Formation of cations and anions upon electron interaction with (doped) helium droplets

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Abstract

Superfluid helium droplets have provided a new perspective for studying electron induced chemistry at extremely low temperatures. Helium droplets represent an ideal environment for the formation of novel and exotic agglomerates of atoms and molecules. Mass spectrometry can be used to detect the resulting ions formed upon electron ionization and electron attachment to doped droplets. In the case of electron ionization a helium atom of the droplet is ionized initially and after few resonant charge transfer reactions between helium atoms the charge finally localises on the dopant. An alternative process is Penning ionization of the dopant, where the scattered electron first electronically excites a helium atom on the surface of the droplet. The attachment of a low energy electron leads to formation of an electron bubble inside the droplet which decays by autodetachment or localization on a dopant, if present in the droplet. In the present minireview a general overview about the field of electron scattering with doped helium droplets is given and a presentation of important recent results related to these electron collision studies is given as well.

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1. The unique world of helium nanodroplets

The first successful attempts by Becker et al. forming intense beams of helium nanodroplets were already in the mid of the last century [1]. Later experiments with helium droplets were motivated by the search for evidence of superfluidity. The formation of helium nanodroplets and their unique properties can be well explained by the phase diagram, which is shown for the bosonic ^4He (nuclear spin $I=0$) in Fig. 1. Helium does not become solid at standard pressures like other liquids, when approaching the limit $T \rightarrow 0$ at very low temperatures. It solidifies only at pressures of more than 2.5 MPa, i.e. below this pressure it always stays liquid or gaseous. The liquid state can be divided in two regions above and below the λ -line ($T_\lambda = 2.173$ K at atmospheric pressure): in the former region He behaves like an ordinary fluid (He I) while for the latter liquid helium changes into the superfluid state (He II). This superfluidity implies a very low viscosity, which allows a frictionless stream of helium through capillaries and thinnest channels and moreover, an infinitely high heat conductivity [3]. The occurrence of superfluidity was explained by Landau in terms of the dispersion curve of the possible elementary excitations in a liquid (phonons and rotons), which occur only above a well defined critical velocity, the so called Landau speed (for helium $v_L = 58$ m/s) [3]. As a consequence, an object moves in a superfluid liquid without any drag, as long as the relative velocity is below the Landau speed. When going from the bulk liquid to nanodroplets (commonly and also in this review the term (nano)droplet is used for sizes $N > \text{a few } 1000$) and down to smaller clusters, the question arises, when superfluidity vanishes? While early experimental and theoretical investigations [4,5] suggested a threshold size of about 60 He atoms for the onset of superfluidity. Later, the proposed threshold cluster size was lowered to $N = 9$ [6]. In addition to the superfluid behavior, helium nanodroplets fascinate by their extremely low temperature of 0.37 K, which was determined for the first time in spectroscopy experiments in 1995 [7]. The binding energy of a helium atom to a droplet is size dependent and approaches the bulk value of 0.6 meV for droplets with $N > 10^4$ atoms [8]. As can be expected *a priori* from a liquid matrix, the zero point motion is high and thus quantum effects like strong delocalization of the helium atoms occur.

For the other stable isotope of helium, the fermionic ($I = 1/2$) ^3He , with a natural abundance of 0.000137 %, also superfluid behavior can be observed, which occurs only at temperatures below 3 mK. Moreover, the lower mass leads to an increased zero point motion compared to ^4He , which alters the binding energy (0.2 meV) and the He density in droplets (in average 24 % lower than for ^4He) [8]. For ^3He droplets a temperature of 0.15 K was determined [4], and

therefore they are not expected to be superfluid since the temperature of the droplets stays above the limit of 3 mK for the occurrence of superfluidity. In the present review the studies presented in more detail have been all carried out using ^4He .

2. Experimental methods to generate superfluid helium droplets

Helium droplets of both isotopes can be formed experimentally in the well known and widely used technique of a free jet expansion [9], i.e. precooled helium gas with a low temperature T_0 is expanded under high pressure through a nozzle into high-vacuum. Due to limited vacuum systems of experiments and the high gas flux through nozzles cooled to $T_0 < 35$ K typical nozzle sizes between 5 and 10 μm are used. Conical shaped nozzles, which often were used for free jet expansions due to favorable conditions for high cluster beam intensities [9] and large cluster mean sizes, are not available in these sizes. Instead commercially available apertures for electron microscopy are often used. These pinhole-type nozzles nevertheless allow the production of intense cluster beams for mass spectrometric experiments. Often experiments have been running with cw-droplet beam sources; in addition, several groups also developed pulsed droplet sources. The latter offer less demands to the pumping system and increased intensities within the pulses compared to cw-sources.

