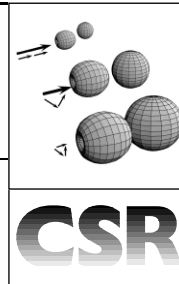


# Structural dependence of electron transfer to non-covalent polar complexes



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**Electron attachment to polar molecules and their non-covalent complexes can lead to different kinds of anions which differ from their excess electron localization. Spectroscopic methods for studying anion structures are reviewed. In many cases, the neutral and anion structures are identical and can be deduced from the electron attachment properties. Examples are given for complexes containing polar solvents or building blocks of biomolecules (nucleobases, amino acid residues...).**

## 1 Introduction

Electron transfer is a fundamental process in several fields such as molecular electronics and chemical or biological processes such as photosynthetic reactions and has been widely studied in condensed phases. The charge transfer is then strongly influenced not only by the electronic and structural properties of the electron donors and acceptors but also by the presence of the environment. Some fundamental aspects encountered in the analysis of large scale physico- or bio-chemical problems can be interestingly scrutinized by restricting the investigations to small model systems studied in gas-phase experiments and interpreted with the help of high-level quantum chemistry calculations. It is then possible to examine electron transfer to species ranging from isolated accepting molecules up to large molecular assemblies whose properties are close to those of the bulk.<sup>1</sup> The influence of donor structures can be greatly reduced by simply using as donors either free electrons or highly-excited atoms. The attention can then be focused on the relationship between neutral and negatively-charged acceptor structures.

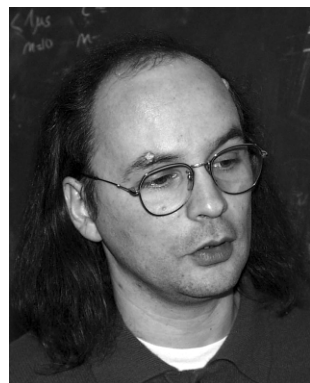
A large fraction of solvents *e.g.* water, pyridine, DMSO, *etc.* and elementary building blocks of biomolecules *e.g.* nucleobases, amino acid side chains, ... possess large dipole moments, and structures of polar acceptors will be emphasised here. In this review, the different electron attachment processes to polar systems leading to several types of anions in the gas-phase will be presented. It will be shown that excess electrons in anions can be located inside molecular orbitals (conventional anions) or outside molecular frames (multipole-bound anions or solvated electrons). A brief survey of the different types of spectroscopy involving either neutral  $\rightarrow$  anion or anion  $\rightarrow$  neutral transitions will be given. Examples will illustrate how the study of electron attachment to neutral polar molecular complexes or photo-detachment from their anions provide structural information.

## 2 Electron attachment to polar systems

### 2.1 Valence anions

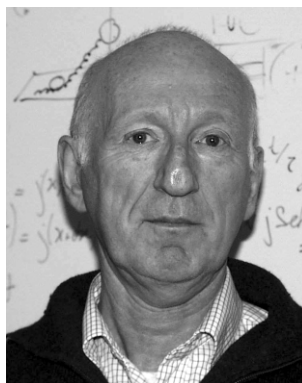
In a valence ( $\ll$  conventional  $\gg$ ) anion, an excess electron is submitted to nuclear attractions and repulsions from other valence electrons.<sup>2</sup> The neutral parent and anion potential energy surfaces cross and different electron affinities must be considered (Fig. 1). The vertical electron affinity  $EA_v$  is the energy difference between the neutral molecular system (plus an electron at infinite distance) and the anion with the same nuclear configuration. The adiabatic electron affinity  $EA_{ad}$  corresponds to the vibrationally relaxed anion. The vertical detachment energy  $VDE$  is the energy difference between the anion in its ground state and the neutral at the same nuclear geometry.

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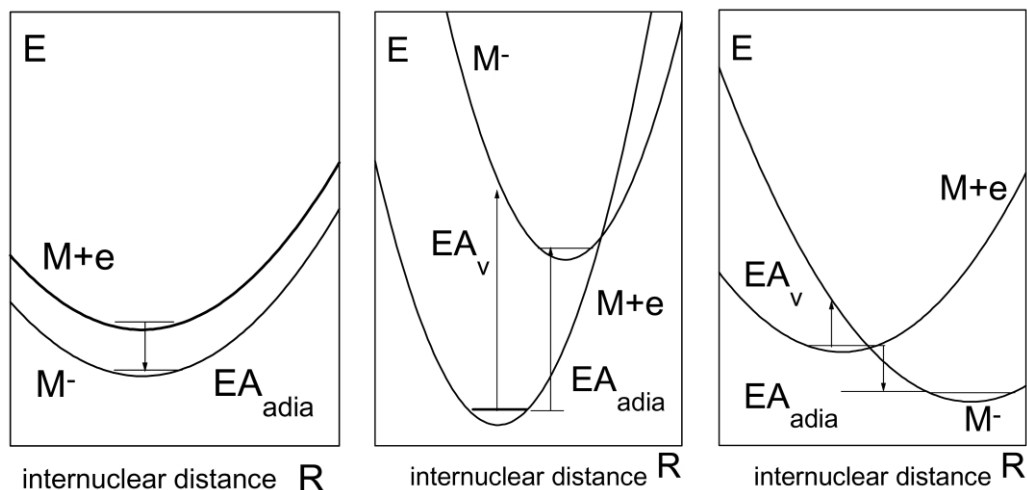


