

## 2.5 Solvated Electron Clusters

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### 2.5.1 Introduction

An electron gains energy if it is brought from the vacuum into a macroscopic dielectric liquid or solid, as shown schematically in Fig. 1. The only exceptions being helium and neon, where after an initial attraction, about 1 eV is necessary to push the electron into the bulk medium. The concepts of a valence- and conduction-band might be better known for crystalline materials, but they can be extended also to amorphous and liquid matter. For semi-conductors and dielectrics the valence band is completely full, and the conduction band empty. Simple solid state theory tells us for this case that no net electric current can flow on application of an electric field. The field gives rise to a flow of electrons which

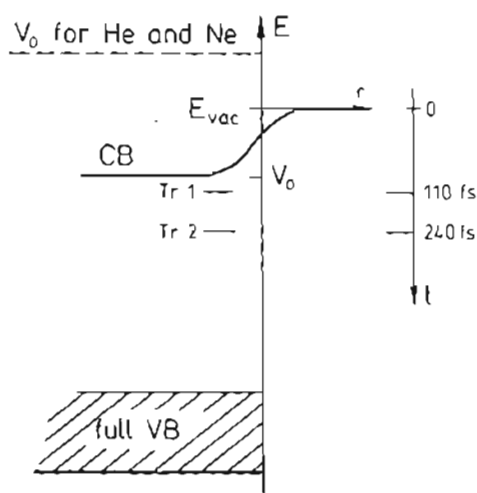


Fig. 1. The energy  $E$  of an electron is plotted as a function of its distance  $r$  from a bulk dielectric surface. A bulk dielectric has a full valence band (VB) and an empty conduction band (CB). The two bands are separated by so large a band gap, that no electron can be thermally excited across it. The energy of the "vacuum level"  $E_{vac}$  is the energy of an electron at rest at infinity. At large distances the interaction between an electron and a dielectric surface is always attractive, as the electron is attracted by the polarisation forces. The difference between the energy of the bottom of the conduction band and  $E_{vac}$  is called  $V_0$ . Only for He and Ne does the conduction band lie above  $E_{vac}$  as indicated by the dashed line. The localised trap states lie below the conduction band. The energies of a shallow (Tr1) and a deep (Tr2) trap state are indicated. The time it takes for an electron in condensed water to localise on the trap states is indicated on the right

is exactly cancelled by the flow of "defect-electrons" or "holes" in the opposite direction. Thus a substance where the highest occupied band is full, is an isolator. For dielectrics the bandgap which separates valence and conduction bands is so large, that no electrons can be thermally excited into the conduction band. But one can of course introduce electrons into the empty conduction band, by injecting them from the outside. Two different things can happen to the electron once it is inside the dielectric:

1. The electron can stay delocalised. It moves as a nearly free electron in the empty conduction band of the dielectric. This rare case will be discussed for Xe clusters below.
2. In the majority of cases the electron will become "trapped" or "localised", i.e. the atoms or molecules of its surrounding react to the changed force field, and move to new positions. The electron becomes bound to this "vacancy", or in chemical language it becomes solvated. This self trapping process has been described pictorially as "the electron digging its own trap". Examples which will be discussed below include He, H<sub>2</sub>O, NH<sub>3</sub>, and NaCl clusters. The energy of the trap states lies below the conduction band, as indicated in Fig. 1

If no chemical reaction occurs after localisation, solvated electrons can be stable for long times. This is the case of electrons in liquid ammonia, where they give the famous "blue solution" discovered in 1864, when Weyl dissolved sodium in liquid ammonia (NH<sub>3</sub>). In modern notation Na<sup>+</sup>(NH<sub>3</sub>)<sub>n</sub> and (NH<sub>3</sub>)<sub>n</sub><sup>-</sup> clusters, with *n* tending to infinity, are formed in the liquid. Under very clean conditions these clusters can be stable for years. But in many cases the electron is first solvated and then undergoes a reaction, either with the host medium or an impurity, giving the solvated electron a finite lifetime, which depends strongly on the impurity content of the solvent.

The celebrated "hydrated electron" was postulated to exist [1] in 1952, and was experimentally identified in the bulk [2, 3] in 1962. It was conceived as an electron self-trapped in bulk water. Its structure will be discussed in detail below. It is produced when ionising radiation interacts with water. As all living material, including us humans, consist mainly of water, some hydrated electrons are formed in our bodies, when e.g. an X-ray is taken, or the body is exposed to some other form of ionising radiation. Due to the strong chemical actions of the hydrated electron, it is important in radiation damage of living material [4]. The hydrated electron might be difficult to study, but it is an ubiquitous species. For example, the surface water of the oceans can contain up to 10<sup>9</sup> hydrated electrons per liter at full sun light [5]. The history of the bulk chemical and biological studies of hydrated electrons has recently been summarised [4]. A collection of newer references can be found in [6, 7].

There exist two different classes of atoms and molecules, which form dielectrics in the bulk:

1. Those which have a negative ion state as a monomer like O<sub>2</sub>, SF<sub>6</sub>, N<sub>2</sub>O, etc. The negative ions of these molecules are stable and well studied. The electron enters into a well defined molecular orbital of the molecule proper. The

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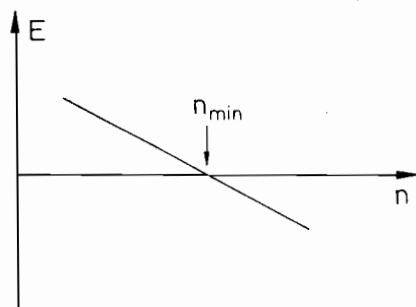


Fig. 2. The binding energy  $E$  of an extra electron is plotted against the cluster size  $n$ . For  $n$  below  $n_{\min}$ ,  $E$  is positive and the electron is not bound. One has a resonance in electron scattering. For  $n > n_{\min}$  the extra electron is bound and a stable cluster can be formed

electron affinity (EA) is positive, where EA is the minimal energy to eject an electron from the negative ion. (For a definition of EA see Fig. 9).

2. Some atoms and molecules on the other hand do not have a stable negative ion state as a monomer. Among these are: the rare gases with the possible exception of xenon,  $\text{H}_2\text{O}$ ,  $\text{NH}_3$  etc. The electron can only be bound by the *cooperative effect* of many atoms or molecules. It is for this latter class of substances only, that one speaks of a solvated electron proper. Some examples are collected in Table 1. All atoms and molecules in this second category have closed electronic shells.