Helium droplet formation occurs in an isentropic expansion [2,10]. Depending on the initial expansion conditions (see Figure 1), different mean cluster sizes can be achieved [2]. Thereby two characteristic regimes are distinguished. In the first regime, the *subcritical* regime, the expansion is started at temperatures close to 15 K or more. The almost linear isentropes cross the phase line from gas phase to the liquid phase. Thus droplets are formed by condensation from the gas phase and cool then further by evaporation of helium atoms to the final temperature of 0.37 K. The size distribution of droplets formed in the subcritical regime can be described by a log-normal function [11,12]. In the second regime, *supercritical* expansion, such low starting temperature is chosen that the expansion follows bent isentropes which approach the gas-liquid transition line from the liquid state. Then already liquid helium passes through the nozzle, which fragments into droplets. Those cool further by evaporation of helium atoms. Thus, in the supercritical expansion very large droplets are produced (larger than $N_{\text{mean}} \sim 10^6$ at $T_0 \sim 8$ K and minimum expansion pressure of 20 bar). Expansions with even lower T_0 ($= 1.6 - 4.2$ K) have been carried out, where droplets sizes up to 10^{12} were achieved [13]. The supercritical size distributions were determined to follow a linear-

exponential distribution. Previously, also a third expansion regime was defined (*critical* expansion) [2], which is at the border between subcritical and supercritical expansions. It should be noted that most experiments have been carried out without neutral size selection; however remarkable diffraction experiments showed non-destructive size selection of neutrals [14].

The resulting mean cluster sizes (N_{mean}) as the function of initial expansion conditions were previously determined by means of deflection experiments utilizing atomic beams, as well as electrostatic deflection of negatively and positively charged droplets. Recent experiments dedicated to the determination of droplet sizes used also the attenuation of neutral droplet beams by electron impact [15]. The resulting size dependencies on the expansion parameters in the supercritical and subcritical regime have been shown in [13]. These data are often used as reference for experiments which do not directly yield N_{mean} . More recently, also mean sizes in the previously less characterized regime of very large helium droplets ($N_{\text{mean}} \sim 10^7$ - 10^{10}) have been determined [16]. The well known cluster-size-law from Hagena $N_{\text{mean}} p_0 \propto d^{1.5}/T_0^{2.4}$ [9] often used for heavier rare gases is hardly used for helium droplets because for the latter the law is only valid in a small temperature range and not applicable for supercritical expansions at all.

At the Institute of Ion Physics and Applied Physics in Innsbruck helium droplets are formed by supersonic expansion of pure ^4He gas (99.9999 %) with high pressure and low temperature through a 5 μm commercial pinhole type nozzle. Currently 3 droplet sources are available which can achieve a wide variety in expansion temperatures and pressures (5 to 15 K and 1.5 to 3 MPa) (see Figure 2 for an illustration of the most recent droplet experiment). The pressure in the droplet formation region is kept below 10^{-2} Pa with one or two turbomolecular pumps; each providing a pumping speed of 1750 l/s.

After the nozzle a skimmer (typical diameter few 100 μm) is placed at the distance of about 0.5 cm in order to avoid an interference of the droplets with shock-waves formed by the expansion. Collision of the expanding gas with these shock waves would cause reheating of the droplet beam. The other main task of the skimmer is to achieve differentially pumped regions since the pressure in the cluster source chamber is usually up to 0.01 Pa, while for the subsequent chambers often a background pressure in the range of 1×10^{-5} Pa should be maintained. This is especially important for experiments where a low pick-up rate is desired. In the pick-up stage the droplets can be doped with various gas phase atoms or molecules. Due to their large geometrical size (for example ~ 10 nm for a droplet with 10^4 atoms) helium droplets possess high pick-up cross sections (for this reason helium droplets are also called

“vacuum cleaners” [1]). By fast evaporative cooling the collision energy, internal energy of the embedded particle and the solvation energy are released and the foreign particle will be quickly cooled down to the temperature of the droplet. This efficient heat bath allows multiple pick-up events. The binding energy of a helium atom to the droplet is about 0.62 meV, i.e. as a rule of thumb ~ 1600 helium atoms are evaporated for 1 eV excess energy deposited in a helium droplet. In general, the pick-up probability P_k is following a Poisson distribution,

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

The parameter k is the number of atoms or molecule picked-up by the droplet and x is the average number of collisions. In case of multiple pick-up by a helium droplet agglomeration into weakly bond sub-clusters in the droplet may occur, which is provided by the high mobility of dopants in the superfluid droplet on the one hand and the finite size of the droplet on the other.

When an atom or molecule is picked-up by a pure helium droplet, the question arises, where the dopant resides in the droplet, i.e. either we have a heliophobic or a heliophilic dopant. As rule of thumb dopants with an electronically closed-shell (most of atoms and molecules) move into the center of the droplets, while for example atomic hydrogen, alkali (Li, Na, ...) and heavy alkaline earth atoms reside close to the surface of the droplet [18]. For heliophobic dopants the Pauli repulsion of the valence electron(s) and the He atoms exceeds the interatomic attractive force. Only for sufficiently large alkali clusters a submersion into the helium droplet was predicted where clusters of alkali atoms start to submerge in the helium droplets after growing to a critical size (e.g., $n=21$ for Na_n and $n=78$ for K) [18]. Subsequent experiments have been in very good agreement with the calculations [19,20].

