Recent progress in the theory of dissociative attachment: From diatomics to biomolecules

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Abstract. We present a summary of recent progress in theoretical studies of low-energy dissociative electron attachment (DEA) to halogen molecules and polyatomic molecules based on the resonance R-matrix theory. It explains many observed features in DEA cross sections including low-energy behavior, threshold resonances and cusps. It also gives correct description of the temperature dependence of the attachment rate coefficients. More recently the theory was applied to two molecules of biological interest, formic acid and glycine. DEA mechanisms in these systems are very similar to those in hydrogen halides.

1. Introduction
Dissociative electron attachment (DEA) processes, in spite of their importance for plasma physics [1, 2, 3], environmental science [4, 5, 6] and radiation damage [7, 8, 9], still do not receive enough attention from theorists. A substantial progress has been made in experimental studies of these processes, mainly due to development of new experimental techniques involving electron beams with high energy resolution [10]. This allowed detailed investigation of threshold phenomena in low-energy dissociative attachment to diatomic and polyatomic molecules: vibrational Feshbach resonances (VFRs) and threshold cusps.

Theoretical description of DEA process requires solving a challenging nuclear dynamics problem involving motion in a nonlocal complex potential [11]. For polyatomic cases a simplifying assumption is always involved: either the nuclear motion is described in the local approximation [12], or a one-mode approximation is used. The local approximation is justified when the resonant state responsible for DEA has a relatively small decay width. The one-mode approximation can be used if there is experimental or theoretical evidence that the DEA process is dominated by one vibrational degree of freedom corresponding to the reaction coordinate. A typical example is a molecule of the type CX$_3$Y where X stands for the H or F atom and Y for a halogen atom. For a description of the reaction

$$e + CX_3Y \rightarrow CX_3 + Y^- \tag{1}$$

the theoretical approach based on inclusion of only C–Y symmetric stretch turned out to be successful [13, 14, 15, 16]. It adequately describes the electron energy dependence and the vibrational energy dependence of the DEA cross sections, and also predicts threshold resonances and cusps which are confirmed by experiments with highly energy-resolved electron beams.
The current state of the theory in principle allows a complete \textit{ab initio} solution in diatomic cases. For example, a complex nonlocal dynamics has been completely investigated for hydrogen halides, and a high level of agreement between the theory and experiment has been achieved [17, 18, 19, 20]. In spite of this, some diatomic cases still present a big challenge. Surprisingly, this is the case for relatively simple halogen molecules. The semiempirical R-matrix calculations [21, 22] for DEA to the Cl$_2$ molecule describe very well the dependence of cross section on electron energy and vibrational temperature. At the same time more recent \textit{ab initio} calculations [23] yield a weaker electron energy dependence and vibrational temperature dependence than that observed in the experiments. The case of low-energy DEA to the even simpler F$_2$ molecule still presents a big challenge [24]. In spite of a 28-year history of theoretical research on this process, there are still major challenges in bringing theory and experiment together.

The present article summarizes major advances in the theory of DEA processes made by the author and his collaborators since the publication of the review of Hotop et al. [10]. Our approach to description of DEA is based on the resonance R-matrix theory [25] which is equivalent to the nonlocal complex potential theory [11]. In this review we discuss only calculations carried out in the one-mode approximation, although some progress on inclusion of several vibrational degrees of freedom has recently been made [26, 27].

2. Attachment to halogen molecules

Until this decade Cl$_2$ presented an enigma because electron-beam experiments showed an attachment feature typical of zero-energy resonances, though weak, while electron capture into the lowest Cl$_2^-$ electronic state requires a $p$-wave process due to its $^2\Sigma_u^+$ symmetry [28]

\[ e^- + \text{Cl}_2(X^1\Sigma_g^+) \rightarrow \text{Cl}_2^-(X^2\Sigma_u^+) \rightarrow \text{Cl}(2P) + \text{Cl}^-(1S). \]

This situation was even more unclear for the analogous case of F$_2$, because the 1987 high-resolution (6 meV) data of Chutjian and Alajajian [29] were demonstrating s-wave attachment, since the cross section $\sigma$ fit the Wigner $\sigma \propto E^{-1/2}$ law appropriate for s-wave attachment as a function of electron energy $E$.

