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Dissociative recombination as primary dissociation channel in plasma chemistry

D. C. Schram, R. A. B. Zijlmans, O. Gabriel, R. Engeln
Department of Applied Physics, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

E-mail: d.c.schram@tue.nl

Abstract. Molecule formation, surface modification and deposition in plasmas can in first order be described as dissociation in the plasma and association of fragments at the surface. In active plasmas ionization and dissociation by electrons is accompanied by excitation. But besides these direct electron processes also a second dissociation channel is active: that by charge transfer followed by dissociative recombination. This latter route is the dominant one in the colder recombining phase of the plasma. Atomic and molecular radicals diffuse or flow to the surface, where new molecules are formed. As a result the original molecules are, after being dissociated in the plasma, converted at the surface to new simple molecules, as H₂, CO, N₂, H₂O, O₂, NO, NH₃, HCN, C₂H₂, CH₄, to name a few in C/H/O/N containing plasmas. There is evidence that the molecular fragments resulting from dissociative recombination are ro-vibrationally (and possible electronically) excited. Also the molecules resulting from association at the surface may be ro-vibrationally or electronically excited. This may facilitate follow up processes as negative ion formation by dissociative attachment. These negative ions will be lost by mutual recombination with positive ions, giving again excited fragments. Rotational or other excitation may change considerably plasma chemistry.

1. Introduction
In many applications the use of plasma [1] relies on the first step in the process sequence: the initial dissociation of injected and produced molecules. Radicals thus formed can be transformed to other more complex radicals, but at the end they will reach the surfaces bordering the plasma. At the surface deposition [2], etching or surface modification [3] takes place. It should be realized that during these surface processes new molecules are produced. If the plasma is very active then any molecule injected or produced is dissociated at least once during the residence time. The situation is then quite different [4] from e.g. chemical vapor deposition or heterogeneous catalysis. In hot gases only very small amount of the molecules is sufficiently hot to dissociate, whereas follow up reactions are fast. Hence the surface is usually only partially occupied. In fact this is essential for catalysis to proceed. In plasmas on the contrary the radical abundance and flux to the surface is so high that surfaces become passivated and fully covered and a different “hot” chemistry can be expected.

1 To whom correspondence should be addressed.
2 present address: Sensor Sense, Heijendaalseweg 135, 6525 AJ Nijmegen
3 present address: PVcomB/Helmholtz-Zentrum Berlin, Schwarzschildstr. 3, 12489 Berlin, Germany
The role of radicals is evident: they form the saturated layer at the surface and they are the active ingredients in the conversion of fragments of injected molecules to new molecules (and are the precursors for deposition, etching etc.). In the formation of molecules the path through charge transfer and dissociative recombination is in many cases more important than the direct dissociation by electrons. As a nice example of this, the optical light from a nuclear fusion device, the JET Tokamak, may serve. Clearly atomic hydrogen Balmer $H\alpha$ line is observed [5]. Even in this fully atomized atmosphere at a low pressure (< 1Pa), a significant part of this atomic line emission comes from dissociative recombination of molecular ions. These ions are a result of charge transfer of atomic ions with molecules coming from the surface. Hence even in this harsh atomic world the effect of the few $H_2$ molecules from recycling of H atoms and $H^+$ ions at the surface is dominantly visible in the emission. The importance of these molecular reactions, denoted by MAR, molecular assisted recombination underlines the importance of charge transfer and dissociative recombination, even in this atomic environment [6].

In earthly plasmas the situation is more molecular and more complex. It is important to realize that a plasma is out of equilibrium: it is created in the active, ionizing phase because of power input and later in time and space it is recombining when the energy sources have decayed. In the ionizing plasma the electron temperature is high to ensure its existence and thus direct ionization, dissociation (and excitation, giving line emission) is important. However, even in the ionizing phase, charge transfer from ions to molecules will give molecular ions, which then decay by dissociative recombination (giving subsequent line emission from excited atomic and/or molecular fragments) [7]. In the much longer persisting recombining phase, the direct electron ionization, excitation and dissociation are absent as the electron temperature is too low. The only reactions occurring are charge transfer and dissociative recombination. Thus for the majority of molecular plasmas dissociative recombination (preceded by charge transfer) is the dominant path for plasma fragmentation. Again (as in the atomic fusion machine) the molecules formed at the surface enter the plasma and undergo charge transfer followed by dissociative recombination (and many times line radiation). In Fig. 1 a sketch is given of a remote plasma and a photo of the actual plasma used in deposition and molecule formation studies.