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Jean Pierre Schermann was born in 1940. He studied at the Ecole de Physique et Chimie de Paris and earned his Ph.D. degree from the Université of Orsay in 1969. After a NSF



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**Fig. 1** Schematic potential energy diagrams of anions ( $M^-$ ) and their neutral parents plus electron at infinity ( $M+e$ ). From left to right are represented multipole-bound anions, molecular systems with negative and positive electron affinities.

Vertical electron affinities  $EA_v$  of molecules are experimentally determined by Electron Transmission Spectroscopy (ETS). Temporary anion formation then appears as a set of resonances in the scattering cross-sections of energy-selected electron beams colliding with molecules.<sup>2</sup> Those resonances are usually extremely short-lived (less than picoseconds), except when they occur at nearly zero-energy for polyatomics.<sup>3</sup>

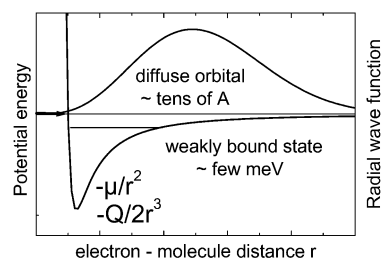
An isolated molecule  $M$  with a negative valence electron affinity  $EA_{val}$  cannot give birth to a stable valence anion. However, when such a molecule is surrounded by  $N$  other solvent species  $S$  which are inert with respect to electron attachment, the electron affinity becomes  $EA(N) = EA_{val} + E_{sol}^{M-}(N) - E_{sol}^M(N)$  where  $E_{sol}^M(N)$  and  $E_{sol}^{M-}(N)$  are the respective solvation energies of the neutral monomer  $M$  and its anion  $M^-$ . When the number  $N$  of solvents increases, the electron affinity becomes less and less negative. When  $N$  becomes larger than a threshold value  $N_{th}$ , the electron affinity  $EA(N)$  of the solvated neutral can become positive. Electron transfer then leads to the formation of stable solvated anions which can be observed. The first solvation shells play a major role and gas-phase properties of small aggregates converge more or less rapidly towards the bulk properties, allowing for the study of solvated anions<sup>4</sup> under conditions reasonably relevant to condensed phase chemistry.<sup>1,5</sup>

When the valence electron affinity  $EA_{ad}(M)$  is too negative, stabilisation cannot take place in the first solvation shell but another mechanism can then be responsible for electron localisation. For example, it has been observed that electrons can be trapped in sufficiently large water, ammonia or acetonitrile homogeneous clusters, due to cooperative interactions with dipoles of the whole assembly. Unfortunately, a satisfying theoretical description of those gas-phase anions which are analogues of solvated electrons in condensed-phase<sup>1,6</sup> is still not available.<sup>7</sup>

## 2.2 Multipole-bound anions

The situation is very different in the case of an anion in which an excess electron is bound by physical rather than chemical interactions. If a low energy electron approaches a molecular system possessing a resultant dipole moment  $\mu$ , a quadrupole moment  $Q$  and a polarisability  $\alpha$ , it experiences, at distances much larger than molecular dimensions, attractive potentials respectively varying as  $-\mu\cos\theta/r^2$ ,  $-Q(3\cos^2\theta - 1)/4r^3$  and  $-\alpha/2r^4$  ( $r$  and  $\theta$  are the excess electron co-ordinates with respect to the axis molecule which is supposed of cylindrical symmetry). In a closed-shell system where available molecular orbitals are already full, the incoming excess electron is

submitted at short distances to the repulsion from the molecular electronic cloud and can then be trapped in the quantum well created by the combination of the long-range and short-range potentials. Solving the Schrödinger equation in such a quantum well provides the excess electron binding energy and its orbital (see Fig. 2). The quantum well is deep and wide enough to



**Fig. 2** Potential well and orbital of the excess electron of a multipole-bound anion.

sustain a bound state, *i.e.* the electron can be trapped, if the dipole moment  $\mu$  or the quadrupole moments  $Q$  are respectively larger than  $\sim 2$ – $2.5$  D ( $D = \text{Debye}$ ) (for comparison, the dipole moment of water is 1.85 D) and  $\sim 50 \text{ D}\text{\AA}$ .<sup>8</sup> Such negative ions into which excess electrons are located in a very diffuse orbital outside the molecular frame are called multipole-bound anions<sup>9</sup> and have been experimentally studied mostly by means of Rydberg Electron Transfer Spectroscopy (RET)<sup>10</sup> and Photoelectron Spectroscopy (PES)<sup>11–13</sup> as described in the next section. Since there is no modification of the geometry of the neutral parent when a multipole-bound anion is created, the electron binding energy EBE or the vertical detachment energy  $VDE$  of the anion are then equivalent to the adiabatic or vertical electron affinity of the neutral parent (Fig. 1).