The problem with Cl$_2$ was resolved in calculations [21] where it was found that the observed attachment resonance peaked not at zero energy but at 50 meV. The cross section followed the Wigner $p$-wave threshold law, $\sigma \propto E^{1/2}$, in rising from zero energy, but dropped rapidly beyond 50 meV due to an unusual rapid decline in the Franck-Condon factor between anion and neutral with increasing electron energy. The resulting cross section peak predicted to lie at 50 meV could easily be mistaken for a zero-energy resonance in experiments which typically have energy resolutions of 50 meV and higher. Explicit verification of these calculations came from high-resolution (1 meV) experiments by Barsotti \textit{et al.} [30] and Ruf \textit{et al.} [22].

More recently the theoretical results for low-energy attachment to Cl$_2$ were confirmed by flowing-afterglow Langmuir-probe measurements [31]. The calculated temperature dependence of the attachment rate coefficient is almost in perfect agreement with the experiment, both in terms of the shape and absolute values. It is interesting, however, that at higher temperatures (above about 1000 K) the theoretical values are somewhat lower than the experimental, although this observation is pertinent to only two measured temperature points, and therefore perhaps not very conclusive. A similar discrepancy was earlier observed for attachment to CF$_3$Br [32], but this was attributed to multimode effects in this target. In any event, one might suggest that the theory does not describe adequately the growth of DEA cross section with the vibrational energy. In this connection it is important to note that in recent \textit{ab initio} calculations [23] of DEA to Cl$_2$ the obtained dependence of DEA cross sections on vibrational energy is even weaker than in the R-matrix calculations [21, 22], and rotational effects were found to be not important [23]. Therefore, although the Cl$_2$ problem is basically solved, for complete clarification further \textit{ab initio} calculations are necessary.
Experiments from the Kaiserslautern group [24] have recently provided high-resolution (5-meV) data for F\textsubscript{2} which clearly show a p-wave threshold behavior for attachment through the F\textsubscript{2}\textsuperscript{−} (Σ\textsuperscript{+}u) ground state, with a peak at 31 meV, in contrast with older work [29]. However, the R-matrix theory that was so successful for Cl\textsubscript{2} failed to properly describe attachment to F\textsubscript{2}. R-matrix calculations with available F\textsubscript{2}\textsuperscript{−} potential energy curves result in a peak position at about 170 meV, consistent with previous dissociative attachment calculations [33, 34, 35]. Attempts to modify the anion curves to make the peak position consistent with the measurements [24] result in unrealistic potential curves and very small attachment rate constants that are inconsistent with drift tube measurements [36].

These studies are illustrated in Figs. 1 and 2 where we present potential energy curves as functions of internuclear distance R given relative to the equilibrium internuclear separation R\textsubscript{e}, and corresponding DEA cross sections. Calculations with the anion curve similar to that obtained by \textit{ab initio} calculations [35] produce the cross section which peaks at E = 170 meV, similar to the result of Brems \textit{et al.} [35]. The cross section which peaks at 50 meV with a significant absolute value can be obtained from the curve which follows very closely the neutral curve to the left of the crossing point, and does not give a deep enough minimum consistent with \textit{ab initio} calculations [37]. Attempts to shift the peak further to lower energies lead to even more unrealistic potential energy curves and very small DEA cross sections.

\textbf{Figure 1.} Potential energy curves for F\textsubscript{2}. The curve anion 1 corresponds to \textit{ab initio} calculations [35], the curve anion 2 to calculations giving a peak at 50 meV.

\textbf{Figure 2.} DEA cross sections corresponding to the anion curves shown in Fig. 1. Solid line, a fit to measured yield [24] up to E = 0.1 eV normalized to the theoretical peak value.

More accurate \textit{ab initio} calculations on this problem are certainly warranted. In particular it is possible that the R-dependence of the anion curve is more complicated than that represented by a simple Morse-potential parametrization used in the semiempirical R-matrix calculations.