![Figure 1](image)

**Figure 1.** Sketch of a cascade arc remote source plasma (horizontal) and photo of vertically arranged carbon deposition machine with pure argon plasma [9-10].

The importance of the dissociative recombination and charge transfer was found in the search for new fast deposition methodologies [8]. Fast deposition requires a large precursor flow and this can only be reached with an efficient plasma source and an equally efficient transformation of the primary energy ($Ar^+$ ions for a-C:H deposition) to injected $C_2H_2$ molecules to radicals as $C_2H$ one of the deposition precursors. Then a remote source approach is beneficial. In this work a high-pressure atomic source expanding in low pressure was chosen because of high source strength at moderate power. A high flux of radicals is produced just after the source by charge transfer and dissociative recombination:
Ar$^+$ + C$_2$H$_2$ $\rightarrow$ C$_2$H$_2^+$ + Ar; C$_2$H$_2^+$ + e $\rightarrow$ C$_2$H + H, but also CH$^*$ + CH and C$_2^*$ + H$_2$.

The dissociative recombination is thus visible in the products and emission of CH$^*$ and C$_2^*$ is thus a sign of the production of these radicals and thus the presence of C$_2$H$_2$ and ions and electrons [9-10]. In many cases also OH$^*$ and CN$^*$ bands are visible, coming from ions of residual H$_2$O and HCN. The process results thus in a high flux of radicals to the surface, which is capable of deposition rates up to 100 nm/s. There is however a downside in particular in the presence of H$_2$. If H$_2$ is used or generated, H radicals will generate H$_2$ at the surface, which will re-enter the expanding plasma, where they will cause a loss of ions, and thus chemistry, from the source.

Figure 2. Hydrogen plasma (from remote cascade arc source) and electron density profiles at 40 Pa, showing the fast decrease by dissociative recombination with increasing amounts of H$_2$ [7].

The strong effect, which molecules have on a plasma is observed if only a small amount of hydrogen is admixed to a pure argon expanding plasma. In the atomic argon plasma the ion recombination (by 3 particle recombination) is weak and ions are preserved, whereas in the hydrogen admixture recombination of molecular ions by (two particle) dissociative recombination is strong. Even atomic ions, which normally do not recombine, are now destroyed, as they are first converted to molecular ions by charge transfer and then recombine:

\[
\begin{align*}
\text{Ar}^+ + \text{H}_2 & \rightarrow \text{ArH}^+ + \text{H}; \text{ArH}^+ + \text{e} \rightarrow \text{Ar} + \text{H}^*(n\leq4) \\
\text{H}^+ + \text{H}_2 & \rightarrow \text{H}_2^+ + \text{H}; \text{H}_2^+ + \text{e} \rightarrow \text{H} + \text{H}^*(n\leq3)
\end{align*}
\]

Thus, if molecules are added to an atomic plasma the situation changes: charge transfer and dissociative recombination become the dominant mechanism and atomic or molecular fragment line emission from the dissociative recombination (indicated by *), forms a sign of parent molecules and the formation of radicals rather than their presence. [9,10]

2. Some ionizing and recombining plasmas

It has been argued above, that plasmas have an ionizing and a recombining phase and that the line emission shows the processes of ionization and of dissociative recombination respectively. We will illustrate this by showing some typical plasmas, varying from low pressure purely ionizing plasmas, mixed systems with ionizing and recombining parts, to purely recombining plasmas at high pressure. At the end we will return to the consequences of a high electron density within a cascade arc recombining plasma.
We will first discuss a low pressure purely ionizing plasma: an inductively coupled plasma (ICP) at low pressure (1 Pa). Such plasmas, used e.g. for atomic layer deposition need to be of low pressure with a large mean free path, of the order of the dimension of the system, to ensure that active particles arrive at the substrate. In such a plasma the electron temperature is high and electron impact is the dominant process for ionization and dissociation. With hydrogen the H$_2^+$ ions and H atoms all arrive at the surface and there new hydrogen molecules are formed by surface association. In Fig. 3 a spectrum in hydrogen is shown, taken from Heil et al [11]. In this ionizing plasma we see in excitation all neutrals present: H$_2$ molecules in the Fulcher bands and H atom in the H Balmer lines. As the electron and ion densities are low (10$^{15}$ m$^{-3}$) the contribution of dissociative recombination to H$\alpha$ emission is relatively small.

