency of this process was shown to be strongly dependent on the vibrational mode excited.

4.4 Metastable clusters

Clusters and complexes composed of multiple molecules may possess several low-lying minima on their potential energy surfaces. If these species are formed by bringing molecules together in a gas phase supersonic expansion, the likelihood is that some or all of these isomers will be present in the final cooled gas mixture. This is because the clusters are formed in three-body collisions near the beginning of the expansion, where the temperature is relatively high and therefore excursions across the various minima are thermally accessible if the barriers are not excessively high. It is through subsequent two-body collisions that the system cools and traps the clusters in the various minima.

Clusters are formed in a very different way in HeDs. Under typical gas pickup conditions, the time between successive pickup events for a single droplet is on the order of tens of microseconds, whereas rotational and even vibrational cooling of molecules by the helium is expected to be many orders of magnitude faster. Thus, as also described in the previous section, clusters will form by the addition of a pre-cooled molecule (at 0.37 K) to the nucleation site. If long range forces exist to steer the added molecule into a particular orientation, there is no significant thermal energy to rotationally re-orient the system at 0.37 K. In this way, the cluster can in some cases be guided into structures with minima significantly above the global potential energy minimum. Energy will be released by the attractive forces as the molecules approach but the continuous and rapid cooling by the helium means that annealing into other potential energy minima is unlikely. Thus HeDs have the potential to trap molecules in metastable structures that are difficult or impossible to explore in any other way.

An excellent illustration of this effect is the self-assembly of polar molecules into linear chains. Nauta and Miller explored this for two linear molecules with substantial dipole moments, HCN and cyanoacetylene (HCCCN).^{53,54} In the case of HCN, it was known previously that gas phase supersonic expansions yield both cyclic and linear isomers of the HCN trimer, whereas for larger clusters the evidence is that only cyclic isomers form. Cyclic isomers are preferred energetically because they are able to form an extra hydrogen bond and they also maximise dispersion interactions because of their compact structures. On the other hand, at large intermolecular distances dipole-dipole interactions favour a structure where the dipoles are arranged in a head-to-tail fashion in a linear chain. At room temperature kT is large relative to the strength of these dipole forces and as the molecules approach more closely they tend to rearrange into cyclic structures. However, HeDs offer the prospect of preserving the linear structures because kT is smaller by nearly three orders of magnitude than at room temperature. Nauta and Miller recorded infrared spectra for (HCN)_n clusters in both the free C-H and hydrogen-bonded C-H stretching regions.⁵³ The resolution was improved by recording spectra of the doped droplets in a strong electric field, which orients the dipole of the overall cluster and inhibits rotational motion, essentially collapsing all of the potential rotational structure into a single

Fig. 9 Infrared spectrum of the free C–H stretching region of $(\text{HCN})_n$ clusters in helium droplets. The spectrum was recorded while the doped droplets were located within a strong electric field (using the apparatus shown in Fig. 5), such that rotational motion was severely restricted and therefore sharper vibrational features were obtained. The peaks are assigned to $(\text{HCN})_n$ clusters in dipole-aligned linear chain structures. From ref. 49. Reprinted with permission from AAAS.

Q-branch feature. The strong dependence of the spectroscopy on an applied electric field already provides compelling evidence for chain structures, since cyclic structures will possess small or zero electric dipole moments. Fig. 9 shows the depletion spectrum obtained in the free C–H stretching region, which shows a smooth convergence of the band positions with cluster size. The magnitude of the shifts of the bands with cluster size are in excellent agreement with those predicted from *ab initio* calculations on the linear clusters and are very different from those predicted for cyclic structures, providing further strong evidence for the formation of metastable linear chains for $n \geq 3$. Long range dipole–dipole steering has also been found to be crucial in the case of the formic acid dimer, which results in an acyclic metastable structure in HeDs, instead of the double hydrogen-bonded cyclic global minimum.⁵⁵

Another remarkable example of a metastable molecular cluster structure in HeDs was the observation of cyclic water hexamer.⁵⁶ This cluster of water is thought to be an important structural unit in liquid water and also in some phases of water ice. However, while cyclic structures are seen for the smaller water clusters in the gas phase, spectra reveal only a three-dimensional cage structure for the water hexamer. However, by recording vibrational spectra in the O–H stretching region the cyclic structure has been successfully found in HeDs, further demonstrating the utility of these droplets for exploring regions of potential energy surfaces that are inaccessible in gas phase studies.