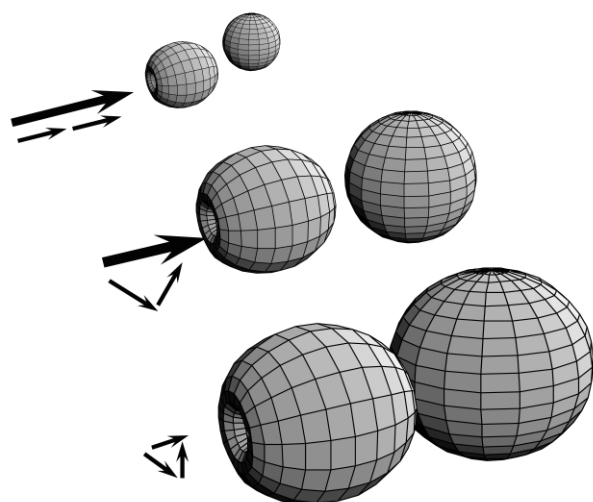
## 3 Spectroscopic techniques

The experimental studies of the structural dependence of electron transfer to non-covalent complexes can be conducted by means of different approaches. One can either investigate electron attachment to neutrals or the reverse process, *i.e.* electron detachment from anions.

### 3.1 Rydberg electron transfer spectroscopy

It is possible to determine the structure of neutral polar electron acceptors by taking advantage of the multipole-binding ionisa-

tion process described above. A given neutral complex constituted by several weakly-bound polar molecules can adopt different geometrical configurations of its neutral components and each configuration possesses its own total multipole moments. At large distances, a very low energy electron approaching this complex experiences a long-range field which mostly results from the sum of the individual molecular electrostatic moments. According to the geometrical configuration of the electron accepting complex, the attached excess electron will thus be more or less bound. By measuring excess electron binding energies and comparing the obtained experimental values to the calculated binding energies corresponding to the different possible dipole configurations, one can directly identify the electron accepting structures. This is realised in a Rydberg Electron Transfer (RET) experiment where a beam of neutral polar complexes is crossed with a beam of laser-excited atoms, with principal quantum number  $n$ . This beam constitutes a precisely controlled tuneable source of very-low energy electrons. For each dipole-configuration leading to a multipole-bound anion, there exists a narrow range of  $n$ -values, characteristic of the electron binding energy to the acceptor (or its electron affinity), where anions are observed. This can be understood, in a first crude approximation, by considering that electron exchange takes place when there is a matching between the diffuse orbitals of the exchange electron in the highly-excited atom and in the multipole-bound anion (Fig. 3).



**Fig. 3** Schematic representation of electron exchange between polar complexes and excited ('Rydberg') atoms. On the left side, three dimers with different resultant dipole moments give birth to multipole-bound anions with different excess electron orbitals. On the right side are represented the outer electron orbitals of the excited atoms which 'match' the anion orbitals. For example, the large resultant dipole moment corresponds to a small size of the anion excess electron orbital which is matched by the orbital of an atom with a low principal quantum number  $n$  value.

### 3.2 Photoelectron spectroscopy

Instead of studying their creation conditions as in RET spectroscopy, anions can be directly investigated by Photoelectron Spectroscopy (PES)<sup>7,14,15</sup> or Anion Infrared Spectroscopy (AIS).<sup>16,17</sup> In PES, excess electrons from a mass-selected beam of anions are photodetached by a laser operating at a fixed-frequency  $\nu$  and energy-analysed. Transitions at energies  $T(\nu, \nu')$  take place from vibrational states  $\nu$  of the anions to different state  $\nu'$  of their neutral parents. If the measured kinetic energies of the photodetached electrons are  $KE(\nu, \nu')$ , the adiabatic electron affinity is determined from the threshold of the photoelectron yield by the energy conservation relationship

$EA_{ad} = h\nu - KE(0,0)$  while the vertical detachment energy  $VDE$  is provided by the maximum of the photoelectron yield. Shapes of the anion creation rate dependence upon the principal quantum number  $n$  in RET or shapes of the photoelectron yield spectral dependence in PES experiments provide clear signatures of the excess electron localisation: in both cases, narrow or broad dependencies respectively correspond to multipole-bound anions (similar neutral and anion structures) or to valence anions (distortion of the neutral structure following electron transfer). A considerably better resolution is obtained if one uses a tuneable photodetachment laser source and records the zero-kinetic energy electron ('ZEKE') yield. The ZEKE electrons are only observed when the photodetachment laser wavelength excites a transition towards a bound state of the neutral system.<sup>7</sup>

Photodetachment of valence radical anions, such as  $C_{2n}H^-$ , in the vicinity of their electron detachment threshold leads to another kind of anion. The excess electron which was initially strongly bound in a valence orbital becomes weakly bound by the large dipole moment of the neutral molecular core, leading to dipole-bound excited state anions (DBS). It has been suggested that those DBS states may play an important role in the formation of anions in interstellar clouds.<sup>18</sup>