![Figure 3. Light emission spectrum showing Fulcher H$_2$ band and H Balmer lines of a low pressure inductively coupled plasma in hydrogen [12].](image)

If this ICP is filled with either CO or CO$_2$ the emission spectra are very similar: they show both the presence of CO. Apparently CO$_2$ is re-formed to CO (and O$_2$) in a sequence of dissociation and surface association. Similarly, CO* is observed in a situation that a CH$_3$ loaded surface is exposed to an O$_2$ plasma [12]. We thus see that in these purely ionizing plasmas at low pressure, with low n$_e$ (n$_e$ $\sim$ 10$^{15}$ m$^{-3}$) and high T$_e$ only direct excitation is visible (low n$_e$). Injected molecules may be totally transformed to other molecules by dissociation in the plasma and association at the surface. The line emission associated with electron excitation can be related to ionization. For e.g. hydrogen (nuclear fusion) this factor has been calculated and (for electron density n$_e$ $\leq$ 10$^{19}$ m$^{-3}$) is typically 10$^{-3}$ – 10$^{-2}$. For higher electron densities this factor decreases with n$_e$, because of saturation of the emission due to upward de-excitation. Thus for higher n$_e$ the emission accompanying ionization becomes relatively small.

In recombining molecular plasmas the situation is different. Now each ion can, by charge transfer, be transformed into a molecular ion. If the electron density is large enough (> 10$^{17}$ m$^{-3}$ for an electron life time, $\tau_e$, of 10$^{-9}$ s), each ion recombines through this channel. Hence for higher n$_e$ in ionizing plasmas and always in recombining plasmas, the light emission associated with dissociative recombination of a molecular ion (formed by charge transfer with a molecule) dominates. It is for this reason that the spectra get empty and contain only very persistent bands and lines: H$^+$ from H$_2^+$, CH$^+$ and C$_2^+$ from C$_2$H$_2^+$, CN$^+$ from HCN$^+$ etc. and thus spectra get very similar for different plasmas. Dissociative recombination induced radiation becomes thus dominant if the electron density is high enough in terms of the electron life time: n$_e$ $\tau_e$ $> 10^{13}$ s/m$^3$. This value is met for most high density plasmas with n$_e > 10^{17}$ m$^{-3}$ and life times of 10$^{-4}$ s. But even the very low density plasmas in dark astrophysical clouds with n$_e$ $\sim$ 10$^2$ m$^{-3}$ and electron life time $\tau_e \leq 10^{11}$ s will emit mostly emission lines from dissociative recombination processes. Hence a molecular plasma is easily in this domain and
dissociative recombination is (preceded by charge transfer) the reaction determining the chemistry and emission of the plasma.

A nice example of mixed ionizing/recombining plasma is displayed in Fig. 5: the planar microwave discharge of INP Greifswald [13]. A detail shows the existence of a small ionizing part close to the window and a larger recombining part. Part of the spectra of these low $n_e \sim 10^{17}$ m$^{-3}$ plasmas, is from ionizing origin and part from the recombining one. This plasma has been used to investigate the generation of molecules in plasmas, a subject, which met renewed interest in the framework of deposition and molecule conversion by plasmas. The role of the plasma is primarily to dissociate injected molecules, whereas the formation of new molecule takes place by association of molecular fragments at the surface. The latter is saturated with radicals from the plasma. These processes should be rather similar in totally differing plasmas as dissociation needs not to be specific and association takes place at passivated surfaces. It proved that one of the easiest methods to address the issue of molecule conversion is to measure the abundances of molecules in situations that the dissociation of molecules is effective. This was done at the planar microwave reactor in INP in Greifswald [13] (and with the earlier mentioned recombining plasma of the ETP method) [14]. The Greifswald experiment (aluminum with quartz windows) is equipped with advanced infrared absorption, with which the formation of new molecules can be measured [15].

![Figure 4](image_url) Sketch of planar microwave discharge at INP Greifswald; detail shows clearly ionizing and recombining regions [13, 15].