\section{3. Attachment to polyatomic molecules}

The one-pole R-matrix theory [25] is very well suited for studying resonances and threshold effects in low-energy DEA to polyatomic molecules. However, even in the one-mode approximation, a challenging part in this approach is the calculation of the R-matrix surface amplitude generating the resonance width as described in the early review [38] of the R-matrix theory. In most calculations performed so far the surface amplitude was adjusted empirically in order to reproduce observed vibrational excitation cross sections or thermal attachment rate
coefficients. After this parameter is fixed, structures in DEA and vibrational excitation can be calculated with high accuracies using the quasiclassical version [25, 39] of the R-matrix theory. The threshold structures are determined by the long-range electron-molecule interaction which in R-matrix theory is included in the logarithmic derivative of the electron wave function in different vibrational channels.

3.1. Summary of recent results for CX$_3$Y molecules

Recent studies [32, 40, 41, 42] of the processes of the type (1) are based on adjusting the R-matrix surface amplitudes to measured thermal attachment rate coefficients. Results obtained for DEA to CF$_3$I, CF$_3$Br and CH$_3$Br illustrate some typical features observed in the process (1).

- Low-energy DEA is dominated by formation of the halogen ion Y$^-$. Because of the high affinity of the halogen atom, all three processes are exothermic, and the DEA cross section at low energy behaves as $E^{-x}$ where $x > 0.5$ is the threshold exponent whose value depends on the dipole moment of the molecule [43]. At ultralow energies below few meV the threshold exponent turns to $x = 0.5$ corresponding to the Bethe-Wigner threshold law. This happens because of molecular rotations – the electron-molecule interaction time becomes so long that molecular dipole moment is averaged out and does not influence the attachment process.

- The vibrational energy dependence of the DEA cross section is determined by the position of the curve crossing between the neutral and anion potential energy curves. In CF$_3$I the crossing point is very close to the equilibrium internuclear separation, and the vibrational energy dependence of the DEA cross section is very weak. The effect becomes very significant in case of CF$_3$Br and really dramatic for CH$_3$Br. In case of CF$_3$Br the anion curve crosses the neutral at the right turning point for the $\nu_3 = 3$ state [32]. This is a typical case for a strong temperature dependence of the DEA cross section. In case of CH$_3$Br the curve crossing occurs at even higher internuclear separation corresponding to the right turning point for the $\nu_3 = 5$ state. Here we expect very low cross sections for attachment to the ground state (or for attachment at low target temperatures), and the temperature effect should be even stronger than for CF$_3$Br.

- The potential curve crossing situation for CF$_3$Br and CH$_3$Br is also typical for formation of the vibrational Feshbach resonance (VFR) [10] which happens when the electron is captured by the long-range (dipolar plus polarization) field of the molecule with its simultaneous vibrational excitation. However, the dipole moment of CF$_3$Br too small for VFR formation. Because of the substantial dipole moment of CH$_3$Br, VFRs appear in this case, as was predicted theoretically [16] and confirmed recently by measurements [24]. In two other molecules, CF$_3$I and CF$_3$Br, cusps are observed at vibrational excitation thresholds.

- Threshold structures (cusps and VFRs) are also seen in vibrational excitation and differential elastic scattering cross section [32, 40, 41, 42].

3.2. Asymmetric dissociation

So far we have been discussing DEA processes dominated by one, obviously dominating, vibrational coordinate. However, there are cases when the choice of the dominating coordinate is not obvious. In particular it might happen that the DEA process goes through formation of a totally symmetric resonant anion state, but this resonance produces an asymmetric dissociation. For example, DEA to the chloroform molecule at low energies is dominated by a shape resonance of $A_1$ symmetry [44, 45]. Therefore one should expect that the resonance drives only totally symmetric vibrations: C-H stretch, symmetric C-Cl stretch, and symmetric CCl$_3$ deformation. However, dissociation of Cl$^-$ is an asymmetric process, therefore for a rigorous calculation of the
DEA process a multimode treatment, including the interaction between the vibrational modes, is necessary.