The relative stability of surface states and interior states can be also described by a dimensionless parameter λ (Ancilotto parameter) [21]. For λ larger than 1.9 interior states are formed while for $\lambda < 1.9$ surface states are favored:

$$\lambda \equiv \frac{\rho \cdot \varepsilon \cdot r_{\min}}{2^{1/6} \cdot \sigma} \quad (2)$$

Thereby ρ is the number density of the liquid, ε is the well depth of the interaction potential between dopant and liquid, $r_{\min}$ is the corresponding equilibrium bond length and σ is the

surface tension of the liquid. For example, for a Li impurity in liquid helium λ is equal to 0.835 and for SF₆ $\lambda = 18.8$ predicting a surface and an interior state, respectively. These predictions have been also in agreement with the experimental observations [7,22].

It should be noted, that the structures of dopant agglomerates grown in helium droplets may also show an exotic configuration. For example, the cage structure of the water hexamer corresponds to the energetically lowest isomer in the gas phase while in helium droplets the higher energy isomer with cyclic structure is preferentially formed [23]. This was explained by freezing of the metastable cyclic structure due to rapid energy dissipation to the surrounding superfluid helium. In addition, also the growth of a chain of polar HCN molecules due to their long range dipole-dipole interaction was reported [24]. Thereby nanoscale oligomers were observed, with length of about 4 nm only limited by the finite size of the helium droplets used. Recently, also track-shaped Ag deposits were identified by electron microscopy after their growth in very large helium droplets. In this case Ag atoms were caught by vortices in the droplets formed in the supercritical expansion of liquid helium [25,26].

It should be also noted that recently also first experiments have been carried out where preformed ions have been embedded in neutral droplets. Cationic species embedded were the protein cytochrome C [27], hemin [28] as well as sodium [29]. In order to embed these ions in He droplets, large droplet sizes $>10^5$ - 10^6 have been necessary.

3. Ionization mechanism in helium nanodroplets by electron ionization

3.1 Pure droplets

Electron ionization is a relatively simple method to form positively charged droplets upon ionization of neutral droplets. Standard ion sources (Nier type) allow electron beam currents up to mA, which is sufficient to obtain ion yields resulting from ionization of helium droplets in the pA regime. Charged droplets allow their detection by mass spectrometry. Detailed electron ionization studies have been reported by the Toennies group in the early 90's [2,30], where the ionization mechanisms in pure as well as doped helium droplets have been investigated. They dedicated their cluster research also to the search for so called magic numbers [9], which are indicated by an exceptional intensity of a specific cluster size or a

large drop in intensity between two neighboring clusters sizes. One intensively discussed question regarding magic numbers was if the cluster size distribution in a mass spectrum with certain magic numbers represents the stability of neutral or of ionized clusters. In the first case the initial neutral cluster distribution has to be preserved also through the ionization experiment. In the second case the ionization process leads to clusters in highly vibrational excited states. These excited clusters relax by evaporation of atoms (fragmentation) and thus the cluster ion spectrum represents the stability of cluster ions. The magic number distribution of helium cluster ions is distinctly different to other rare gas systems due to the absence of magic numbers for larger cluster sizes (like 55, 147, etc., ascribed to icosahedral shell closures [9]). Helium cluster ions show magic numbers only for small cluster sizes $n \leq 14$ [30,31,32,33,34] (see Figure 3). In this case helium atoms are rigidly bound by ion-dipole forces to an ionized core of He^+ or He_2^+ . This leads to the formation of well-known snowball structures. This difference to other cluster systems can be explained by the phase of helium cluster ions. The latter are solid only for small cluster sizes while then the cluster becomes liquid-like.

Helium has the largest ionization energy (24.59 eV) of all atoms and molecules. An electron with kinetic energy above this value may ionize a helium atom of the droplet in the following inelastic scattering process,

Subsequently a resonant charge hopping process occurs, where the electron hole “jumps” to neighboring helium atoms [35]. In the case of pure helium droplets this process can be characterized as a random walk. Finally formation of a positively charged helium dimer occurs, which terminates the charge hopping process. Ellis and Yang calculated that in a pure droplet approximately 11 charge hops are possible before He_2^+ formation occurs [35]. He_2^+ formation turned out to be the most probable cluster fragment ion (30-70% of the total ion yield) [34]. He_2^+ can also act as nucleation site for the growth of small He_n^+ cluster ions. In the latter species a finite number of helium atoms are tightly bound to the ionic core leading to formation of snowballs. In addition, ion formation always releases a substantial amount of excess energy (2.35 eV), which leads to the (thermal) evaporation of helium atoms from an ionized droplet. However, a complete thermal evaporation of the surrounding helium is

unlikely for larger droplets; thus He_2^+ and He_n^+ are likely ejected out of the droplet as proposed in [34].

