Dipole-bound states as doorways in (dissociative) electron attachment

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Abstract. This communication starts with a comparison of dissociative recombination and dissociative attachment placing emphasis on the role of resonances as reactive intermediates. The main focus is then the mechanism of electron attachment to polar molecules at very low energies (100 meV). The scheme considered consists of two steps: First, an electron is captured in a diffuse dipole-bound state depositing its energy in the vibrational degrees of freedom, in other words, a vibrational Feshbach resonance is formed. Then, owing to the coupling with a valence state, the electron is transferred into a compact valence orbital, and depending on the electron affinities of the valence state and possible dissociation products, as well as on the details of the intramolecular redistribution of vibrational energy, long-lived anions can be generated or dissociation reactions can be initiated. The key property in this context is the electronic coupling strength between the diffuse dipole-bound and the compact valence states. We describe how the coupling strength can be extracted from \textit{ab initio} data, and present results for Nitromethane, Uracil and Cyanoacetylene.

1. Electron-induced processes
In this introductory section we consider dissociative recombination and electron-molecule scattering from a general point of view. Both can be understood as pathways through very similar reaction schemes, and both schemes contain an electronically metastable resonance state as central intermediate.

Let us begin with dissociative recombination. In the initial step an electron is captured by a cation, and a neutral resonance state is formed. Clearly, the resonance can simply decay by electron re-ejection, but provided its lifetime is sufficiently long, energy can be transferred to the nuclei paving the way to dissociation. Alternatively long-lived or stable neutrals can be formed if the system possesses a large number of of internal degrees of freedom such that the recombination energy can be dissipated, say the cation is part of a cluster or a large molecule. This reaction scheme is shown in figure 1 and unites processes such as dissociative recombination, associative ionization, photo dissociation, and photo ionization around a central resonance state that plays the role of a reactive intermediate.

A completely analogous scheme applies when the total charge $Q$ is decreased from $Q = 0$ to $Q = -1$, that is in electron-molecule scattering (figure 2). If an electron is captured by a neutral molecule, and the resulting negative ion resonance lives sufficiently long, energy can be transferred to the nuclei, and dissociations can proceed or long-lived anions can be formed. The names of the different pathways through the reaction scheme are now dissociative attachment, associative detachment, and photo detachment, but the overall scheme and the role of the resonance as a central intermediate are identical.

There are clearly many differences when the total charge is changed. Colliding ions or neutrals, and detecting then neutral or ions, respectively, involves very different experimental techniques. The same is
Figure 1. Electron-induced processes for total charge $Q = 0$ using the H$_2$O molecule as an example. This scheme contains amongst other processes dissociative recombination and photo ionization.

Figure 2. Electron-induced processes for total charge $Q = -1$ using a chloroalkane as an example. This scheme contains amongst other processes dissociative attachment and photo detachment.

true for theory. Since for $Q = 0$ and $Q = -1$ the resonance states have typically one-particle-one-hole and one-particle character, respectively, the challenges in building wavefunctions are very different. But it is equally clear that despite the differences a higher vantage point has its merits, and that approaching both schemes as electron-induced processes can be very beneficial.
2. Negative ion resonances

In this section we discuss two fundamentally different ways of attaching electrons to neutral molecules and the correspondingly different types of resonance states in view of their capability as intermediates in electron-induced processes. Here and in the following we will concentrate primarily on the electronic structure viewpoint. The computed cuts through multidimensional potential energy surfaces allow us to draw qualitative conclusions and provide the necessary input for treating the nuclear motion using e.g. the $R$-matrix or the projection operator formalisms that yield cross sections for vibrational excitation or dissociative attachment [1,2].

The by far most common anion type, at least in chemistry textbooks, is the valence or conventional anion. The extra electron occupies a compact valence orbital which is – as a rule – antibonding in character, and thus the equilibrium structure of the anion is typically very different from that of the neutral. For example, Cyanoacetylene $\text{H}–\text{C}≡\text{C}–\text{C}≡\text{N}$ is a linear molecule while its valence anion is strongly bent ($\angle(\text{HCC}) \approx 120^\circ$, $\angle(\text{CCC}) \approx 130^\circ$). On the other hand, an electron can be attached to a molecule by long-range forces, dipole bound states representing the most prominent example [3–5]. Here the extra electron occupies a very diffuse orbital localized essentially outside the molecular framework. Occupation of such an orbital has very little influence on the bonding, and the equilibrium structures of neutral and anion are therefore almost identical. Let us note that there is a smooth transition between the two bonding modes. A sharp distinction is impossible, and there are borderline cases such as NaCl$^-$ that can be understood either as dipole-bound or as valence (attachment into a Na 3s/3p hybrid orbital) anion.