Still, with the goal to describe the correct threshold behavior of low-energy DEA to CHCl$_3$, we adopted a simplified approach [46]. First we identify the symmetric vibrational mode which is most important for the DEA process. High-resolution experimental data [46] obtained with the Laser Photoelectron Attachment method indicate a strong coupling between the attachment channel and the symmetric CCl$_3$ deformation mode $\nu_3$. This coupling appears in the form of a pronounced Wigner cusp in the measured DEA cross section at the threshold for the $\nu_3$ excitation.

Based on this observation and the observation of a direct anion dissociation process following Rydberg electron transfer to CHCl$_3$ [47], we assume that the electron capture initially drives the $\nu_3$ mode and that the primary temporary anion state is stabilized rapidly by direct dissociation along the $\nu_3$ coordinate. Then, mediated by intramolecular vibrational energy redistribution (IVR), the excess energy is channelled into the C-Cl stretch which eventually leads to the dissociation into the fragments Cl$^-$ and CHCl$_2$. The attachment process is thus treated in a one-dimensional approximation, assuming coupling of the anion state with only the $\nu_3$ mode. This approach is similar to our effective-range-theory treatment of electron attachment to SF$_6$ [48].

The theoretical results for different gas temperatures obtained from this model are presented in Fig. 3, together with experimental data obtained at room temperature by combined Laser Photoelectron Attachment - Extended Laser Photoelectron Attachment (LPA/EXLPA) method [49]. The R-matrix surface amplitude was adjusted to reproduce the measured [46] attachment rate coefficient, $k(T=300\,\text{K}) = 3.9(2) \times 10^{-9} \, \text{cm}^3/\text{s}$. Because of a very strong variation of the DEA cross section with the vibrational quantum number $\nu_3$ [46], we observe a strong temperature dependence in the low-energy region. However, the position of the peak between 0.4 and 0.5 eV virtually does not change with the gas temperature that is confirmed by measurements [46].

According to the threshold law for exothermic reactions at very low energies [43], the DEA cross section should be proportional to $E^{-x}$ where the threshold exponent $x$ depends on the molecular dipole moment. For the CHCl$_3$ molecule one obtains $x = 0.623$. As observed in Fig. 3, the vibrationally-averaged R-matrix cross sections are distinctly steeper at very low energies. This can be explained by the presence of a weakly bound or a virtual state due to the combined dipolar and polarization interactions, making the region of validity of the threshold
law extremely narrow. For the methyl iodide molecule, for example, the calculated DEA cross section grows much faster towards lower energies than predicted by the threshold law and reaches the correct slope only in the region below 0.1 meV [43]. A similar effect is observed in the present case. However, whereas in the methyl iodide case this effect is caused by a bound state leading to the vibrational Feshbach resonance (VFR) below the first vibrational excitation threshold [15], in the case of chloroform no evidence for a VFR and a bound state is present, therefore the effect is due to a virtual state. We should note also that the discussed behavior is pertinent to collisions with molecules with fixed orientation. In reality the molecules rotate, and when rotation is taken into account, the Bethe-Wigner law $x = 0.5$ should be restored in the sub-meV region [43].

Similar calculations were recently performed for the environmentally important molecules SF$_5$CF$_3$ [50] and CF$_2$Cl$_2$ [51].

4. Notes on Arrhenius equation

It is well known that the temperature dependence of the rate coefficient for many chemical reactions is described by the Arrhenius equation

$$k(T) = A e^{-\frac{E_a}{T}},$$

where $T$ is the temperature in energy units, $A$ is a constant, and $E_a$ is the so-called activation energy. In numerous cases, activation energies have thus been determined from plots of $\ln k$ versus $1/T$. In general, the prefactor $A$ might be temperature-dependent too, but this dependence is normally much weaker than exponential.