If  $n$  is varied in, say,  $(\text{H}_2\text{O})_n^-$  from 1 to a very large number, the development of bulk hydrated electron can be studied. Several interesting questions and phenomena arise in this study:

1. Solvated electron clusters can only be formed in nonconducting, dielectric fluids and solids. But insulating materials are formed by condensing closed shell atoms and molecules, which most often do not have a bound negative ion state as a monomer. (Exceptions are the alkali-halides and possibly xenon.) The interaction of a slow electron with a closed shell atom or molecule leads to a resonance in the electron scattering continuum. A transition from a resonance in electron scattering to a bound electronic state must therefore occur as a function of cluster size, as indicated in Fig. 2.
2. What is the minimal number  $n_{\min}$  of atoms and molecules necessary to support a bound state, and how does  $n_{\min}$  vary from one substance to the other? (Compare Fig. 2 and Table 1.)
3. How is the macroscopic limit attained? Does the structure of the cluster between  $n_{\min}$  and  $n \rightarrow \infty$  evolve more or less continuously or are there interesting transitions?
4. What happens if the cluster size becomes equal to the diameter of the electronic charge distribution?
5. Is the electron inside or on the outside of the cluster?
6. Does the chemical reactivity change with cluster size?

### 2.5.1.1 Solvated Electrons in the Condensed Phase

A wealth of information is available from experiment and theory on solvated electrons in the condensed phase. Dipolar and nonpolar vapours, liquids and

solids have all been studied [6, 7]. The high interest has a physical and a chemical origin. Questions asked are: What are the electronic states in disordered materials? How does electron localisation happen? How can one understand the metal to non-metal transition at high sodium content in Na/NH<sub>3</sub> solutions? How is the electron's mobility changing from the gaseous to the liquid state? Are there differences in the optical absorption spectrum of electrons solvated in liquid water and ammonia? How does a liquid-state environment influence the quantum behaviour of matter? What is the influence on electron transfer reactions in solutions, etc.? Because of its radiological relevance, a short summary is given here on how solvated electrons are formed in liquid water. Other applications are treated in the chapter by *Belloni et al.* in this book.

If a fast electron is injected into liquid water four different processes can be distinguished:

*Thermalisation.* The kinetic energy of the fast electron is quickly reduced by ionisation and electronic excitation until its energy is in the 5 eV range. Then excitation of vibrations (phonons) and hindered rotations become important. It takes about 10 to 20 fs to thermalise an electron in liquid water. (1 fs = 1 femtosecond =  $10^{-15}$  s).

*Localisation.* The electron now moves for 110 to 180 fs in the empty conduction band of water (compare Fig. 1), until it finds a shallow trap state (Tr 1 in Fig. 1), on which it can localise. A strong absorption in the near infra red appears.

*Solvation.* The molecules around the newly trapped electron experience a new force field. The H<sub>2</sub>O molecules rotate until they have found the new position of lowest energy. This takes about 240 fs. A strong absorption in the red part of the visible spectrum appears. The fast times cited above have been measured by generating the electron and probing its absorption by fs laser pulses [8, 9].

*Recombination or Reaction.* Not only the electron, but also the ion is solvated. They attract each other by the Coulomb force, which is screened by the water molecules lying between the two charge centers. If the attraction becomes strong enough, the electron and the ion can recombine. Alternatively the solvated charges can be destructed by a chemical reaction.

## 2.5.2 Case Studies

The different possibilities for electron localisation in and on small clusters of closed shell atoms and molecules will be discussed for several prototypes. Stress will be laid on the experimental observations.

### 2.5.2.1 Helium

Calculations indicate that excess electrons can be bound to the surface of very large He clusters [10]. These states are similar to the well studied electronic surface states on liquid helium. Due to the very low polarisability of He and Ne the interaction of an extra electron with bulk He or Ne is repulsive. For clusters containing more than  $10^5$  He atoms, the potential well between the attractive polarisation force and the repulsive bulk potential is just strong enough to support a bound state for an extra electron. There exist many interesting theoretical questions concerning these states. But definite experimental verification will become very difficult [11]. Large helium clusters are known to soak up any molecule they encounter on their way through a vacuum chamber. This makes for a terrible background problem. For example some  $O_2$  is always present in a vacuum system. The  $O_2$  molecule has a high positive electron affinity, thus forming easily negative ions. As  $O_2$  has nearly the same mass as eight He atoms, one would need a mass spectrometer with a resolving power of nearly  $10^9$  in order to distinguish between  $He_{n+32}^-$  and  $He_n O_2^-$ , with  $n \geq 10^5$ .

### 2.5.2.2 Xenon

The bottom of the (normally empty) conduction band of solid xenon lies 0.4–0.5 eV below the vacuum level. Or stated differently, the electron affinity of solid xenon is 0.4 to 0.5 eV, a value obtained in two independent experiments [12, 13]. The extra electron is not self trapped, it can move freely in the otherwise empty conduction band.

For the atom it is not yet finally clear, if the recently observed [14] negatively charged xenon atom is in the electronic ground state or in an electronically excited metastable state. In any case the electron affinity of the Xe atom is either very small or negative.

Several theoretical treatments have attacked the problem of electron attachment to xenon clusters. The interaction of the extra electron with the Xe atoms has to be treated quantum mechanically. The interaction of the atoms among themselves is either treated classically [15], or a continuum model is used [16]. The calculated minimal cluster size is in the 6–10 atom range.

For the experimental test [14] of these predictions a mixture of Xe with Ar and  $N_2$  was expanded from a pulsed supersonic beam and 100 eV electrons were injected at position A of Fig. 14 of "Experimental Methods". The fast electrons eject secondary electrons from the beam. These are quickly decelerated by collisions. The nitrogen gas is necessary, as it serves as a "moderator" for the electrons, extracting their kinetic energy via the short lived negative ion resonance:  $N_2(v=0) + e^- \rightarrow N_2^- \rightarrow N_2(v \geq 0) + e^-$ . After the collision the electron has lost kinetic energy and the  $N_2$  molecule is vibrationally excited. It seems, that only very low energy electrons can attach to the xenon clusters.

A Xe mass spectrum shown in Fig. 3. Some intensity is observed on all cluster masses down to the monomer. According to theory, the extra electron is repelled from the interior of an Xe atom. The space available to the extra electron are the "channels" between the atoms and the surface of the cluster. This is obviously a delocalised electron state. If there are more or deeper or wider channels for the electron to move in, its binding energy increases. For  $\text{Xe}_{13}^-$  a compact icosahedral structure has been calculated. The central atom with its two pentagonal caps of six atoms each can be seen in Fig. 4. For  $N = 19$  one has an icosahedron with an additional pentagonal cap. These icosahedral shapes are more compact than their neighbours, with narrower channels between the xenon atoms and consequently lower electron binding energy. If the electron affinity is lower it is plausible that an electron is less often attached and more often detached in the expanding jet. This results in a low intensity on masses  $N = 13$  and 19. Similarly the open structure of  $N = 12$  and  $N = 18$  leads to a higher electron affinity and to the higher experimental intensity. On this qualitative level experiment and theory are in agreement.