Turning to autodetaching resonances, both valence and diffuse anionic states typically give rise to a distinct class of metastable states. If attachment into a valence orbital yields an unbound state, one speaks of a shape-type resonance. Shape-type resonances are associated with almost all unoccupied orbitals of almost all small molecules at their respective equilibrium structures. Well known examples include the $\pi^*$ resonances of N$_2$, C O$_2$, and benzene as well as the $\sigma^*$ resonances of chloroalkanes and chloroalkenes [6, 7]. Owing to the anti-bonding character of the extra electron’s orbital, upon vertical attachment, the anion finds itself far from its equilibrium geometry, and there will be large forces on the nuclei. This is the usual picture for rationalizing vibrational excitation or dissociative attachment mediated by a shape-type resonance and the basis of all “resonance models” in electron molecule collision theories [1].

Dipole-bound states, on the other hand, give rise to vibrational Feshbach resonances (VFR) [2]. Since the dipole-bound orbital is essentially non-bonding, the potential energy surfaces of neutral and anion run almost parallel in a substantial region around their virtually identical equilibrium structures. Thus, dipole-bound anions are electronically stable at all relevant geometries, and in a Born-Oppenheimer picture there is no autodetaching resonance but only an electronically stable anion. But the total energy of a vibrationally excited state of this anion can obviously be above the vibrational ground state of the neutral, and these vibrationally excited states can autodetach and are referred to as VFRs [2]. At this point two remarks are in order. First, VFRs are clearly not limited to dipole-bound states; electronically stable valence anions can also be excited vibrationally above their detachment threshold leading to autodetachment. However, for stable valence anions typically a large number of vibrational quanta must be absorbed before the autodetachment region is reached, and whereas these states are important for vibrationally induced detachment they can play no role in electron-induced processes. Second, autodetachment from a VFR is associated with a vibrational transition, and mediated by non-adiabatic coupling elements $\langle \psi_\text{el} | d/dQ_j | \psi_\text{el} \rangle$ where $\psi_\text{el}$ is the electronic wavefunction and $Q_j$ is a nuclear coordinate [8,9]. This is true for both typical dipole-bound states such as H$_3$CCN$^-$ and for stable valence anions such as NH$^-$ [10] or the acetaldehyde enolate anion [11], i.e., whenever there is only one anionic state below the surface of the neutral.

While the standard “resonance” picture of electron-induced processes invokes shape-type resonances as reactive intermediates, there are presently only few examples where VFR have been shown to strongly influence cross sections for vibrational excitation or dissociative attachment [2, 12–14]. We note that VFRs have recently also been invoked as reactive intermediates in [15]. However, if there is only a
dipole-bound state, then there is no direct mechanism to transfer significant amounts of energy to the nuclear degrees of freedom through a VFR. In contrast to shape-type resonances, for dipole-bound states the surfaces of neutral and anion run essentially parallel, and moreover, the change of vibrational state upon attachment is only efficient for small energy differences between the initial and final vibrational levels [16]. Thus, by itself a VFR seems to be a cul-de-sac regarding dissociation or other reactions. This is however not true if the anion in question does also have a low-lying valence state. From Rydberg electron transfer experiments it is known that the initially populated dipole-bound states provide a “doorway” into the valence states of systems such as Nitromethane and Nitrobenzene [17, 18]. Thus, in principle a VFR can – as a doorway to a valence state – mediate reactive processes in free electron attachment, provided that the transition to the valence state can successfully compete with electron re-ejection.