3.2 Doped droplets

Direct electron ionization of a molecule deeply embedded in a cold helium droplet by a colliding electron is very unlikely. Instead, the removal of an electron from the dopant occurs in the droplet via charge transfer from He^+ . The initial ionization event can be described by reaction (3) like for a pure droplet. However, the resonant charge hopping process is modified because a random walk only occurs for rather large doped droplets ($n > 10^5$), where a hole localization on the dopant becomes then unlikely. Instead, for smaller droplets the direction of the hole migration is pointed towards the dopant due to induced long range dipole interaction [35].

In addition to charge transfer ionization, also Penning ionization of dopants may be a possible ionization mechanism in doped helium droplets. Above the electron energy of 19.82 eV an electronically excited helium atom can be formed by an inelastic collision of an electron with a helium atom of the droplet,

The corresponding lowest excitation state of helium is the 2^3S_1 state which is metastable with a lifetime of 8000 s [30]. The second metastable state of helium is 2^1S_0 with an energy of 20.62 eV and a lifetime of 20 ms. These lifetimes mentioned refer to collision free conditions. When reaction (4) occurs in a droplet, the formed metastable He^* exciton resides in a bubble and migrates in the droplet. In a pure droplet it may combine with another helium atom to form a vibrationally excited He_2^* after 15 μs [30] and the droplet remains neutral. In presence of a dopant in the droplet Penning ionization may occur,

which leads to dopant ion formation in the droplet, provided that the ionization energy of the dopant is below the excitation energy of helium (which is the case for all known molecules).

More details about Penning ionization, which has been investigated in molecular beam studies and theory, can be found in [36]. If the kinetic energy of an incoming electron is sufficient to produce two helium excitations in one droplet, even double ionization of a dopant may occur if the excitation energy is higher than the double ionization energy of the dopant [37]. In contrast, sequential double ionization of a dopant by two He^+ ions can be excluded due to the Coulomb repulsion of the ionic species after the first dopant ionization.

3.3 Recent studies on electron ionization of doped helium droplets

Electron ionization is known to be a “hard ionization” reaction which leads to vibrationally hot ions. This results often in the non-observation of a molecular ion in electron ionization mass spectrometry and substantial fragmentation of ionized molecules. Due to the remarkable properties of helium droplets discussed above one major line of the mass spectrometric research with doped helium droplets has been devoted to the study of the fragmentation pattern of ionized molecules in helium droplets. It is well known that both the temperature and the environment are important parameters for the control of chemical reactions. Due to the low temperature environment and fast evaporative cooling one may expect substantial quenching of molecular fragmentation in helium droplets upon ionization. However, one needs to keep in mind that the high ionization energy of helium (24.59 eV) exceeds substantially the ionization energies of molecules (for organic molecules ionization energies are mainly between 8 and 12 eV). This obvious large difference in the ionization energies, which corresponds to the excess energy deposited in the formed ion, may lead nevertheless to severe fragmentation of the dopant ion formed. The question is then, to which extent fragmentation can be buffered by the dissipative He environment. One of the earlier investigations has been devoted to SF_6^+ which is not stable on mass spectrometric timescales under isolated conditions. A first tentative report [38] of stabilization of SF_6^+ in helium droplets was not confirmed later [39]. More recently, the group of R.E. Miller [40] showed that sufficiently large helium droplets provide rapid cooling to reduce fragmentation of vibrationally hot molecular ions. They studied electron ionization of helium droplets doped with triphenylmethanol (which is an important molecule in synthetic chemistry) in helium droplets. Compared to electron ionization of the bare molecule, they observed a strong enhancement of the molecular ion intensity in helium droplets. They also recorded the ion yields as a function of the helium droplet size where a steady increase of molecular ion signal was observed with increasing droplet size (the size regime investigated covered up to 10^4

helium atoms). Based on these size dependency studies it was also possible to assign fragment ions of triphenylmethanol to first or second generation fragments (the latter are formed in sequential decays). Therefore electron ionization studies of molecules embedded in helium droplets may also give valuable insight into the dissociation dynamics of gas phase molecular ions. We also recently studied electron ionization of perfluoroether molecules embedded in helium droplets and bare in the gas phase [41]. Perfluoroethers like perfluorotriglyme have a molecular mass around 400-600 u and represent model compounds of perfluoropolyethers known as excellent lubricants. While the mass spectra of the isolated molecules show predominantly light fragment ions, the helium droplet mass spectra exhibit predominantly heavy fragment ions as well as increased ion yields of the corresponding molecular ions as shown in Figure 4. The conclusion from this result is that ionic fragmentation-intermediates are frozen and subsequently stabilized in the He environment. Helium droplets can therefore effectively transform short lived decomposition intermediates into stable fragment ions which then appear as strong signals in the mass spectrum.