Rare gas atoms are known to have very long lived, metastable excited states which sometimes can attach an electron. For example the metastable triplet state of helium,  $\text{He}(1s2s, ^3S)$ , can form a long lived negative ion state. If similar states would exist in the xenon atom and cluster, they could give rise to the mass spectrum in Fig. 3. An energy of about 10 eV is necessary to excite the metastable state. The kinetic energy of the electron beam is a factor of ten higher. So the excitation of a metastable Xe state, which could in principle attach an electron, cannot be ruled out.

An experiment with photo-electrons which utilised electron energies below 1 eV gave a smallest cluster of  $n = 6$ . Smaller  $\text{Xe}_n^-$  clusters could have been there,

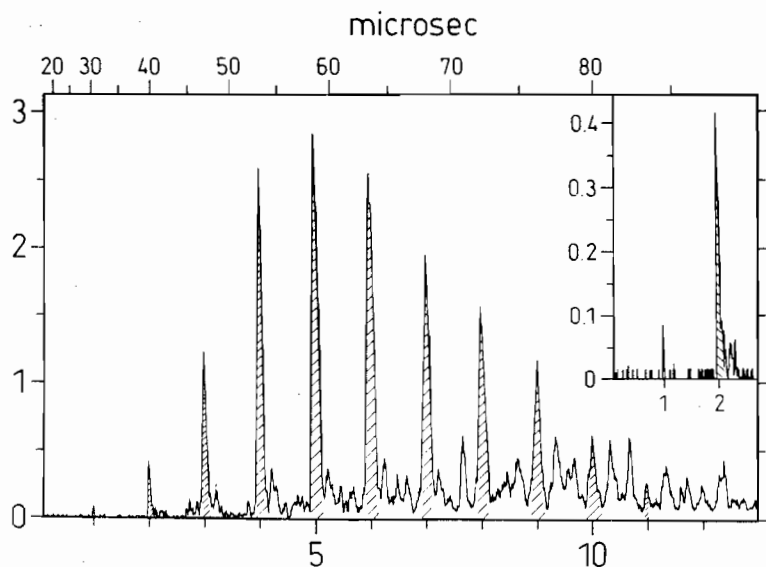


Fig. 3. Mass spectrum of negatively charged Xe clusters. The marked peaks are  $\text{Xe}_n^-$  clusters, the other ones are impurity peaks. The insert shows the  $n = 1$  and 2 peaks on a large scale

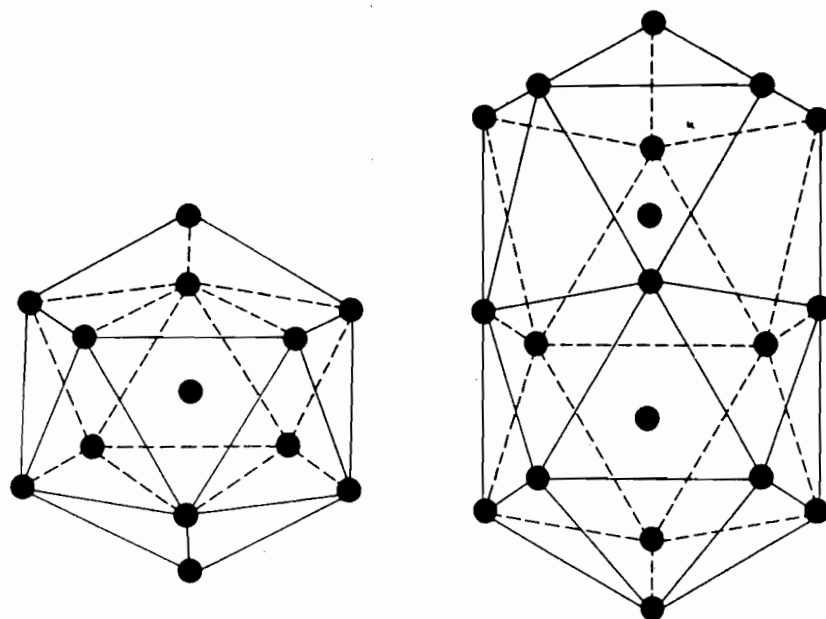


Fig. 4. Calculated structures for  $Xe_{13}^-$  and  $Xe_{19}^-$ . The  $n = 13$  cluster has the shape of an icosahedron, an inner atom having two pentagonal caps. For  $n = 19$  another pentagonal cap is added. As explained in the text the compact structure of the icosahedra can explain the high intensity on mass  $n = 12$  and 18, and the low intensity on mass 13 and 19 in Fig. 3

but could not be seen due to a large interfering background. It is not impossible, that even the atom could support a negatively bound stable state. Some  $n_{min}$  values are collected in Table 1 below.

### 2.5.2.3 Water and Ammonia

Cluster models for electrons solvated in water and ammonia clusters had been popular with theorists long before experimental studies became feasible. As the electron localises on a few molecules it is theoretically often easier to treat a finite number of molecules, rather than the infinite bulk. By the early 1980's the first successful mass spectrometric studies had been performed, in a time when one had to learn how to synthesize these clusters. Later photo-detachment and photo-fragmentation studies proved a good meeting ground of theory and experiment.

#### 2.5.2.3a) Mass Spectra

Figure 5 shows a mass spectrum of  $(NH_3)_n^-$  clusters. Above some  $n = n_{min}$  the intensity increases rapidly by nearly 3 orders of magnitude, and tails off slowly for larger  $n$ . The decrease at high  $n$  is at least partially due to the detection

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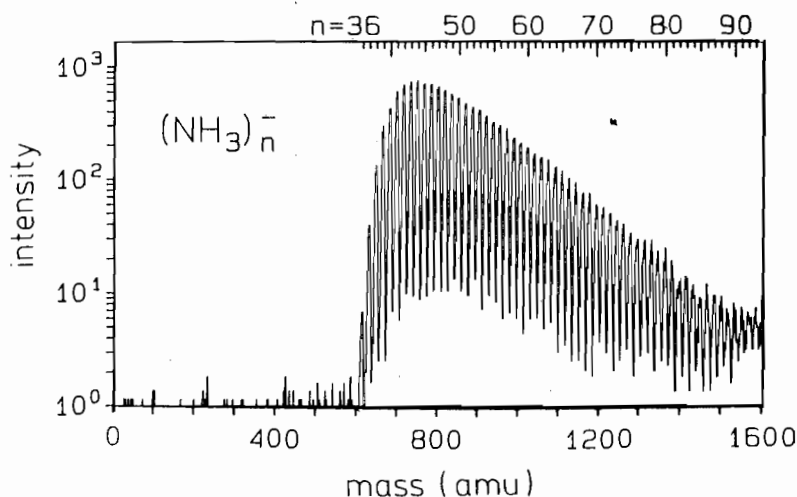


Fig. 5. Mass spectrum of negatively charged  $\text{NH}_3$  clusters. No  $(\text{NH}_3)_3^-$  clusters were ever observed with  $n < 34$

problems discussed in Chapter 3.2. Larger clusters are always less efficiently detected.