3. The coupling between dipole-bound and valence states

The property governing the transition from a dipole-bound to a valence state – and vice versa – is the electronic coupling or electronic interaction between these states. Dipole-bound and valence states are by construction diabatic states [19] which are coupled by the electronic Hamiltonian, and the coupling matrix element $W$ determines in Golden-rule-like first-order treatments the associated transition rate. Clearly, first order perturbation theory is only appropriate if the coupling is weak, but the same matrix elements will determine the transition rate in more elaborate treatments of the dynamics albeit in a less obvious manner. To get a reasonable estimate of the coupling we chose straight line cuts corresponding to a linear transition form the equilibrium structure of the neutral to that of the valence anion, computed the two lowest adiabatic potential energy curves of the anion along this cuts, and fitted a simple diabatic model potential to our \textit{ab initio} results [20, 21]. We emphasize that the \textit{ab initio} calculation of the adiabatic surfaces is far from straightforward. First, for attachment states electron correlation effects are in general very important. Second, a carefully balanced description of two states with very different electronic structure is needed. For the dipole-bound state there is little orbital relaxation, whereas for the valence state relaxation effects are huge. And last but not least, close to the crucial crossing region the upper adiabatic state crosses the potential energy surface of the neutral and is transformed into a resonance state (figure 3). Details regarding suitable \textit{ab initio} methods and the diabatic model potential can be found in [20].

Presently we have results for four molecular systems: Nitromethane [20], Cyanoacetyleene, Uracil, and 5-Chlorouracil [21] (table 1). The respective coordinates of the chosen cuts are essentially a NO$_2$
Table 1. Electronic coupling matrix elements between dipole-bound and valence anions. The \textit{ab initio} method employed to compute the adiabatic surfaces is indicated.

| Molecule                  | $W$   | \textit{ab initio} method |
|---------------------------|-------|--------------------------|
| H$_3$C–NO$_2$             | 30 meV| EOM-CCSD                 |
| H–C≡C–C≡N                 | 32 meV| EOM-CCSD                 |
| Uracil                    | 43 meV| ADC(2)                   |
| 5-Chlorouracil            | 43 meV| ADC(2)                   |

Wagging motion for Nitromethane, an anti bending motion of H and the CN group for Cyanoacetylene, and ring puckering modes for Uracil and 5-Chlorouracil. To compute the adiabatic surfaces two different \textit{ab initio} methods have been employed: (1) the equation-of-motion coupled-cluster with single and double substitutions (EOM-CCSD) method [22], and (2) the algebraic diagrammatic construction of the one-particle Green’s function in second order (ADC(2)) [23]. In all cases we found a relatively sharp avoided crossing. It turned out that with our model potential we can only determine the value of $W$ at the intersection, and these values are listed in table 1.

Based on our results we can conclude that the dipole-bound states of all investigated molecules are very efficient doorways to the respective valence states. The first-order transition rate is essentially $W^2$ times a Franck-Condon factor, and thus the transfer-time can be of the same timescale as molecular vibrations if the Franck-Condon factors are very favorable. Unless the Franck-Condon factors are extremely unfavorable the transfer will be very fast on a mass spectroscopic timescale explaining the exclusive observation of valence anions after Rydberg electron transfer in Nitrobenzene [18]. In general, this mechanism can be used to rationalize how polar species with a substantial valence adiabatic electron affinity capture electrons and form very long-lived species.

Regarding the relevance of VFR as intermediates in electron-induced reactions one needs to compare with the associated autodetachment rates. Unfortunately, only very little is known about autodetachment lifetimes of the VFR class considered here, and the few known numbers cover a wide range [10–12, 24]. The best comparison comes probably from dipole-bound states of acetaldheyde and acetone enolate anions [11,24] despite the open-shell ‘core’ of these systems. For these enolates the lifetimes depend on the particular rovibrational state but fall roughly into the 1 to 100 ns range. Moreover, typical rates for vibration-induced electron detachment have been estimated to fall into the huge $10^2$–$10^{10}$ s$^{-1}$ interval [9]. If these rates translate into typical autodetachment rates from closed-shell core VFR, and presently we can see no reason for lifetimes in a completely different order of magnitude, we can conclude that the transition to a valence state will most probably be considerably faster than autodetachment, again, unless the Franck-Condon factors are very unfavorable. Be this as it may, the coupling between dipole-bound and valence state has been found to be in the order of several tens of meV translating into a wide open doorway, and thus, provided the anion possesses a low-lying valence state, one can expect VFR to be well able to play the role of reactive intermediates in electron-induced processes.

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[22] Reference for EOM-CCSD method.
[23] Reference for ADC(2) method.
[24] References for acetaldheyde and acetone enolate anions.
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