### 3.3 Anion infrared spectroscopy

Anion Infrared Spectroscopy (AIS),<sup>16,17</sup> offers the possibility to determine the location of the electron accepting system  $M$  in an inhomogeneous negatively-charged complex. In such a complex  $M^- \cdot S_N$ , an anion  $M^-$  can be either surrounded by solvent molecules  $S$  ( $\ll$  interior states  $\gg$ ) or solvated on the surface, according to the relative strengths of the anion-solvent and solvent-solvent interactions. AIS studies mostly rely on the observation of spectral shifts induced by the establishment of ionic ( $M^- \cdot S$ ) or hydrogen ( $S \cdot \cdot S$ ) bonds. Let us suppose that the solvent molecules are  $S = H_1-Y-H_2$  ( $Y = O, C$ ). In the  $M^- \cdot (H_1-Y-H_2)_N$  complex, a red-shift of the  $H_1-Y$  vibration can be induced while the  $Y-H_2$  vibration remains free if the first solvation shell is unfilled. A shift of the  $Y-H_2$  vibration is observed when the second solvation shell starts to be filled. In order to obtain quantitative structural data, it is necessary to compare experimentally measured frequency shifts calculated to elaborate *ab initio* calculations. The different spectroscopic techniques which have been developed for studies of electron attachment to polar clusters or photodetachment of complex anions are summarized in Table 1.

**Table 1** Comparison between anion spectroscopies

Spectroscopy	Anion type	Measured molecular parameter
Electron Transmission spectroscopy (ETS)	Valence anion	$EA_\nu$
Photoelectron spectroscopy (PES)	Multipole-bound anion	$EA_{ad}$ ( $> 30$ meV)
Anion Infrared Spectroscopy (AIS)	Valence anion	$VDE$
		Spectral shifts of ionic and hydrogen bonds
Rydberg electron transfer spectroscopy (RET)	Multipole-bound anion	$EA_{ad}$ (0.1–100 meV)
	Valence anion	$EA_{ad}$ ( $< 0$ )

## 4 Structural dependence of electron transfer to non-covalent polar complexes

We now first present examples of determination of polar neutral complex structures by means of the RET and PES spectroscopy

pies. In order to establish a link between pure gas-phase species such as multipole-bound anions and condensed phase anions, we then examine transitions between the different electron transfer processes, as a function of complex size.