The  $\text{NH}_3$  clusters were produced by injecting very slow electrons into the very first part of a supersonic expansion (point A of Fig. 3.15). The clusters can grow around the electron. By playing with the diameter and temperature of the nozzle, and the percentage and nature of the seeding gas it was determined that below  $n_{\min} = 35$  no negatively charged  $\text{NH}_3$  clusters could be synthesized. The  $n_{\min}$  values of several molecules and atoms are collected in Table 1.

Alternatively one can attach electrons at point B of Fig. 3.15. The smallest cluster observed is always larger than  $n_{\min}$ , even when the extremely low energy electrons available in Rydberg atoms are used [17]. The physical reason will be discussed below for the similar case of water clusters.

The case of water is more complex. First the results for a pure, unseeded water expansion will be treated. Attaching low energy electrons either at point

Table 1. The table gives the minimal number of atoms and molecules needed to support a bound negative ion state. Both the very large difference between water and ammonia, and the ammonia isotope effect are presently not understood

Molecule	$n_{\min}$	Atom	$n_{\min}$
NaF	1	Mg	3
$\text{H}_2\text{O}$	2	Hg	3
$\text{D}_2\text{O}$	2	Xe	6
HCl	2		
$\text{H}_4\text{C}_2(\text{OH})_2$	2		Possibly 1
$\text{NH}_3$	34		
$\text{ND}_3$	41		



A or B, the minimal cluster size is 11 to 12, as shown in the middle part of Fig. 6. If the electron's kinetic energy is increased, dissociative electron attachment



can take place. The stable negative ions  $\text{OD}^-$  and  $\text{OH}^-$  can attach any number of water molecules, leading to the upper spectrum of Fig. 6. This proves that indeed all cluster sizes are present in the beam. It will be argued below, that smaller  $(\text{D}_2\text{O})_n^-$  are actually formed, but have too short a lifetime, to be visible in this experiment.

The authors [18] estimate with arguments similar to those leading to Eq. (3.21) that their cluster temperature is about 180 K. Once the electron is attached the water dipole moments start to rotate, seeking the new position of lowest energy. This will increase the clusters temperature further. What will be ejected by this high internal vibrational energy, an electron or a molecule? The two following processes are possible:



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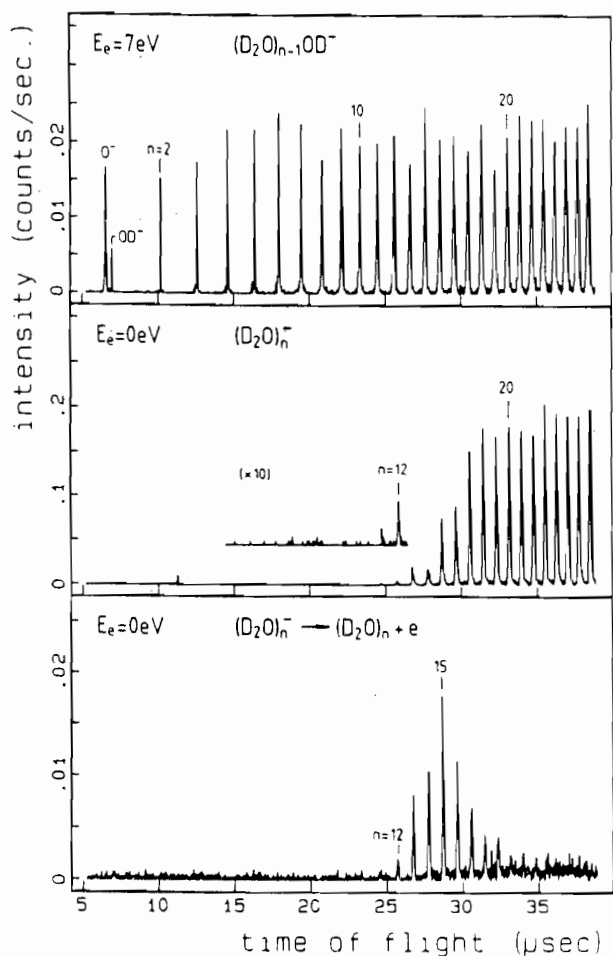


Fig. 6. The middle spectrum shows heavy water cluster anions obtained by attaching low energy electrons to cold water clusters. The lower spectrum shows the metastable clusters, those which have survived the acceleration into the mass spectrometer, but have subsequently ejected an electron. The upper spectrum is obtained if the energy of the electrons is raised

In the first case a neutral molecule, in the second one an electron is ejected. In the metastable time window  $0.1 \cdot \text{TOF} \leq t \leq \text{TOF}$ , where TOF is the flight time of the  $(\text{D}_2\text{O})_n^-$ , the channel according to Eq. (2.5.3) is dominant. The mass spectrum of the remaining neutrals is shown in the lower part of Fig. 6. The clusters have lost their electron in the field free region of the TOF mass spectrometer. They have the same velocity as the charged ones, but as neutral particles no longer react to electric fields, and can easily be discriminated from the ions in the beam. Neutral particles with sufficient kinetic energy can also eject an electron from a metal surface, so that a mass spectrum can be recorded.

Figure 7 shows the electron attachment probability as a function of the kinetic energy of the electron. A resonance near zero kinetic energy is measured for the solvated electron cluster production, proving that the attachment is indeed a resonant process. This experiment proves that slow electrons can be attached to cold clusters, where they can be trapped, in what has been termed "preexisting traps", traps for the electron, which have been present in the neutral cluster. This question had controversially been discussed in the literature on solvated electrons in bulk media. For electron energies between 2 and 5 eV the electron attachment cross section is very low. Afterwards it increases due to the dissociative attachment processes (see Eq. (2.5.1)).