A general result is that in mixtures some dominant molecules are formed from fragments of injected molecules. In e.g. N$_2$ and O$_2$ mixtures (but also in a NO gas) the main product molecules are N$_2$ and O$_2$, but with a significant 2-5 % NO. In mixtures with H/N NH$_3$ is formed besides N$_2$ and H$_2$. With H/N/O mixtures H$_2$O appears and with carbon, CO is the dominantly produced molecule.

As an example we show in Fig. 5 the decay of formation of NH$_3$ and the increase of H$_2$O in hydrogen/nitrogen plasma to which oxygen is added. It proves also that the formation of NO is not much changed, if H$_2$ is added to a N$_2$/O$_2$ gas feed [14]. The explanation is that dissociated molecular fragments do stay a finite time at the surface. There they form together molecules, which subsequently desorb from the surface.

In pure gases e.g. hydrogen H$^+$ + H$^+$ → H$_2$ hydrogen atoms (H$^+$ is surface hydrogen) are re-cycled that way. In mixtures it depends on the radical fragments residing on the surface. In the absence of oxygen N and H radicals can build up to NH$_2$, which then, with an H atom, can form NH$_3$. With oxygen the OH radicals become dominant and H$_2$O is produced.
Figure 5 Decrease of NH$_3$ effective mol fraction and increase of H$_2$O with O$_2$ flow [14]

In the totally different Eindhoven experiment, expanding thermal plasma with stainless steel walls, very similar results have been obtained [16]. One way to explain this is that in plasma environment the surfaces are passivated and that thus the chemical specificity is decreased.

In a third very different experiment, a high-pressure plasma in a water bubble in water by P. Bruggeman [17], the light emission is primarily a result from the recombining phase. The ionization duration is short, whereas the recombination phase takes a long time. Only some bands/lines are visible in the spectrum from 200-800 nm: OH$^*$ band, H lines and a Na (or K) line in ‘salt’ water. Thus only two molecular ions make themselves visible in the dissociative recombination path: OH$^-$ and H$^+$ from H$_2$O$^-$ (or H$_3$O$^+$) and Na$^+$ probably from NaH$^+$. Seeing the complexity of this experiment, the spectrum is thus remarkably simple and this leads us to a general rule: One observes the 

recombination of dominant molecular ions

(in this case H$_2$O$^+$). Another fact, which becomes clear from the UV part of the spectrum in fig 6 is that a large overpopulation is visible in the OH band. In this figure also a simulated spectrum is shown with Trot ~ 1900 K necessary to cover the spectrum to 315 nm and a vibrational temperature of 7000 K to represent the peak at 315 nm. The part of the spectrum above 315 nm is due to higher J transitions and indicates a second temperature of ~ 8000 K.
Figure 6 OH band emission spectrum from a high pressure plasma in a water bubble recorded by Bruggeman [17]. The emission at $\lambda = 315-340$ nm points to a strong non-thermal overpopulation of high rotational levels (J>14).

This experiment is at atmospheric pressure and thus this non-equilibrium excitation points to direct observation of the dissociative recombination process $\text{H}_2\text{O}^+ + e \rightarrow \text{OH}^* + \text{H}$.

Apparently dissociative recombination of molecular ions leads to a strong overpopulation in rotation. The low levels are collisionally coupled, but the higher levels with energy differences above kT are heavily overpopulated [18]. This is an interesting fact, as this overpopulation can be rather persistent and offers a secondary energy reservoir for chemical reactions. Dissociative attachment is highly facilitated and thus the production of negative ions.

4. Recombining low $T_e$ plasmas in remote plasma processing

We will now return to the expanding purely recombining plasmas with a remote source used for fast plasma deposition and molecule conversion developed at the Technical University of Eindhoven. In this low temperature ($T_e \leq 0.2$ eV) plasma, electron excitation is absent and charge transfer and dissociative recombination are the most important reactions. Recombination is very strong and was called initially anomalous [7]; later in the fusion community it is referred to as MAR processes [6].

We described above that this recombination forms also the main source of line emission. This sequence of charge transfer from atomic ions to molecules, forming molecular ions, which dissociatively recombine, is very present in hydrogen plasmas. The spectrum shows a large series of atomic hydrogen Balmer lines, as is shown in Fig. 7, even though the main constituents are hydrogen molecules, associate at the surface [7].