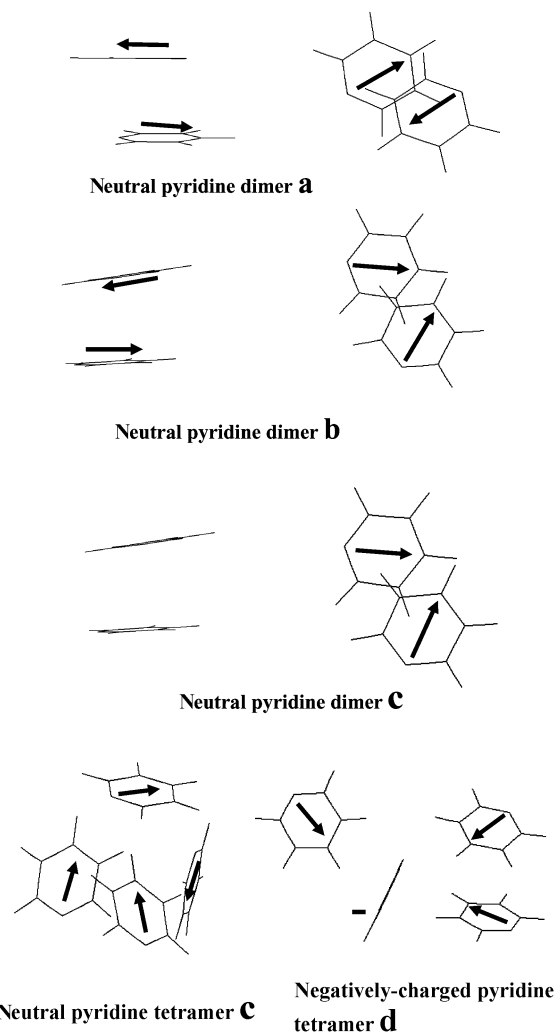
#### 4.1 Homogeneous complexes

As a first example of the influence of structure upon electron attachment to polar systems, we here consider homogeneous pyridine complex anions. ETS measurements have shown that the pyridine (Py) molecule has a negative vertical affinity *ca.*  $-0.6$  eV. Its dipole moment of 2.2 D is slightly lower than the critical moment for multipole-binding electron attachment. Pyridine cluster structures are interesting due to the competition between dipole-dipole and stacking interactions. For a given cluster  $(\text{Py})_N$ , several structures can coexist in a beam and spectroscopic techniques are required to establish a structural discrimination. The first experimental study of low-energy electron attachment to  $(\text{Py})_N$  clusters was performed with Rydberg atoms in undefined quantum states and pyridine tetramer anions were the smallest observed species (see ref. 19). Several neutral dimer configurations have nearly the same energies (Fig. 4A) but a single one has a large enough dipole moment of 3.4 D corresponding to a weak electron affinity of 17 meV and is thus observed in a RET experiment. In a PES experiment,<sup>19</sup> both dipole-bound and valence tetramer anions have been simultaneously observed. The DB anion signature is a narrow peak in the photoelectron spectrum corresponding to a small value of *VDE* (or *EA<sub>ad</sub>*) = 0.13 eV. The structure of the neutral parent of this anion is displayed in Fig. 4c. The valence anion signature is a broad peak around 0.65 eV. The structure of this valence anion is that of a solvated anion with an excess electron localized on a pyridine molecule surrounded by three pyridine whose dipole moments are pointing towards the negative charge (Fig. 4d).

Nucleic acid bases are other examples of molecular systems which can give birth to both multipole-bound and valence anions and they can act as traps in cell nuclei for electrons produced by ionising radiation.<sup>20</sup> Among nucleobases, uracil is the most peculiar since it possesses a valence electron affinity which is positive but very weak ( $\approx 60$  meV), smaller than the multipole-binding electron affinity ( $\approx 80$  meV).

#### 4.2 Inhomogeneous complexes

Biomolecules can recognise each other with an amazing specificity by establishing non-covalent interactions. Gene expression and control, for example, is the result of recognition of precise sequences of nucleobases in DNA by specialised proteins. There is a current large interest in the design of artificial ligands capable of binding to unique sites of DNA. Hairpin polyamides containing pyrrole, 3-hydroxypyrrole and imidazole have demonstrated their ability to fulfil such a role<sup>21</sup> by distinguishing all four Watson-Crick base pairs in the minor groove of DNA. The modelling of those artificial ligands has been performed with the help of force-field methods whose parameters are derived from X-ray crystallographic and NMR structures of large systems. We here consider a microscopic approach providing information about interactions between a nucleobase adenine (A), and imidazole (Im) or pyrrole (Py), in the absence or presence of water (W).<sup>22</sup> The configurations of the different neutral complexes: A-Im, A-Py, Im-W, Py-W can be calculated by exploring the corresponding empirical potential energy surfaces. In our calculations, the intermolecular potential energy comprises atom-atom Coulombic terms between partial atomic charges, atom-atom van der Waals terms, specific hydrogen bond terms for the concerned atoms and polarisation terms for each atom. The partial atomic

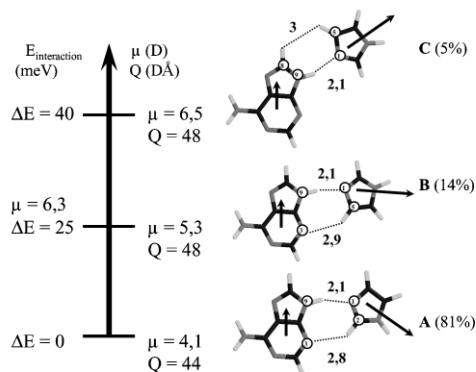


**Fig. 4** (A) Structures of neutral pyridine dimers. Configuration **a** is the most stable gas-phase configuration with a binding energy of 190 meV and a very small dipole moment of 0.12 D. Configuration **b** which is slightly less stable has a binding energy of 170 meV and a dipole moment equal to 3.4 D. This configuration gives birth to an observed multipole-bound anion with the same geometrical configuration. (B) Structures of neutral and negatively-charged pyridine tetramer complexes. Configuration **c** which is the most stable neutral configuration has a binding energy of 860 meV and a dipole-moment of 3.51 D. This configuration gives birth to an observed multipole-bound anion with the same geometrical configuration. In the tetramer valence anion configuration **d**, the negative charge is localized on a single pyridine molecule.

charges are adjusted in order to reproduce the values of dipole and/or quadrupole moments of the isolated molecules when they are available. Exploration of the potential energy surfaces is conducted by means of a genetic algorithm which provides the different local minima. To each isomer configuration of the neutral systems corresponds a set of resultant multipole moments from which electron affinity can be calculated (see Section 2). By comparing experimental and calculated electron affinities, it becomes possible to assign to each observed multipole-bound anion its neutral parent configuration. An example is displayed in Fig. 5 for the adenine-imidazole complex.

#### 4.3 Transition from multipole electron binding to valence electron binding

The mechanism of electron transfer to a polar system containing molecules with negative affinities can lead to different types of anions, according to the cluster size. Let us consider indole-water cluster anions  $(\text{In-W}_N)^-$ . Indole (In) is the residue of



**Fig. 5** The different configurations of the neutral adenine–imidazole complex are represented together with their Boltzmann distributions in a supersonic beam ( $T \approx 150$  K). Those configurations have different total dipole and quadrupole moments which are given on the left side. The hydrogen bond lengths are given in Angstroms. The experimentally observed anions correspond to the lowest energy configuration A which is taken as energy reference.