In addition, the fragmentation process of an ionized molecule in a matrix may be also influenced by cage effects where the matrix favors the escape of small, energetic fragments over heavier ones with low kinetic energy. Such an effect has been also reported for helium droplets by Yang et al. [42,43]. Based on electron ionization mass spectra of alcohols and ethers embedded in helium droplets they suggested a cage effect by the helium droplet, which favors the escape of the dehydrogenated parent cations over other fragmentation channels [43].

Since helium droplets are an ideal matrix to form pure clusters of dopant atoms or molecules and even exotic species, i.e., mixed clusters of various atoms or molecules embedded, a number of electron ionization studies with various molecular clusters formed in helium droplets have been carried out in recent years. For mixed clusters the fragmentation pattern may not be only altered the surrounding helium (though fragmentation may occur like for the corresponding monomers [44,45,46]) but also by the presence of the second dopant (cluster) as well. For example, recently core-shell effects have been reported for ionization of water clusters surrounded by an atomic or molecular shell [47,48]. In case of N₂, O₂, CO₂ or C₆D₆ shells the fragmentation of the water cluster (leading to the protonated water cluster which is the dominant product of ionization of pure water cluster and water cluster in helium droplets [49]) was reduced in favor of unprotonated water cluster ions. It was also suggested by Ren and Kresin [50] that the electric dipole moment of a molecule to be protected by a shell of water molecules plays an important role. They studied electron ionization of mixed clusters

containing fragile molecules like glycine, alkanes or alkanethiols and water formed in helium droplets. Ren and Kresin observed quenching of fragmentation only for first two systems, while fragmentation of alkanethiols remained unaffected. Alkanethiols have a much higher dipole moment than glycine, or alkanes and therefore they concluded that the reduction of fragmentation is also controlled by the strength of the dipole moment of the impurity [50] which generally steers the charge hopping process in the droplet [51].

Our group also investigated electron ionization of helium droplets containing mixed clusters of the fullerene C_{60} and water (see Figure 5) [52]. Ionization leads predominantly to small $C_{60}^+(H_2O)_n$ cluster ions with $n < 6$. However, quantum chemical calculations on the structure of the mixed clusters revealed no water shell formation around the C_{60} but instead a loosely bound water cluster to the fullerene. Since the ionization energy of C_{60} is substantially lower than that of water (7.6 eV vs. 12.6 eV), the charge transferred from He^+ will localize mainly on the C_{60} moiety. This leads then to the suppression of the autoprotection reaction in the attached water cluster leading to $C_{60}H^+(H_2O)_n$.

The dehydrogenated cluster ions (particularly abundant is $C_{60}OH^+$) seem to be a counterexample to the notion that fragmentation of clusters embedded in helium is suppressed. However, since the double ionization energy of C_{60} (19 eV) is below the single ionization of helium the formation of $C_{60}OH^+$ may proceed via following reaction scheme:

In this reaction scheme initial charge transfer from He^+ produces C_{60}^{2+} (6a). Subsequent charge transfer to the water moiety induces fragmentation of the water cluster ion (6c) before charge separation occurs (6d). Thus fragmentation products can be observed which are not formed in the absence of helium.

The formation of snowballs (characterized by an ionic core with compressed shell of neutrals) was not only investigated for pure helium cluster ions but also for mixed cluster ions with a dopant atom [53], molecule or cluster as ionic core. For example, in Ref. [54] a list of (alkali earth) metal cations with the corresponding numbers of He shell closures can be found. He solvation was also found for molecular ions [55,56,57], starting from small systems up to

fullerenes [58]. In a recent paper on helium solvation of various diatomic molecules and their clusters in helium droplets a much stronger solvation of intact cluster ions compared to the respective monomer ion was reported [55]. This result was ascribed to higher cooling capabilities of the cluster species.