In Fig. 8 it is shown that not only red emission ($\text{H}_\alpha$) but also blue emission from the higher n Balmer lines is observed. This emission is likely caused by mutual recombination of $\text{H}^-$ and $\text{H}_n^+$ ions [8]. Blue emission is considered a signal of negative ion formation.
Figure 7. Measurement of Balmer series in a hydrogen expanding plasma [7]. The principal quantum number of the emitting state is indicated.

Figure 8. Left: Expanding plasmas in Ar and in Ar/H₂ plasmas at pressure of 40 Pa. Right: expanding plasma in H₂ at higher pressure, showing the blue periphery around the red central expansion.

A necessary ingredient for the process of dissociative attachment is the presence of ro-vibrationally excited molecules H₂(r,v). To investigate their presence we have used VUV laser induced fluorescence, calibrated using earlier measurements with CARS. Results shown in Fig. 9 give clearly evidence for an appreciable excitation in H₂(r,v) [18]. In this figure only rotational levels for v= 0, 1, 2, 4 and 6 are shown; in ref [19] more detail and also rotational levels of higher vibrational levels are given.

The main chemical route in these recombining plasmas is thus: Dissociation by plasma, transport (and possibly modification) of radicals to surfaces and then association at the surface to molecules, which can be excited. In this process the high radical flux plays also another role: it leads to a passivated and thus modified surface with possibly different chemistry. One suggestion is the existence of mobile,
weakly bound, H atoms, which by “hot-LH” reactions produce the excited hydrogen molecules. These excited H$_2$(r,v) molecules give then the possibility to form e.g. negative ions. Additionally, the presence of H$_2$(r,v) may facilitate the conversion of H$^+$ to H$_3^+$, which is then converted to H$_3^+$, even in very cold atmospheres. The presence of H$_2$(r,v) may thus indirectly promote further chemistry.

More evidence of excited molecules produced at the surface can be found in cold recombining plasmas in nitrogen, where substantial radiation is observed (N* lines, first positive system of N$_2$(B$\rightarrow$A) and the first negative system of N$_2$ (B$\rightarrow$X)). The N* emission is assigned to the weak three particle recombination of N$^+$ ions. The molecular bands cannot be explained by volume processes. One possibility, suggested by extra emission close to a substrate, is that N atoms create excited molecules at the surface, possibly in the B or a’ state [20]. By B$\rightarrow$A radiation these decay to metastable N$_3$(A) molecules. We note that also here high rotational excitation is observed. Charge transfer from N$_3$(A) molecules to N$^+$ ions can then lead to excited molecular ions N$_2^+$(B), which decay through the first negative system N$_2^+$(B$\rightarrow$X). Hence also this observation of excited molecules, being desorbed from the surface could indicate the existence of weakly absorbed “hot” fragments at the surface. Another example is the appearance of the orange shuttle glow close to the surface in N$_2$/O$_2$ downstream plasmas, which is attributed to NO$_2^*$ [21]. Also this emission can only be explained, if weakly bound pre-cursors at the surface cause the generation of excited molecules.

6. Conclusions

In cold strongly recombining plasmas, as present in downstream plasmas used in remote source plasma processing, dissociative recombination in combination with charge transfer is the main channel for dissociation of molecules injected or produced. Dissociative recombination is thus a dominant process in chemical plasmas. It is there the most important source of visible and UV emission and we observe thus the dissociation process. Many times the molecular products prove to be highly excited (in particular rotationally). High rotational excitation is possibly rather stable and can facilitate further chemistry. Dissociative recombination can also be used to register the formation of new molecules by the footprint they give in emission, as CN$^*$ for HCN$^{(+)}$, OH$^*$ for H$_2$O$^{(+)}$, H$^*$ for H$_3^+$ etc.. In low-pressure plasmas with a high radical flux, molecule formation proceeds primarily by association of molecular fragments at saturated surfaces. In this process substantial (rotational) excitation has been observed and the example of H$^*$ formation indicates the importance of this excitation for further chemistry. Likewise rotational excitation can facilitate the process of dissociative
recombination. Hence a study of rotational excitation influence and consequence would be an important subject for plasma chemistry.

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