Decay processes according to Eq. (2.5.2) and (2.5.3) do occur also on smaller and longer time-scales than discussed above. If the decay time is longer, the cluster ions appear as stable. They contribute to the middle spectrum in Fig. 6. But if the lifetime is shorter than  $0.1 \cdot \text{TOF}$ , they decay already in the ion source or acceleration region. There exist no plausible reason why small  $(\text{D}_2\text{O})_n^-$  are not formed in the interaction of slow electrons with water clusters at 180 K, but their lifetime is so short that they decay before detection. The internal energy leading to the fast decay has three contributions, the temperature (180 K per degree of freedom), the electron affinity, and the reorientation energy of the water molecules. The sum of these three contributions has to be reduced if the smaller, less stable clusters are to appear. This can be done by attaching slow electrons at position A of Fig. 3.15. At point A the density of water and seed gas is so high, that multiple collisions occur, so that a yield curve like in Fig. 7

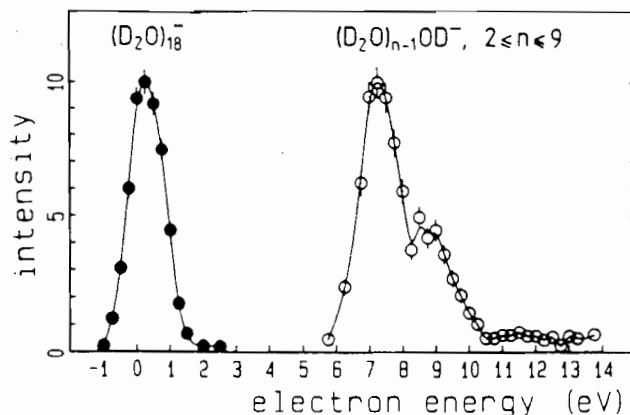
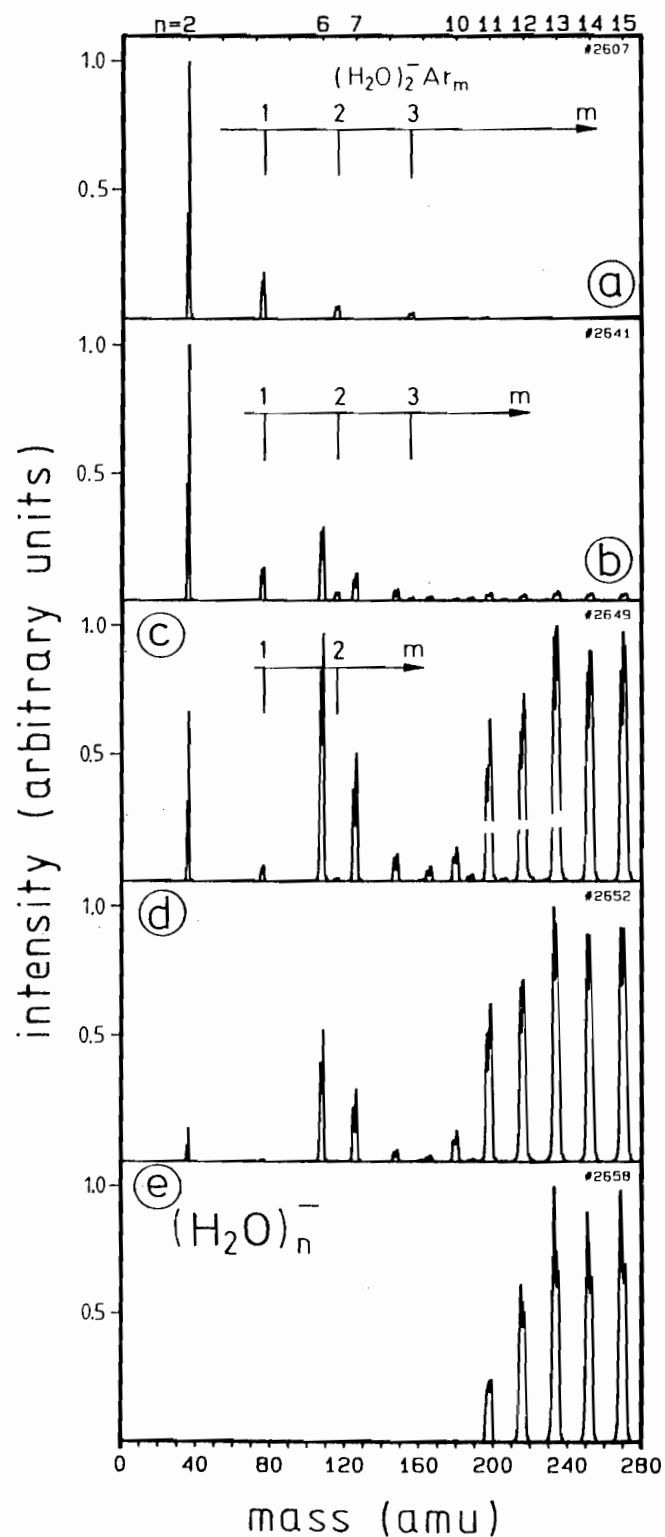


Fig. 7. Yield of specific cluster ions as a function of the kinetic energy of the attaching electrons. For electron energies below 1 eV solvated electron clusters are formed. Energies above 6 eV lead to dissociative electron attachment. The intensity below 0 eV is an artifact of the experiment

cannot be measured. The electron acts as a condensation point for the clusters, which grow around the charge in an already relaxed configuration. The clusters are cooled by collisions with the seed gas. The smaller the water content, the cooler the expansion will be, and the smaller clusters can be synthesized. This



**Fig. 8.** For the production of small negatively charged water clusters a large surplus of rare gas is needed. The smaller the water content, the lower is the temperature in the expansion, and the smaller  $(\text{H}_2\text{O})_n^-$  clusters can be synthesized. From top to bottom the partial water pressure was only 0.0008, 0.008, 0.016, 0.022, 0.04 parts of the 7.5 bars argon pressure. If the water content is very low, mixed clusters like  $(\text{H}_2\text{O})_2^- \text{Ar}_n$  can be formed. Only if one sees these mixed clusters one can sure that the clusters are cold

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expectation is confirmed by the experimental result shown in Fig. 8. At 4% water content  $(\text{H}_2\text{O})_n^-$ ,  $n = 10$  is the smallest cluster visible. Reducing the water content all clusters with the exception of  $n = 4$  can be observed. For the dimer,  $(\text{H}_2\text{O})_2^-$ , the measured vertical detachment energy is only 47 meV [19]. If some vibration or rotation is excited, an energy transfer (by a non-Born–Oppenheimer process) to the electron is possible, and it can be ejected. Therefore, these fragile species can only be synthesized in very cold beams.

This feature has been utilised to measure a vibrational spectrum of  $(\text{H}_2\text{O})_2^-$ . An IR-laser was used to excite a vibrational frequency, leading to an ejection of the electron [20].

### 2.5.2.3b) Photodetachment

Although a considerable amount has been learned from mass spectrometry, a more quantitative knowledge is available from the study of photo-interactions with mass selected clusters.