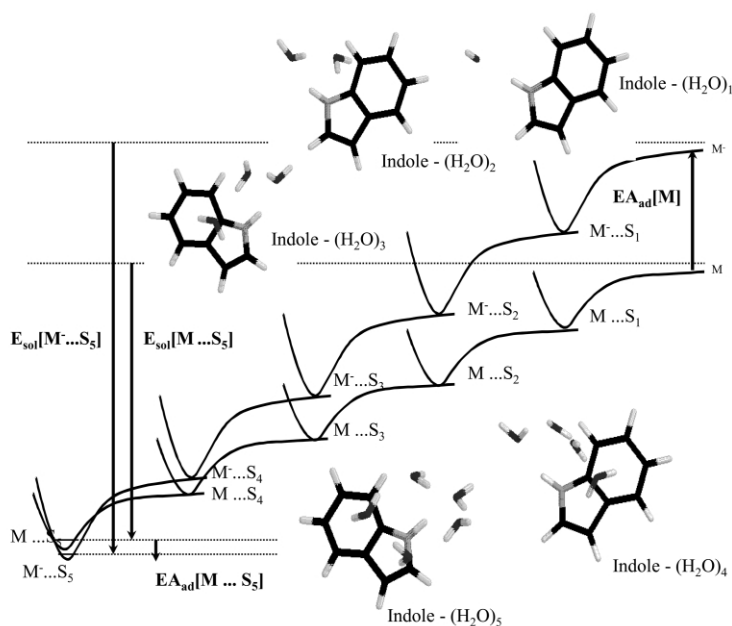
tryptophan and the influence of hydration on the properties of this chromophore molecule must be taken into account in the understanding of protein fluorescence. For  $N = 0, 1$  and  $2$ , only multipole-bound anions are observed, corresponding to neutral parents with large enough dipole and quadrupole moments to bind excess electrons in diffuse orbitals. This is no longer the case for  $N = 3$  and  $4$ . In the lowest energy configuration of the ( $\text{In}-\text{W}_3$ ) neutral complex, the water molecules form a bridge between the N–H bond and the electrons of the double ring of the indole molecule. This H-bonded chain is rather flexible but the total dipole moment of the complex varies between  $1.2$  and  $1.8$  D, below the critical value for electron binding. Similarly, the lowest energy configurations of the ( $\text{In}-\text{W}_4$ ) neutral complex possess total dipole moments less than  $2.2$  D and ( $\text{In}-\text{W}_{3,4}$ )<sup>−</sup> anions are not observed. The threshold value  $N_{\text{th}}$  for production of valence anions is equal to  $5$  and all ( $\text{In}-\text{W}_{N \geq 5}$ )<sup>−</sup> anions are observed (see Fig. 6). The valence electron affinity  $EA(N_{\text{th}} = 5)$  is very small but positive and the valence electron affinity of isolated indole can be deduced from the following relationship:  $EA_{\text{ad}}(\text{In}) \approx E_{\text{sol}}^{\text{In}}(N_{\text{th}}) - E_{\text{sol}}^{\text{In}^-}(N_{\text{th}})$ . The same method which has been described in Section 4.2 can be used to

calculate the solvation energies  $E_{\text{sol}}^{\text{In}}(N_{\text{th}}) - E_{\text{sol}}^{\text{In}^-}(N_{\text{th}})$  and  $E_{\text{sol}}^{\text{In}}(N_{\text{th}}) - E_{\text{sol}}^{\text{In}^-}(N_{\text{th}})$ , leading to a value of  $EA_{\text{ad}}(\text{In})$  which is equal to  $-1.03 \pm 0.05$  eV. Usually, negative electron affinities are measured by means of electron transmission spectroscopy (ETS)<sup>2</sup> through experimental observation of resonances in the energy dependence of the free electron scattering cross-sections (see Section 2.1). The vertical electron affinities are then determined but negative adiabatic electron affinities can be much more difficult to obtain for polar species due to the importance of elastic scattering in their energy range which tends to mask formation of temporary anions. The here presented alternative method for determination of adiabatic negative electron affinities which takes advantage of solvation effects has been employed in several cases such as DNA bases.<sup>23,24</sup>

#### 4.4 Transition from multipole-bound cluster anions to solvated electrons

Although isolated water or ammonia molecules do not individually bind electrons, solvated electrons are observed in the liquid phase.<sup>6</sup> It has been first suggested that an excess electron is then localised in a cavity surrounded by hydrogen atoms which constitute the first solvation shell. Recently, this cavity model has been challenged and it has been shown<sup>25</sup> that the solvated electron species might be a solvated  $\text{H}_3\text{O}$ , consisting of a localized electron cloud connected to a hydronium cation by a water molecule network. If one considers finite systems such as water and ammonia clusters, anion mass spectra exhibit minimum sizes  $N_{\text{min}}$  above which continuous mass distributions are observed ( $N_{\text{min}}$  is respectively equal to  $11$  and  $34$  for water and ammonia).<sup>26</sup> Linear plots of the cluster vertical detachment energy  $VDE(N)$  measured by PES as a function of cluster size  $N^{-1/3}$  converge to the photoemission threshold energies for bulk solvated electrons, suggesting that  $(\text{H}_2\text{O})_{N \geq 11}^-$  and  $(\text{NH}_3)_{N \geq 34}^-$  clusters might be gas-phase analogues of solvated electrons.<sup>14</sup> However, up to now, there does not exist any satisfying theory predicting those threshold numbers  $N_{\text{min}}$ .<sup>7</sup>

