RECENT DEVELOPMENTS IN THE THEORY OF DISSOCIATIVE RECOMBINATION
AND RELATED PROCESSES

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Dissociative recombination of molecular ions:

\[ \text{AB}^+ + e \rightarrow A + B \]

has been presented and discussed by B. Mitchell, in the same volume. The current chapter will comment on some interesting features of this process and present recent theoretical developments in this field. Examples and extension to related processes will close this chapter.

I. INTRODUCTION

As an introduction, I will ask a naïve question: what do we learn from Dissociative Recombination (DR*) studies, experimental or theoretical? Of course, we hope to obtain reliable values of the cross-section \( \sigma \) or of the rate coefficient \( \alpha = \langle v \rangle \) (\( v \) is the incident electron velocity and the average is taken over the velocity distribution, usually Maxwellian). They are very important to understand or predict the electronic density of numerous ionized media, in laboratory plasmas, ionosphere or interstellar medium. But beyond its own interest, DR may shed light on the dynamics of excited molecular states, in particular those which cannot be studied by conventional (i.e. one photon) spectroscopy due to parity or multiplicity selection rules. More generally, the dissociative recombination pertains to a broad class of processes which proceed through the formation of a "molecular complex" (Fig. 1a) in which all the particles (electrons and nuclei) are close together and may interact strongly. All kinds of energy exchanges are thus possible, leading to various decay channels (Fig. 1b). In dissociative recombination, the kinetic energy of the incident electron is transferred to the motion of the nuclei, not directly but via a rearrangement of the whole electronic cloud, resulting in the formation of a dissociative (or predissociated) state of the neutral molecule. It is to be noted that such an excited state, lying above the ionization and dissociation limit of the molecule (they are sometimes called "superexcited states"), generally plays a role in other processes (associative ionization, atomic collisions, photoprocesses) involving the same molecular complex.

* Not to be confused with Dielectronic Recombination, denoted also DR by atomic physicists, e.g. Y. Hahn in the same volume! A comment on "molecular" DR versus "atomic" DR will be made in Section II.2 below.
II. COMMENTS ON DISSOCIATIVE RECOMBINATION CROSS-SECTIONS

1. What determines the intensity of the process?

The strength of the DR process hinges mainly on the existence of a dissociative valence state (doubly excited state) of the neutral molecule, intersecting "favorably" the potential curve of the ion initial state (generally the ground one). Two factors are then determinant: the strength of the electronic interaction $V_{el}(R)$ between the mono- and diexcited electronic configurations, and the size of the overlap between the nuclear wavefunctions of the ion initial level ($\chi_{v+}$) and of the dissociative state ($F_d$). The basic mechanism for DR, first proposed by Bates \cite{Bates}, has been explained in detail by B. Mitchell in this volume, and by S. Gubermann in Ref. 2. They show that the DR cross-section may be written approximately as the product of a capture cross-section and a survival factor $S_F$, which represents the probability of dissociation following the electronic capture ($S_F \leq 1$):

\[
\sigma = \sigma_{\text{capt}} \times S_F = \frac{4\pi^3}{k^2} g \frac{v^2_{el}}{} |\langle \chi_{v+} | F_d \rangle|^2 S_F
\]  

where $g$ is the ratio of the final and initial state multiplicities and $k = \sqrt{2e}$ (in a.u., $e$ being the energy of the incident electron) is the electron wave number.

Here I just want to make a few remarks about this widely used approximate expression:

i) a more exact expression of the capture cross-section, avoiding the "Frank-Condor approximation" is:

\[
\sigma_{\text{capt}} = \frac{4\pi^3}{k^2} g \int \chi_{v+} (R) V_{el} (R) F_d (R) dR |^2
\]  

Fig. 1: Formation (a) and decay (b) of an excited molecular complex