4. Negative ion formation in helium droplets

4.1 Pure droplets

The attachment of a low energy electron (with a few eV kinetic energy) to a helium droplet, independent if doped or undoped, has a particular characteristic due to electron bubble formation. The reaction differs substantially from electron capture by clusters with a positive electron affinity. Moreover, presence in helium droplets affects the measured resonance energies of dopant anions, which do not necessarily correspond to the electron energy in vacuum. The electron - ground state helium interaction is dominated by the short-range repulsive exchange forces because of the small atomic polarizability of helium [1]. Such repulsive interaction can be also found for other liquid-like droplets like hydrogen and neon droplets. In general, considering the electronic band structure of a droplet (or the bulk), the electron energy at the bottom of the conduction band, V_0 , serves as an indicator of the balance between the repulsive and attractive interactions between an electron and a medium like a droplet. For bulk liquids V_0 decreases in the order $\text{He} \rightarrow \text{Ne} \rightarrow \text{Ar} \rightarrow \text{Kr} \rightarrow \text{Xe}$ ($1.06 \text{ eV} \rightarrow 0.67 \text{ eV} \rightarrow -0.17 \text{ eV} \rightarrow -0.37 \text{ eV} \rightarrow -0.65 \text{ eV}$) while the electron mobility increases in the same order, i.e. these parameters turned out to be correlated [59]. Thereby a negative value means that the vacuum level, i.e. the energy of a free electron at rest far away from the medium, is in the conduction band. In other words, the electron affinity of the medium is positive. In contrast, liquid helium and neon possess a $V_0 > 0$, i.e. the surface of these liquids represents an energetic barrier for the incoming electron. In this case the bottom of the conduction band, which represents the lowest delocalized state for an excess electron in the condensed media is above the vacuum level. Previously the value of V_0 was determined for helium droplets by measuring the yield of electronically excited clusters as a function of the electron energy. Martini et al. [60] derived a value of $1.03 \pm 0.2 \text{ eV}$ for He droplets. A more recent value is $V_0 = 1.15 \pm 0.025 \text{ eV}$, which was valid for cluster sizes from 2×10^3 up to 50×10^3 [61]. The result of a larger value than for the bulk ($V_{0,\text{bulk}} = 1.06 \text{ eV}$) is rather

surprising since the atom density becomes smaller, when going from the bulk to smaller clusters and thus can be expected that V_0 will slightly decrease with decreasing cluster size [1].

Once injected into liquid helium a low energy electron thermalizes in a few picoseconds by creating a charged bubble, where the electron resides in a cavity. For He the bubble radius was estimated to be 17 Å (bulk value) which slightly decreases for droplets with finite size [62]. However, this electronic bubble state is a metastable state, where the lifetime is finite due to possible electron detachment (where the electron escapes back into vacuum via tunnelling). Moreover, a minimum droplet size was predicted for the formation of a bubble state ($N \approx 4500 \pm 700$) taking into account the energetic stability (the size dependent total electron bubble energy at equilibrium configuration must be lower than V_0) and dynamic stability (tunnelling effects) [63]. The metastability implies also basic consequences for the mass spectrometric observation of negatively charged helium droplets. It turned out that large droplet sizes are required ($N > 7.5 \times 10^4$) in order to form negatively charged (pure) helium droplets observable on mass spectrometric timescales [64,65]. The electron energy dependence of He_N^- ($N > 9.3 \times 10^4$) was determined by Henne and Toennies [61]. For the smallest droplet size measured the anion efficiency curve showed a sharp rise above a threshold of 1.3 eV with a peak maximum at $E_{\text{max}} = 1.8$ eV. This maximum gradually shifted with increasing droplet size up to 2.3 eV for the largest droplet size studied ($n = 1.5 \times 10^7$). Moreover, the anion efficiency curves also showed self scavenging processes with peaks at about $E_{\text{max}} + n \times 20 \text{ eV}$ ($n = 1-4$), where the incoming electron scatters inelastically from one or more helium atoms. So the incident electron is slowed down to ~ 2 eV which seems to be the optimum energy for being self-trapped via bubble formation [61].

4.2 Doped droplets

For doped helium droplets the electron bubble may localize on the dopant, which may lead to thermodynamically stable anions [66]. Moreover, the droplet size criterion for observation of negative ions is overruled and smaller droplet sizes lead to a higher probability of localization on the dopant in competition to electron detachment from the droplet. Like in case of positive ion formation it is of course then the question to which extend molecular (or cluster) fragmentation of the so called temporary negative ion state (TNI) formed can be quenched by

the helium environment. In the following, prime examples of electron attachment to helium droplets doped with polyatomic molecules are presented.