Before a discussion of the experimental results is possible some definitions have to be introduced: the adiabatic and vertical electron affinity ( $EA_a$ ,  $EA_v$ ) and the vertical detachment energy (VDE). A schematic sketch is shown in Fig. 9. The adiabatic electron affinity is defined as the energy difference between the ground states of  $X_n$  and  $X_n^-$ :

$$EA_a = E(X_n, v = 0) - E(X_n^-, v' = 0) \quad (2.5.4)$$

The binding energies  $E$  are taken negative here, so that the EA of a stable negative ion is positive. The geometries of the lowest energy states of  $X_n$  and  $X_n^-$  might occasionally be so different, that the corresponding vibrational

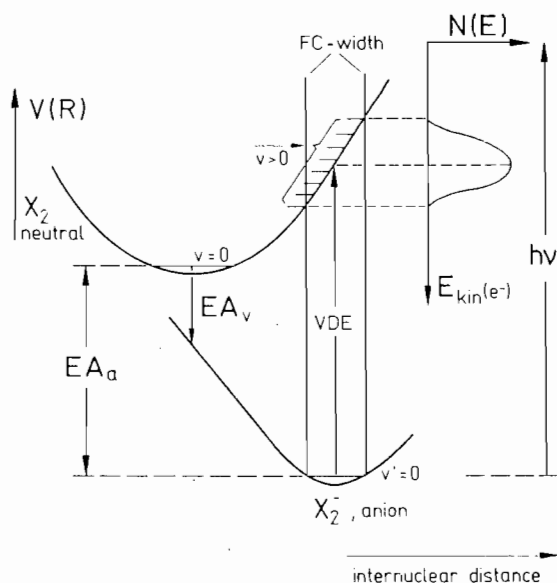
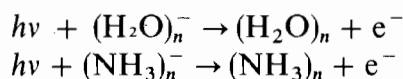


Fig. 9. Definition of the adiabatic and vertical electron affinity ( $EA_a$ ,  $EA_v$ ) and of the vertical detachment energy (VDE) for a diatomic molecule  $X_2$ . Electrons with different kinetic energies are emitted if a photon  $h\nu$  induces an electronic transition. The minimal and maximal kinetic electron energies compatible with the Franck–Condon principle are indicated

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wavefunctions  $|v\rangle$  and  $|v'\rangle$  do not have an overlap, i.e.,  $\langle v|v'\rangle = 0$ . It is this overlap which controls the strength of an optical transition; its square is called the Franck–Condon factor [21]. If the Franck–Condon factor is zero between the two states on the right hand side of Eq. (2.5.4), the electron affinity cannot be measured optically, as the transition probability connecting the two states vanishes. But for higher vibrational states  $v = n > 0$  the Franck–Condon (FC) factor can become finite (compare Fig. 9). The FC-factor increases at first, reaches a maximum and decreases afterwards. This is directly reflected in the kinetic energy spectrum of the emitted electrons. The vertical detachment energy (VDE) corresponds to the most probable part of this transition. The difference,  $\delta E = \text{VDE} - \text{EA}_a$ , is often called the rearrangement energy. It is the energy needed to rearrange the atoms in  $X_n$  so that the optical transition from  $X_n^-$  attains its largest value.

The word “vertical” in  $\text{EA}_v$  and VDE has the following origin. The Born–Oppenheimer approximation of molecular and solid state physics tells us, that the nuclei do not move during an electronic transition, i.e.  $\delta R = 0$ . In a potential energy diagram, where the potential energy  $V(R)$  is plotted against the internuclear position  $R$ , the VDE corresponds to a *vertical* transition from the potential curve of  $X_n^-$  to the higher one for  $X_n$ , without any change in  $R$ . After these preliminaries the photo processes in



can be discussed. The geometry of the neutral or negatively charged clusters may be very different. If the  $v' = v = 0$  vibrational wavefunctions would not overlap, only the VDE and not the  $\text{EA}_a$  could be measured optically.

Figures 10 and 11 show the measured VDE for water and ammonia clusters [19, 22, 23]. A continuous, mass selected negative cluster ion beam was crossed with a high intensity laser beam. The energy spectrum of the emitted electrons was measured. The peak maximum of the spectrum gives the VDE. In Figs. 10 and 11 the data are plotted against  $n^{-1/3}$  which is proportional to the inverse of the cluster radius [24]. For water above  $n = 11$  and for all ammonia data points, the experimental results are well represented by straight lines, which extrapolate to the correct bulk values for  $n \rightarrow \infty$ .

From a simple electrostatic calculation for the energy to eject an electron from the center of a homogeneous dielectric sphere one obtains [25]:

$$\text{VDE}(n) = \text{VDE}(n = \infty) - \frac{e^2}{2R} \left( 1 + \frac{1}{D_{\text{opt}}} - \frac{2}{D_{\text{stat}}} \right) n^{-1/3}, \quad (2.5.5)$$

where  $D_{\text{opt}}$  and  $D_{\text{stat}}$  are the optical and static dielectric constants and  $R$  the effective radius of water or ammonia. Equation (2.5.5) tells us, that a straight line is expected for the VDE on a  $n^{-1/3}$  plot if electrostatic effects prevail and if the electron is in an interior state inside the cluster. Save for the small water cluster sizes, the experimental results can be very well fit by straight line. Inserting the

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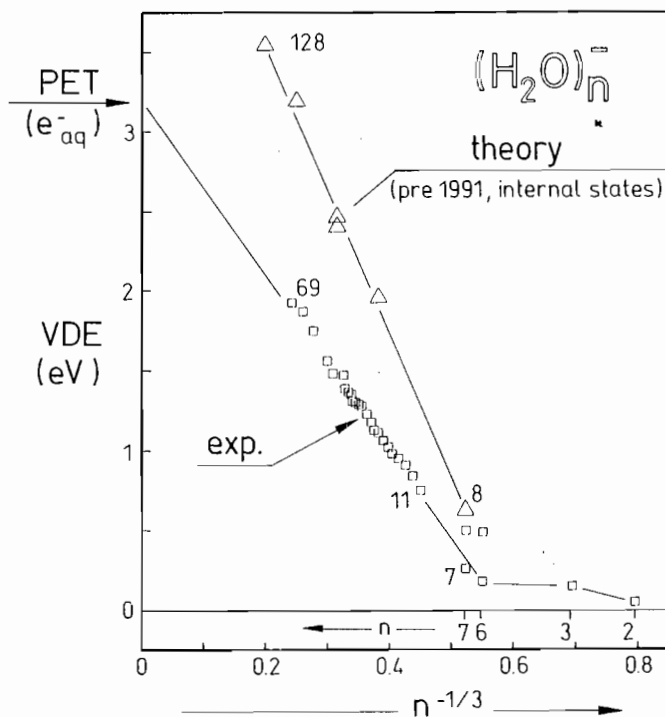
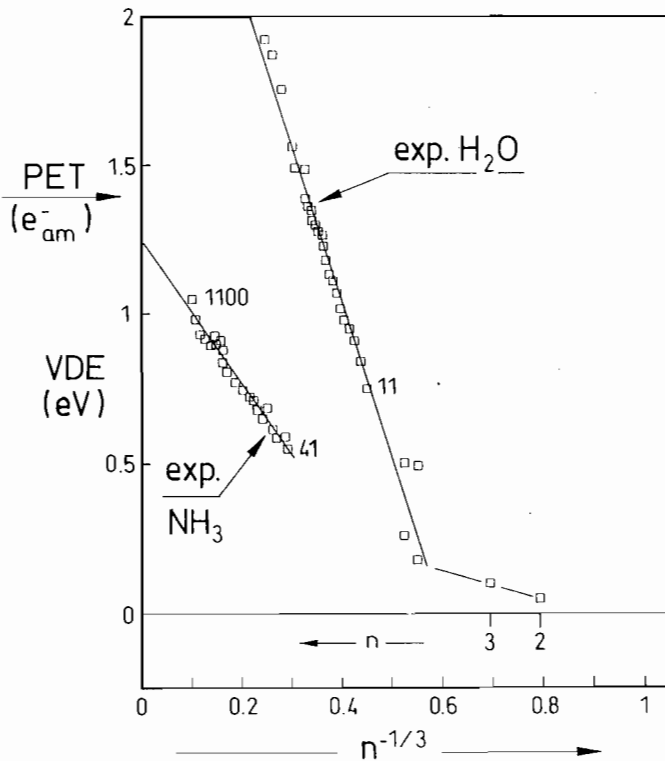