In order to study the respective influence of dipole configurations and dispersion interactions in cluster analogues of solvated electrons, *ab initio* calculations of the structures of  $(\text{H}_2\text{O})_{12}^-$  and  $(\text{HF})_3^-$  anions have been performed. For  $(\text{H}_2\text{O})_{12}^-$ , the  $VDE$ s of



**Fig. 6** This figure illustrates the principle of the solvation method for determination of negative adiabatic electron affinities (Section 4.3 in the text). The valence electron affinity of the isolated indole molecule is negative (right). In the presence of five water molecules, the electron affinity becomes positive and valence anions are observed. The structures of the neutral indole–water complexes are represented.

several different anion conformers were compared<sup>27</sup> to the experimental value (0.88 eV) determined by PES. An important result is that the excess electron not only interacts with the dipole moments but also with H atoms which are not engaged in H-bonds ( $\llcorner$  dangling H  $\lrcorner$ ). Several possibilities are then offered. All H atoms can be engaged in H-bonds and the excess electron is then in a  $\llcorner$  surface  $\lrcorner$  state similar to a multipole-bound state. Although the corresponding neutral structures possess very large dipole moments ( $>20$  D), the calculated VDE values are too small. In structures whose VDEs are close to the experimental value, the excess electron is partially or totally engaged in an  $\llcorner$  interior  $\lrcorner$  state, interacting with the dangling H-atoms. IR spectroscopy would be very useful to support these predictions. In  $(\text{HF})_N^-$  anions, the transition between dipole-bound and solvated electrons already occurs at such a small size as in between the dimer and the trimer.<sup>28</sup> PES and *ab initio* calculations show that the trimer anion has two stable configurations with respect to the cyclic neutral configuration, a lowest energy configuration which is a chain-like dipole-bound state with an electron binding energy *ca.* 200 meV and a solvated electron configuration with a VDE of *ca.* 600 meV. It is important to note that for  $(\text{HF})_3^-$ , as for  $(\text{H}_2\text{O})_{12}^-$ , *ab initio* calculations predict that dispersion interactions can be nearly as important as electrostatic interactions between an excess electron with dipole and/or quadrupole moments.

## 5 Time-resolved spectroscopic studies of electron transfer

Ultrafast spectroscopy combined with PES spectroscopy of mass-selected solvated anions allows for the investigation of the dynamics of electron transfer. One of the most studied systems is the hydrated iodine anion.<sup>29,30</sup> Initially, each water molecule of a  $\text{I}^- (\text{H}_2\text{O})_N$  ion is H-bonded to another water molecule and the dangling hydrogen is bound to the  $\text{I}^-$  core. A first pump UV laser electronically excites mass-selected  $\text{I}^- (\text{H}_2\text{O})_N$  anions and, following a variable time-delay (0–2000 fs), photoelectrons are produced by a second laser and energy-analysed. In a first step, anion excess electrons are photo-excited from a valence state of  $\text{I}^-$  towards short-lived diffuse states. The solvent water molecules are still in the same configurations as they were before photo-excitation and which are strongly influenced by the presence of  $\text{I}^-$ . The excess electrons are then bound by the water network resultant dipole moments which are rather important (*e.g.* 4.4 D for  $N = 4$ , as compared to the null dipole moment of the water tetramer). It has been shown that those diffuse excited states into which electrons are bound by a small number of solvent molecules in clusters are precursors of excited states known in liquids as charge-transfer-to-solvent-states (CTTS). Following the initial excitation of those CTTS states, the solvent molecules rearrange over a time scale of 1000 fs towards configurations into which electrons become more strongly bound. In analogy with water cluster anion calculations described in the previous section, it has been suggested<sup>31</sup> that the initial photo-excited ( $\llcorner$  CTTS  $\lrcorner$ ) states are equivalent to dipole-bound ( $\llcorner$  surface  $\lrcorner$ ) states which further evolve towards ( $\llcorner$  interior  $\lrcorner$ ) partially solvated electron states on a time scale characteristic of the solvent reorganisation.