4.2.1 Electron attachment to helium droplets doped with chloroform

Chloroform (CHCl_3), belongs to the class of halogenated hydrocarbons which are of relevance in atmospheric chemistry [67]. Especially the electron induced chemistry is of great interest as halogenated hydrocarbons possess high attachment cross sections for low energy electrons [68]. Halogenated compounds always dissociate upon electron attachment (most efficiently below 1 eV) with the captured electron localizing at the halogen atom. This is attributed to the high electron affinity of the halogen radicals ($\text{EA}(\text{X}) = 3.40, 3.61$ and 3.36 eV for $\text{X} = \text{F}, \text{Cl}$, and Br , respectively). For many halogenated molecules the dissociative electron attachment (DEA) process becomes then energetically exothermic, i.e. the dissociation limit of the halogen anion and the neutral fragment is below the ground state of the neutral molecule. In previous DEA studies to gas phase chloroform 10 fragment anions have been observed in total [69]. The high electron capture efficiency makes the molecule to an ideal candidate for studying the formation of anions in helium droplets [69]. Figure 6 shows the negative ion mass spectrum of chloroform cluster anions close to 1.5 eV. This electron energy was chosen for the mass spectrum because the strongest signal of anion formation was observed at this energy (in contrast to the gas phase, where ~ 0 eV peaks are the strongest ones). Another important result was that non-dissociated cluster anions of chloroform can be observed while for the isolated molecules the parent anion is not stabilized due to autodetachment or dissociation occurring on shorter timescales. However, more intense are the ion yields of anions formed via fragmentation of chloroform clusters upon DEA. These results show that both, the molecular cluster as well as the helium droplet, do not substantially quench dissociation. In this case the chlorinated cluster anions are the most abundant fragment anions observed upon DEA to chloroform embedded in helium droplets. Figure 7 shows the ion yield of the chlorinated cluster anions as a function of the initial electron energy. In addition to the major peak close to 1.5 eV, additional (weaker) resonances can be found close to 10 eV and 22 eV. The disappearance of the zero eV resonance and the occurrence of peaks between 1 and 2 eV can be explained by the initial interaction of the incoming electron with the helium droplet. Like in the case of a pure helium droplet, the electron requires a minimum amount of energy to penetrate into the droplet before entering the bottom of the conduction band and

localization in a bubble. Now in the case of a doped droplet, the electron may finally localize on the dopant before the metastable electron bubble decays spontaneously. Therefore the position of the energetically lowest resonance observed for all anions of chloroform in helium droplets is very close to the position of the first resonance in the ion yields of pure helium droplet anions which showed their first resonance at about 1.8 eV (see the previous section). The resonance at ~ 10 eV can be ascribed to (cluster) fragmentation after electronic excitation of chloroform while the resonance at ~ 22 eV is a clear reminiscence of the presence in the helium droplet. In this case the incoming electron loses additionally substantial amount of kinetic energy by electronic excitation of helium before attachment to the chloroform cluster takes place.

Compared to gas phase studies one can conclude that the presence of the helium droplet has a strong effect on the resulting cross section of chloroform anion formation: Gas phase Cl^- is formed via s-wave electron attachment close to ~ 0 eV with a very high cross section due to the reciprocal energy dependence of this reaction [69]. However, this strong ion signal observed close to zero eV for the gas phase is quenched when the electron attachment reaction occurs within the helium droplet. Instead, at the electron energy of 2 eV, which is required for the electron to penetrate into the He droplet, the electron capture cross section is already orders of magnitude lower compared to zero eV. On the other hand a shift of 2 eV for resonances at higher electron energies would yield a much smaller effect on the capture cross section. Such effect would account for all systems where the localization of the dopant (cluster) occurs deeply inside the droplet (see section 3).

4.2.2 Electron attachment to helium droplets doped with aromatic molecules like thymine or trinitrotoluene:

The results for chloroform embedded in helium droplets indicated that also for negative ions a change of fragmentation pattern may occur. For another class of molecules, biomolecules, this effect may be very important since many electron attachment studies with biomolecules have been carried out under isolated conditions [70,71]. The research with biomolecules has been also motivated by the discovery that low energy electrons may cause DNA single and double strand breaks by resonant electron attachment [72]. Moreover, low energy secondary electrons are formed abundantly upon the interaction of energetic radiation (α , β , γ , ions, etc) with biological matter. Analogously to chloroform, electron capture by an isolated nucleobase

always leads to dissociation of the TNI or alternatively electron emission. The question is then, if this will also occur if the nucleobase is embedded in a matrix, because then the excess energy released upon TNI formation may be transferred to the surrounding matrix by vibrational redistribution. As very first approach experiments with nucleobases embedded in an inert matrix like helium droplets may allow some predictions [73,74]. Indeed, a remarkable change of the anion abundances was observed in electron attachment experiments with nucleobases embedded in helium droplets. In contrast to the gas phase, a parent anion can be observed on mass spectrometric timescales (i.e., longer than few μs). This effect results from the quick transfer of the excess energy (basically the kinetic energy of the incoming and the electron affinity of the anion formed) into the surrounding helium matrix. In addition, we studied the anionic fragmentation pattern of single thymine molecules embedded in helium droplets as a function of the electron energy [73]. The pattern changes in favor of the dehydrogenated parent anion and while for the isolated molecule $(\text{M-H})^-$ is formed in considerable amounts just below 4 eV, the abundance in the droplets is strongly increased above this energy [73]. This becomes possible by suppression of ring cleavage reactions. The latter also leads to NCO^- formation, which is the dominant anion at electron energies >4 eV for the isolated molecule. The effect observed for nucleobases stems from the different dissociation mechanism for H-loss and NCO^- formation: while the former undergoes direct dissociation along a purely repulsive potential energy surface, the latter is accompanied by cleavage of multiple bonds and possibly considerable rearrangement of the molecule. Thus NCO^- formation is a time-consuming process and can be effectively quenched by the helium environment. However, the hydrogen loss reaction cannot be quenched and the dehydrogenated parent anion is therefore an intermediate fragmentation product becoming frozen in helium droplets by energy relaxation (see Fig. 8).