Many of the DEA reactions

$$XY + e \rightarrow X + Y^{-},$$

where $X$ and $Y^{-}$ are neutral and ionic fragments, not necessarily monoatomic, were found to obey the Arrhenius equation albeit over rather limited temperature ranges. The Arrhenius equation is usually associated with a reaction barrier which might be due to either the endothermcity of the DEA process or due to a barrier separating the initial $XY$ state from the exothermic final $X + Y^{-}$ state. In the endothermic case we assume that the activation energy is identical with the reaction threshold. In the exothermic case the reaction barrier is usually associated with the energy of the crossing point between the neutral and anion potential curves. The vibrational states of the neutral molecule lying below the energy of the crossing point are expected to have small DEA cross sections. This happens because for these vibrational states at low electron energies the Franck-Condon overlap between the neutral and anion states is small, and for higher energies the electron capture occurs far from the crossing point, and the intermediate anion state is likely to decay before reaching the crossing (stabilization) point. Therefore it is usually assumed that the activation energy is identical with or close to the reaction barrier, i.e. the difference $E_B$ between the energy of the crossing point and the energy of the neutral ground vibrational state.

However, upon a closer inspection of Arrhenius plots for DEA processes [52], one observes that the validity of the Arrhenius equation is certainly limited towards low temperatures and probably towards high temperatures as well. Because of these limitations, the question arises what is the relation between the activation energy and the reaction barrier. We recently performed a detailed study of validity of the Arrhenius law for the DEA process [52]. We were particularly interested in the relation between the activation energy and the reaction threshold (for the endothermic case) or the reaction barrier (for the exothermic case).

The results of this study show that the Arrhenius equation for description of the DEA processes should be used with caution. For endothermic DEA processes and favorable curve crossing, the Arrhenius equation has a rather wide range of validity limited by high temperatures.
The upper temperature limit depends on the threshold energy $E_t$ and becomes quite low for low $E_t$ and low vibrational frequency. The activation energy in the Arrhenius equation is close to $E_t$.

In the case of exothermic DEA processes with an intermediate barrier the range of validity of the Arrhenius equation is also limited towards low temperatures where the rate coefficient as a function of $T$ becomes flat. The activation energy $E_a$ is found to be lower than the reaction barrier $E_B$, and the relative difference $(E_B - E_a)/E_B$ decreases towards higher $E_B$. This behavior is partly due to the relatively slow growth of the partial rate coefficient with rising vibrational energy for vibrational levels just below the barrier. The other reason for the difference between $E_a$ and $E_B$ is the uncertainty in the definition of the reaction barrier: due to the long-range electron-molecule interaction the adiabatic anion curve peaks at lower energies than the diabatic curve. This effect is more significant for stronger long-range contributions to the electron-molecule interaction.

The above conclusions are pertinent to DEA cases where $s$-wave attachment is allowed. However, low-energy DEA to halogen molecules is dominated by the $p$-wave. In this case a separate analysis is necessary which was done recently for the Cl$_2$ molecule [31]. Like in the case of $s$-wave attachment, the contribution of the ground vibrational state to the rate coefficient is dominant at low temperatures. However, in contrast to $s$-wave attachment, the $p$-wave attachment cross section is proportional to $E^{1/2}$ and the rate coefficient proportional to $T$. Therefore, the temperature dependence in the low-temperature limit is not flat for the $p$-wave case, nor does it exhibit Arrhenius behavior typical of high temperatures. In fact, the temperature dependence in the low-energy region is substantially weaker than linear because the $E^{1/2}$ dependence of the cross section holds only in the very low-energy region below about 15 meV [22].

These observations are illustrated in Fig. 4 for four molecules: CF$_3$Br, CHCl$_3$, CH$_3$Br, and Cl$_2$. Detailed comparison with experimental data is given in Refs. [24, 31, 32, 46]. Here we just comment on the major features observed in these plots.

DEA process for all molecules presented in the figure is exothermic. However, due to a rather large reaction barrier, the CH$_3$Br plot exhibits a substantial activation energy $E_a = 249$ meV which is in a good agreement with swarm measurements [53, 54]. In contrast, the activation energy for CF$_3$Br and CHCl$_3$ is rather low, and the Arrhenius equation for these species holds in a very limited range of temperatures. This leads to some uncertainties in determination of $E_a$. 