Fig. 10. The measured and calculated vertical detachment energies for  $(\text{H}_2\text{O})_n^-$  clusters are plotted against the inverse of the reduced cluster radius. A fit by Eq. (2.5.5) using bulk data gives a surprisingly accurate fit to the data. The calculated volume states show the same linear behaviour, but the slope and the asymptotic value are too high

known values into Eq. (2.5.5) one finds a surprisingly good agreement with the experiment for water. For ammonia the agreement is poorer. For example, the  $R$ -value for water is within 5% of that calculated for a density of  $1 \text{ g/cm}^3$ . The data for the small water cluster sizes do not fall on this line. But all other data can be well fit by a straight line, which has a slope calculated from Eq. (2.5.5) and the correct bulk limit. So this seems to be consistent with the picture of an electron solvated in ever increasing cluster sizes. A difficulty with this interpretation is discussed below.

The VDE ( $n = \infty$ ) of Eq. (2.5.5) is not measured directly, but it should be equal to the photoelectric threshold (PET) energy of the bulk solvated electron. For water the PET is about 3.2 eV, and the photodetachment data extrapolate to a VDE ( $n = \infty$ ) of 3.3 eV. Similarly one finds for ammonia, that an upper limit of PET( $\text{NH}_3$ ) is about 1.4 eV, while the detachment data extrapolate to about 1.25 eV. Above  $n = 11$  for water and  $n = 41$  for ammonia, the negatively charged clusters seem to evolve directly to the bulk solvated electron. No experimental evidence for a transition to another structure is seen.

One must be cautious in applying Eq. (2.5.5). It is derived by assuming that the solvated electron radius is much smaller than the cluster radius. This condition does certainly not hold for the smaller  $(\text{H}_2\text{O})_n^-$  clusters, where a straight line with the correct (bulk) parameters still gives a good fit. A recent



**Fig. 11.** Comparison of experimental vertical detachment energies for negatively charged water and ammonia clusters. While  $(\text{H}_2\text{O})_n^-$  is stable down to  $n = 2$ , for  $(\text{NH}_3)_n^-$ ,  $n = 34$  is the smallest one observable. Because of the low signal intensity no data exist for  $n$  between 34 and 41. The straight lines result from a least square fit to the data. The water data extrapolate to the correct bulk value, as shown in Fig. 10

model calculation using a mean spherical approximation for  $\text{I}^-(\text{H}_2\text{O})_n$  revealed that Eq. (2.5.5) might be obeyed only for  $n \geq 125$ , or so [26]. For the smallest clusters the VDE versus  $n^{-1/3}$  curve oscillates. A close inspection of the data do in fact show some very weak oscillations. Whether they correspond to the calculated ones is not known. One is left with the dilemma, that Eq. (2.5.5) gives a beautiful fit to the data in a size region, where it should not be applicable.

Quantum path integral calculations have been performed on negatively charged water [27] and ammonia [27, 28] clusters. In essence the interaction of the assumed rigid water or ammonia molecules among themselves is treated classically, while quantum mechanics is used to describe the electron-molecule interaction. For large cluster sizes (e.g.:  $n$  above 64 for water) the calculations find "internal states" for the extra electron in water cluster anions [27]. The electron is primary localised in the center of the cluster for these volume states. The early calculated VDE values for the volume states of  $(\text{H}_2\text{O})_n^-$  are included in Fig. 10. They agree qualitatively with the experimental results, and show the same straight line behaviour on a VDE versus  $n^{-1/3}$  plot. But their slope and extrapolated bulk value are too high. Very new results, using improved potentials, give a better agreement, but the slope and intercept are still too high [29].

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For small water cluster anions the calculations show that the electron is localised on a "surface state" [27, 28]. The very small water clusters ( $n = 2-8$ ) do quite possibly belong to this class, as these small clusters are composed of surface only. Why there is no experimental signature of a surface state is unknown for the moment. It could be that surface states of the larger clusters are not formed experimentally. The dimer ion,  $(\text{H}_2\text{O})_2^-$ , is a surface state, and it can be formed. On the theoretical side, the complicated water-water and water-electron interaction is not known exactly, or the assumption of a rigid water molecule might not be tenable.

### 2.5.2.3c) Angular Distribution of the Photo-electron

One experiment has been performed to measure the angular distribution of the emitted electrons. In simple cases the symmetry of the extra electrons wavefunction can be deduced from such a measurement. In this experiment a polarised laser beam is overlapped with an unpolarised  $(\text{H}_2\text{O})_{18}^-$  beam, and the angle  $\theta$  between the laser polarisation and the velocity vector of the emitted electron is varied. The experimental result, shown in Fig. 12 has been fitted to the theoretical prediction:

$$I(\theta) = \sigma_{\text{total}}[1 + \beta P_2(\cos \theta)] \quad (2.5.6)$$

where  $P_2(u) = (3u^2 - 1)/2$  is the second Legendre Polynomial and the asymmetry parameter  $\beta$  can take values between  $+2$  and  $-1$ . A fit to the data gives  $\beta = 0.92$ . For a pure s-type orbital (zero orbital angular momentum of the extra electron) one expects  $\beta = 2$ , while  $\beta = -1$  is obtained for a p-orbital. No calculation exists to which this experiment could be compared.