The effect of freezing dissociation channels is even more extreme in the case of electron attachment to monomers of trinitrotoluene (TNT) embedded in helium droplets [75]. TNT is an explosive compound and shows the characteristic behavior of explosive compounds upon electron attachment. In this case an extremely rich fragmentation pattern already close to about $\sim 0\text{eV}$ electron energy can be observed. Such low threshold even for formation of fragment anions via ring cleavage indicates substantial rearrangement processes to compensate the energy required for multiple bond cleavages. In the case of TNT embedded in the helium droplets the resulting mass spectra only show the undissociated molecular anion and cluster anions [75]. No fragmentation can be observed within the detection limit of the apparatus. The quenching of these dissociation channels by the helium environment gives also

for this molecule insight in the dissociation mechanism. For TNT vibrational predissociation governs the dissociation where sufficient redistribution of vibrational energy into particular reaction coordinate is required to access energetically possible dissociation channels. This results in a slow dissociation process compared to direct electronic dissociation, sometimes extending to the metastable (ms) timescale associated with the appearance of products resulting from multiple bond cleavages and rearrangement. Such metastable decay reactions due to vibrational predissociation were also observed recently for other molecular anions, offering a reasonably large number of vibrational degrees of freedom, but TNT is a remarkable example where vibrational predissociation governs to most extent the dissociation mechanism.

5 Summary and future perspectives

In a previous article helium droplets have been called “flying nano-cryo-reactors” [77]; a term which probably describes the potential of helium droplets in forming new targets for electron collisions in the most appropriate way. Electron ionization combined with mass spectrometry offers thereby excellent opportunities to characterize the systems formed in the nanodroplets. The pick-up method allows to generate a large variety of species in the droplets which offer a broad horizon for future studies. Ionization and fragmentation of a dopant in helium droplets can be seen as interplay between the substantial deposition of excess energy in the charge transfer process from He^+ process of dopants in helium droplets and the fast cooling by helium evaporation. Therefore it was concluded that helium droplets cannot provide a soft ionization method to be used for wide application in analytical chemistry, which is an effect of the large difference of the ionization of dopant and helium [43,78].

Concerning electron attachment it should be noted that observed cross sections (or ion yields) seem to be orders of magnitude lower than for isolated molecules. What is shown by the presently discussed electron attachment studies for chloroform, nucleobases and for trinitrotoluene (TNT): extensive and slow fragmentation processes seem to be quenched effectively in the droplet, while direct dissociations via repulsive potential energy surface upon DEA cannot be avoided. It should be noted that the obvious low cross section for electron attachment means a high challenge for experimental investigations compared to electron ionization. In addition, in currently running experiments standard ion source are used,

which lack on high energy resolution. Future high resolution studies would allow precise determination of resonance energies may lead to further understanding of electron attachment processes in doped helium droplets.

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Fig. 1: Solid lines: Phase diagram of ^4He . The dashed lines indicate the isentropes for a free jet expansion starting from a stagnation pressure of 2 MPa for different stagnation temperatures T_0 . Adapted from [2].

Fig. 2: Scheme of the most recent experimental He-droplet setup in our institute. The apparatus includes 4 different stages, (i) helium droplet source, (ii) pick-up stages, (iii) ion source and (iv) time-of-flight mass spectrometer. Adapted from [17].

Fig. 3: Mass spectrum of small helium cluster ions formed upon electron ionization of pure helium droplets [33]. The spectrum was taken at the electron energy of 70 eV. The magic numbers 7, 10 and 14 are indicated by a star.

Figure 4: Electron ionization mass spectrum of perfluorotriglyme (PT, mass 502 u), when isolated (top) and when the molecule is embedded in ultracold helium droplets (bottom). Adapted from [41].

Figure 5: High resolution mass spectrum recorded in presence of C_{60} and D_2O in helium droplets. The triangles mark the peaks at mass 738 u and 739 u which can be assigned to $C_{60}OD^+$ ions. Adapted from [49].

Figure 6: Negative ion mass spectrum of chloroform embedded in helium droplets [67] recorded at the electron energy of 1.5 eV. The spectrum is dominated by parent cluster anion and chlorinated parent cluster anions (see text).

Figure 7: Ion yield of chlorinated chloroform cluster anions ($n=1-3$) as a function of the initial electron energy. The anions have been formed upon electron attachment to chloroform embedded in helium droplets [67].

Figure 8: Ion yield of the dehydrogenated parent anion $(T-H)^-$ formed upon electron attachment to single thymine in helium droplets (full line) and in the gas phase (full line with open circles). The comparison with the sum of all other gas phase fragment anion shows that at electron energies $> \sim 4\text{eV}$ $(T-H)^-$ is a dissociation intermediate frozen in helium. [73]

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