4.5 Large clusters and nanoparticles

To date the majority of studies of doped helium droplets have focused on individual atoms or molecules as dopants, or have explored relatively small clusters or complexes. However, some work has been done on large dopant clusters and recent developments suggest that these may become an increasingly important area of research.

The first reports of large clusters inside helium droplets focused on metals, with one of the primary motivations being to identify electronic effects on the stability of particular metal cluster sizes.

Fig. 10 Vibrational spectra in the N–H stretching region of $(\text{NH}_3)_n$ clusters with average values of n , expressed as $\langle n \rangle$, shown beside each spectrum. Reprinted with permission from ref. 54. Copyright 2010 American Institute of Physics.

A good example is the work by Döppner *et al.*, in which magnesium cluster ions with up to several thousand atoms were identified in mass spectra following ionization by a femtosecond laser pulse.⁵⁷ To form large dopant clusters it is necessary to start with relatively large HeDs and Döppner *et al.* chose source conditions which delivered helium droplets containing $\sim 10^5$ helium atoms, on average.

Large molecular clusters can also be constructed in this way and a recent illustration is the observation of ammonia clusters composed of up to 10^4 NH_3 molecules by Slipchenko *et al.*⁵⁸ Vibrational spectra of these clusters (see Fig. 10) were recorded in the N–H stretching region using depletion spectroscopy and by altering the droplet size, such that the average number of molecules picked up varied from <1 to *ca.* 10 000, the evolution of the spectroscopy from a single molecule through to essentially a bulk sample of ammonia ice could be followed. One of the interesting findings from this study was that the vibrational spectrum of the largest ammonia cluster closely resembled the spectrum of crystal-line ammonia and is distinctly narrower than that of amorphous solid ammonia. This is quite surprising given the very low temperature in HeDs, which might be expected to yield amorphous solid ammonia. However, Slipchenko *et al.* suggest that as each

Fig. 11 Schematic illustration of the apparatus used to deposit metal clusters on solid targets. Reprinted with permission from ref. 56. Copyright 2011 American Chemical Society.

NH_3 molecule is added each molecule is steered into the correct position by dipole–dipole interactions, yielding a crystalline structure held together primarily by hydrogen bonding. This dipole–dipole steering echoes some of the issues discussed in the previous section. The use of HeDs for exploring trends in behaviour from small molecules through intermediate clusters sizes to large clusters has so far seen few applications but it offers a rather general way of bridging the gap between small molecular clusters and species that are essentially bulk-like.

Given the ability to grow large clusters within helium nanodroplets, one might ponder the possibility of using the droplets to grow new types of nanostructures, which can then be removed from the droplets. In fact helium droplets provide a ready-made means of achieving the latter since the exceptionally weak He–He binding means that any collision of a doped helium droplet with a surface should lead to rapid evaporation of helium atoms, thus exposing the droplet contents. The first practical demonstration of this was reported in 2007 when Mozhayskiy *et al.* observed deposition of Au and Ag clusters, as well as mixed Au–Ag clusters, onto a solid target.⁵⁹ In this initial study conditions were chosen which delivered metal clusters composed of several hundred metal atoms and the growth of these particles was inferred from their deposition onto a quartz crystal microbalance. In subsequent work the first images of such nanoparticles, recorded using transmission electron microscopy, were obtained.⁶⁰ The apparatus used to make the nanoparticles is illustrated in Fig. 11 and micrographs recorded,

in this case for Ag_n nanoparticles, are shown in Fig. 12. Conditions were chosen to deliver Ag_n nanoparticles with an average size of 6000 Ag atoms and the particle sizes measured from the micrograph data are consistent with this selection.