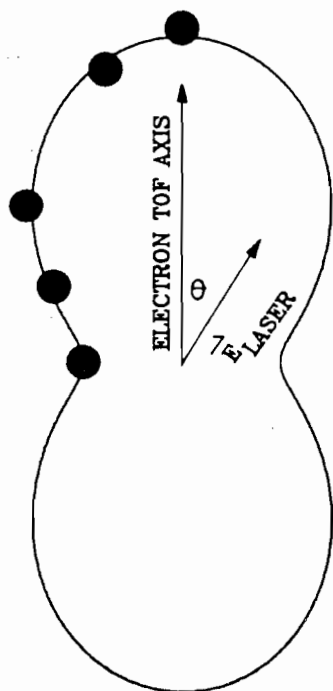


Fig. 12. Angular distribution of ejected photo-electrons. The angle  $\theta$  is spanned between the polarization vector of the photon and the velocity vector of the electron



### 2.5.2.3d) Photofragmentation

In the context of Eqs. (2.5.2) and (2.5.3) the question was asked, what does a highly excited negatively charged cluster emit, an electron or a molecule? This problem was studied in more detail for  $(\text{H}_2\text{O})_{25}^-$ . The cluster was photoexcited and the two decay channels studied [30]. The energetic threshold for photodissociation (e.g. Eq. (2.5.2)), is  $\approx 0.48$  eV, while that for photodetachment is 0.8 eV. Photodetachment dominates for photon energies above 2 eV. Photofragmentation is seen only within about 1 eV above the detachment threshold. Probably the water molecules in the cluster have to move before the electron can leave at low photon energies. Otherwise the concurrence of the two time scales is difficult to understand. The influence of the clusters' internal excitation on the fragmentation pattern could be demonstrated [31].

### 2.5.2.3e) Summary and Remaining Problems

Although enormous progress has been made in the understanding of the negatively charged water and ammonia clusters, several questions remain open, and are the focus of intense research:

1. What is the origin of the very different  $n_{\text{min}}$  values in Table 1?
2. What is the experimental signature of the calculated surface states? Why is there no experimental evidence for their existence at larger sizes?
3. What kind of physical information does the  $\beta$  value of the angular distribution contain?
4. Above which  $n$  do doubly negatively charged solvated electron clusters become stable? Are both the singlet and the triplet state bound?

### 2.5.2.4 Alkali-Halide Clusters

The excess electron states in alkali halides are somewhat different from those discussed above. The clusters are neutral and the monomer anion exists. But these systems, in both the cluster and the bulk, are similar in some ways to  $\text{H}_2\text{O}$  and  $\text{NH}_3$ , so that they are discussed here.

#### 2.5.2.4a) Excess Electron States for the Molecule and the Solid

The chemical bonding in alkali halide molecules, say  $\text{NaF}$ , is well described by treating the molecules as ion pairs,  $\text{Na}^+\text{F}^-$ . The valence electron of the metal fills the hole in the halogen's valence shell, giving two closed shell ions bound by the strong Coulomb attraction. In the monomer anions the extra electron goes into the alkali valence orbital, which is strongly polarized by the halogen ion [32]. The charge density of the extra electron is mainly located "behind" the

positive metal ion core, well shielded from the halogen ion. Thus, in contrast to the examples discussed above, the monomer itself does have a positive electron affinity.

The excess electron states in the bulk are the well known F-centers. The electron occupies the position of a missing halogen molecule. Its charge density is concentrated mainly near the eight neighbouring positively charged metal ions. The F-centers are well studied and characterised, as explained in many textbooks on solid state physics [33].

#### 2.5.2.4b) Calculations of Excess Electron States in Molecules and Clusters

The interaction potential used in calculations on alkali-halide molecules, clusters and crystals is the so called Rittner potential and its variants [34–36], which describes the Coulomb attraction of the ions counterbalanced by an exponential repulsion, which arises when the two closed electronic shells overlap. The calculated most stable structures often have cube or chair-like structures. Theoretically and experimentally it is observed, that cluster ions have especially stable cubic structures, if they contain an odd number  $2n - 1 = j \cdot k \cdot l$  of atoms, with  $j$ ,  $k$ , and  $l$  all odd integers. Examples are  $\text{Na}_{14}\text{F}_{13}^+$  or  $\text{Na}_{23}\text{F}_{22}^+$ , with  $2n - 1 = 3 \cdot 3 \cdot 3$ , or  $3 \cdot 3 \cdot 5$ . The clusters form a filled cubic microlattice with 3 or 5 atoms on one side. Adding 1 extra electron to this cluster, makes a neutral cluster. The extra electron is so weakly bound that it has to be treated quantum mechanically [35, 36]. The electron distributes its charge density uniformly around the cluster, if the position of the nuclei is clamped fixed during electron attachment. If the atoms are allowed to move the excess electron localizes, forming a weakly bound surface state (binding energy  $\approx 1.8$  eV). These states have been termed Class I in [36]. The cluster analog of the bulk F-center belongs to Class II. They again have the stable near cubic structures. Their detachment energies are in the 3–4 eV range. Excess electrons in noncubic clusters (Class III) have binding energies of  $\approx 3.8$  eV. The excess electron is probably bound to a single Na atom, similar to the alkali halide molecule. Most of these predictions have indeed been verified experimentally.

#### 2.5.2.4c) Observation of Excess Electron States in Alkali-Halide Clusters

For the production of alkali-halide clusters one may use laser vaporisation of Na metal into a helium flow containing 1%  $\text{SF}_6$  [36]. The molecule is dissociated in the hot, laser produced plasma and NaF molecules and clusters are formed. The electronic structure of the excess electrons and the cluster geometry is probed by one and two photon laser spectroscopy, giving a satisfactory agreement between theory and experiment [35, 36].

### 2.5.3 Outlook

Only a few of the questions asked in the introduction have been answered satisfactorily to date. The field is one of active research, which has profited much from the interaction of theory and experiment.

### 2.5.4 Recent Developments

(1) Recently, it has been pointed out [37] that the  $(\text{NH}_3)_n$ -VDE data fit Eq. (2.5.5) rather well when the dielectric constants for solid ammonia are used. Under the conditions utilized to form these cluster anions, they are very likely to be solid [38]. Also, more recent measurements [39, 40] of the bulk PET for ammoniated electrons in dilute solutions find it to range between 1.27–1.45 eV, in even closer agreement with the 1.25 eV extrapolated from experiment [19]. (2) The species  $(\text{H}_2\text{O})_{n=2,6,7}$ , were observed via collisions of water clusters with laser-excited Rydberg atoms [41]. (3) Ethylene glycol cluster anions were studied by photodetachment [42]. (4) Mixed cluster anions of ammonia and water were studied by photodetachment [42]. Also, the dipole-bound dimer anion,  $(\text{H}_2\text{O})(\text{NH}_3)$ , was predicted and then observed [43]. (5) Several alkali halide cluster anions were studied by photodetachment [44, 45] and evidence for both F and F' centers was seen.

*Acknowledgments.* The authors acknowledge the support of a NATO grant (#861307) and KB acknowledges the support of the US NSF under grant CHE-9007445.

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have recently bombarded a He beam with electrons. They observed a negative ion signal, which was not mass analyzed. It is interpreted as being due to an electron in a metastable "bubble state" inside a He-cluster. It cannot be the very weakly bound surface state, which would field detach in the electric fields of the mass spectrometer.

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