## 6 Conclusion

Electron transfer to non-covalent complexes can be investigated by means of several complementary experimental techniques. One can either focus on the formation of complex anions in order to determine structures of the neutral parents or one can

study the reverse process of detachment of the excess electron to deduce anion structures. One of the main goals of cluster studies has been the establishment of links between gas-phase and solutions but this proves sometimes to be difficult. As discussed in Section 4.4, the relationship between structures, spectroscopic and dynamical properties of small water anions and those of hydrated electrons is still not fully understood. New gas-phase anion species such as octupole-bound anions and dianions<sup>32</sup> have been very recently investigated. The case of the well-known  $\text{SO}_4^-$  dianion provides another illustration of some non-trivial aspects of solvation. The isolated  $\text{SO}_4^-$  dianion cannot be observed because it is electronically unstable and a minimum number of three water molecules is required to stabilise this dianion.<sup>32</sup> Interpretation of these measurements requires more and more elaborate quantum calculations<sup>33</sup> which are today limited to systems containing a rather restricted number of atoms ( $<100$  atoms) and are thus still far from solution chemistry.

## References

- 1 J. Jortner, *Z. Phys. D*, 1992, **24**, 247.
- 2 J. Simons and K. H. Jordan, *Chem. Rev.*, 1987, **87**, 535.
- 3 J. M. Weber, E. Leber and M. W. Ruf, *Eur. Phys. J. D*, 1999, **7**, 587.
- 4 C. K. Takashima and J. M. Riveros, *Mass Spectrom. Rev.*, 1998, **17**, 409.
- 5 D. Chandler and K. Leung, *Annu. Rev. Phys. Chem.*, 1994, **45**, 557.
- 6 P. Kambhampati, D. H. Son and T. W. Kee, *J. Phys. Chem. A*, 2002, **106**, 2374.
- 7 U. Boesl and W. J. Knott, *Mass Spectr. Rev.*, 1998, **17**, 275.
- 8 H. Abdoul-Carime and C. Desfrancois, *Eur. Phys. J. D*, 1998, **2**, 149.
- 9 M. Gutowski and P. Skurski, *Recent Res. Dev. Phys. Chem.*, 1999, **3**, 245.
- 10 C. Desfrancois, H. Abdoul-Carime and J. P. Schermann, *Int. J. Mod. Phys.*, 1996, **10**, 1339.
- 11 J. H. Hendricks, S. A. Lyapustina and H. L. d. Clercq, *J. Chem. Phys.*, 1998, **108**, 8.
- 12 J. Kim, I. Becker and O. Chesnowsky, *Chem. Phys. Lett.*, 1998, **297**, 90.
- 13 S. Y. Han, J. K. Song and J. H. Kim, *J. Chem. Phys.*, 1999, **111**, 4041.
- 14 A. W. Castleman and K. H. Bowen, *J. Phys. Chem.*, 1996, **100**, 12911.
- 15 I. Becker and O. Chesnowsky, *J. Chem. Phys.*, 1999, **110**, 6288.
- 16 P. S. Weiser, D. A. Wild and E. J. Bieske, *J. Chem. Phys.*, 1999, **110**, 9443.
- 17 O. M. Cabarcos, C. J. Weinheimer and T. J. Martinez, *J. Chem. Phys.*, 1999, **110**, 9516.
- 18 F. Güthe, T. Pino and M. Tulej, *Astrophys. J.*, 2001, **555**, 466.
- 19 S. Y. Han, J. H. Kim and J. K. Song, *J. Chem. Phys.*, 1998, **109**, 9656.
- 20 X. Li, Z. Ci and M. D. Sevilla, *J. Phys. Chem.*, 2002, **106**, 1596.
- 21 S. White, J. W. Szweczyk and J. M. Turner, *Nature*, 1998, **391**, 468.
- 22 S. Carles, F. Lecomte and J. P. Schermann, *J. Phys. Chem. A*, 2000, **104**, 10662.
- 23 J. Schiedt, R. Weinkauff and D. M. Neumark, *Chem. Phys.*, 1999, **239**, 511.
- 24 V. Périquet, A. Moreau and S. Carles, *J. Electron. Spectrosc. Relat. Phenom.*, 2000, **106**, 141.
- 25 A. L. Sobolewski and W. Domcke, *Phys. Chem. Chem. Phys.*, 2002, **4**, 10.
- 26 H. Haberland, H. Schindler and H. G. Worsnop, *Ber. Bunsen-Ges. Phys. Chem.*, 1984, **88**, 270.
- 27 J. Kim, J. M. Park and K. S. Oh, *J. Chem. Phys.*, 1997, **106**, 10207.
- 28 M. Gutowski and P. Skurski, *J. Phys. Chem.*, 1997, **101**, 9143.
- 29 G. Markovich, R. Giniger and M. Levin, *J. Chem. Phys.*, 1991, **95**, 9416.
- 30 L. Lehr, M. T. Zanni and C. Frischkorn, *Science*, 1999, **284**, 635.
- 31 D. Sexner, C. E. H. Dessent and M. A. Johnson, *J. Chem. Phys.*, 1996, **105**, 7231.
- 32 M. Gutowski, P. Skurski and X. Li, *Phys. Rev. Lett.*, 2000, **85**, 3145.
- 33 P. Skurski and J. Simons, *J. Chem. Phys.*, 2000, **112**, 6563.