There are a number of fascinating possibilities with this approach to nanoparticle deposition. The first thing to note is the prospect of growing nanoparticles in a layer-by-layer fashion. With two distinct pickup cells, dopants can be added sequentially. Given the relatively long time taken for HeDs to travel between pickup cells ($>100 \mu\text{s}$), the formation of a solid core of the first dopant *via* pickup in the first cell will be followed by formation of a clean solid shell as material is added in the second pickup cell. In principle a huge range of core–shell combinations could be achieved by this means. A second feature of this approach is the potential for soft-landing nanoparticles as they hit a solid target. The velocity of the droplets as they hit the target is quite low – typically $200\text{--}300 \text{ m s}^{-1}$ – and the resulting energy per atom should be well below the energy required to rupture atom–atom bonds in a metal nanoparticle. Consequently, the nanoparticles should land intact and the initial evidence from TEM studies is that they do.⁶⁰ A third aspect of the helium droplet approach is the ability to control the particle size *via* the vapour pressure of the dopant(s) and the mean size of the helium droplets. This will not deliver fine control, given the statistical nature of the dopant pickup process and the variation in actual HeD sizes, but it does offer

Fig. 12 TEM images showing Ag_n nanoparticles deposited on an amorphous carbon TEM grid. Samples were obtained by exposure to the He droplet beam doped with Ag clusters consisting of about 6000 Ag atoms for 0.5 (a), 2 (b), 32 (c), and 120 min (d). Micrograph (e) was obtained by exposing the grid surface to an effusive beam of Ag atoms emanating from the oven for a period of 32 mins, kept at the same temperature as in experiments producing samples in (a)–(d). The size of the particles shown is consistent with mean Ag_n particles of ~ 6000 atoms. Reprinted with permission from ref. 56. Copyright 2011 American Chemical Society.

a means of biasing the particle size towards smaller or larger particles.

An important caveat will need to be borne in mind when seeking large nanoparticles *via* this synthetic route. The assumption above is that a single nanoparticle grows by the sequential addition of metal atoms. However, if metal atoms are added at a rate which is faster than the rate at which they are able to nucleate on the original nanoparticle, then a more likely scenario is nucleation at multiple sites within the droplet, with each mini-cluster eventually coagulating to form a nanocluster aggregate. Evidence for this process has been found by Loginov *et al.*, who recorded depletion spectra of Ag_n in HeDs in an attempt to observe the surface plasmon resonance of Ag_n clusters as a function of particle size.⁶¹ From an interpretation of changes seen in the spectra it seems that the time taken for atoms to reach a central nucleation site is long relative to the time required for local nucleation for HeDs with more than 10^6 helium atoms. This will lead to multicentre aggregation and, given the very low droplet temperature, will ultimately result in the formation of a granular composite. This applies, for example, to the Ag_n particles consisting of roughly 6000 atoms mentioned earlier. The TEM images were not able to identify this granularity, but in any case it is possible that the granules coalesce into a single close-packed structure once energy is delivered *via* collision with the deposition surface.

Lastly, we note the very recent report of metal cluster chains deposited from very large HeDs (diameters >300 nm), which have been taken as the first experimental evidence for the existence of quantum vortices inside helium droplets.⁶²

5. Conclusions

Helium droplets offer a somewhat exotic and cold environment in which to study individual molecules and collections of molecules. In this review we have attempted to give succinct descriptions of the properties of these droplets, how they can be formed and doped, and how dopants can be studied when attached to or are within the droplets. This was followed by a series of themed applications, with the primary emphasis on topics which would specifically appeal to chemists. There are many other fascinating topics that we would like to have included in this review but space limitations precluded this.

We think it appropriate to close with some personal thoughts about where we see the field of helium nanodroplets moving to in the next few years, with once again a particular bias towards the chemical sciences. In our view the study of molecular clusters and molecular complexes in helium droplets is still in its infancy. In particular many chemically relevant complexes, such as salt–water or acid–base complexes, are ripe for investigation. Helium droplets provide a convenient way to explore the variation in properties with the number of solvent molecules and may also allow identification of unusual metastable structures. This applies not only to neutral species but also to ions. Another area where there is enormous scope for development is in the study of time-resolved phenomena in helium droplets, such as determining how fast energy is

disposed into the helium matrix following laser excitation. Although there are plausible estimates for the dynamics, there is little or no supporting experimental data at present. We also see a greater role for laser pump–probe experiments for inducing and controlling chemical reactions in helium droplets, as indicated towards the end of Section 4.3. Finally, we see enormous potential for using helium droplets as a growth medium for an extraordinary range of new nanomaterials which are difficult or impossible to synthesise by wet chemical techniques. The future for helium nanodroplets as a chemical tool is an exciting one.

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