![Figure 4. Attachment rate coefficients for CF$_3$Br, CHCl$_3$, CH$_3$Br and Cl$_2$ molecules.](image-url)
and to substantial disagreement between the theoretical and experimental values for activation energy. For example, for CF$_3$Br [32] the theory predicts $E_a = 52$ meV whereas the experimental value is $E_a = 75$ meV. Another reason for disagreement is a rather slow growth of the theoretical attachment rate coefficient with vibrational temperature, as compared with the experiment. This drawback of the theory might be due to one-mode approximation as discussed in Ref. [32].

5. Attachment to formic acid and glycine

Low energy electron interactions with biological molecules in the gas phase have proved to be a challenge for experimentalists and theorists alike. Although the field has been highly motivated by applications to radiation damage [7, 8, 9], it warrants fundamental interest because of the remarkable variety of bond-breaking reactions produced through the DEA process.

Progress in understanding interactions with large systems such as DNA strands and proteins must be grounded on an accurate analysis of the DEA process in the simplest components of these systems. Surprisingly, in the case of the amino acids and closely related molecules such as formic acid (HCOOH), there is not yet a consensus on the mechanism by which electrons with energies near 1.2 eV produce the sole fragment (M-H)$^-$, where (M-H) represents the target molecule minus an H atom. We recently presented [55] a theoretical treatment of this process in the two compounds that have been studied most extensively, formic acid and glycine, the simplest of the amino acids. We showed that the existing experimental results can be explained by invoking a single $\sigma^*$ valence anion state in which the additional electron is largely located on the OH bond [56]. This state has an extremely large width of about 6 eV or higher which precludes its direct observation in the total electron scattering cross section but which is clearly manifested in the DEA [55] and vibrational excitation [57] cross sections at much lower energies. We concluded that in formic acid and glycine, and by implication the other amino acids, capture into the $\pi^*$ orbital followed by $\pi^*/\sigma^*$ coupling, as suggested by Rescigno et al. [58], is not required to account for the bond breaking.

To simplify the DEA treatment, we employed again a one-dimensional model according to which the H dissociation occurs along the O-H bond coordinate roughly corresponding to the normal O-H coordinate in the neutral molecule. To find the R-matrix parameters for formic acid, we started with a calculation of the resonance scattering phase shifts using the finite element discrete model (FEDM) method described by Nesbet [59] combined with an approximate version of the variational technique for quasi-bound states developed by Froelich and Brandäs [60].

The R-matrix scattering phase shifts for three values of the O–H distance are presented in Figs. 5 and 6. The resonant contribution is growing so slowly that this growth is completely offset by the dipole contribution. As a result, the total phase shift is decreasing monotonically, although some indication of the resonance contribution appears at the distance $R = 1.2$ Å which is closer to the position of the crossing point between the neutral and the anion curves. These features are very similar to those observed for hydrogen halides [17, 18, 19, 61, 62, 63] where the DEA and near-threshold vibration excitation is also dominated by a very broad $\sigma^*$ resonance.

The corresponding DEA cross section is shown in Fig. 7, together with comparison with experiments [64, 65]. Due to some uncertainties in the fitting procedure, the calculated cross section suffers from some uncertainties as well which were discussed in more detail in Ref. [55]. However all analyzed R-matrix models are able to reproduce the general shape and absolute magnitude of the DEA cross section. We believe that, together with the experimental evidence of Allau [57], this proves the dominant role of the $\sigma^*$ resonance in excitation of the O–H vibrations and in the near-threshold DEA process.

Similar, albeit semiempirical, calculations [55] were performed for glycine. They reproduce the major features in the DEA cross section measured by Abouaf [66].
6. Conclusion

To summarize, substantial progress has been made during the past five years in our understanding of the basic mechanisms of DEA and in quantitative description of these processes. The resonance R-matrix theory has been successful in explaining major features in the electron energy dependence and vibrational energy dependence of DEA cross sections. Threshold resonances and cusps in DEA cross sections appear to be typical in polyatomic molecules, including molecules of biological interest. In particular we have found similarities in the attachment mechanism for formic acid and hydrogen halides.

Further development of the theory is certainly required. More accurate \textit{ab initio} calculations of the input parameters, resonance positions and widths as functions of nuclear geometry, are necessary. At the same time we need incorporation of multimode effects which still present a big challenge, particularly for the nonlocal version of the resonance theory.
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