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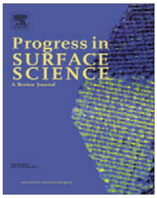

Review

Electron driven processes in ices: Surface functionalization and synthesis reactions

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ABSTRACT

The ability to control and orientate chemical reactivity in the condensed phase is a major challenge of modern research. Upon interaction with condensed molecules electrons drive bond cleavage thus generating a population of very reactive species in the condensed medium. These reactive species may interact either within the volume leading to the synthesis of new molecules or with the substrate surface by forming strong chemical bonds. The former reaction is known as electron induced synthesis and the latter one as electron induced surface functionalization.

High-energy electrons achieve only a low chemical specificity due to the large number of dissociating open channels. In contrast, electrons with energies below ionization threshold of the irradiated matter are capable of high selectivity because of the dissociative electron attachment mechanism.

In this review recent studies of electron interaction with condensed molecules on hydrogenated diamond substrates will be described. In particular electron induced functionalization of diamond surfaces by CH_2CN groups, decarboxylation reactions in condensed films of pure organic acids RCOOH (R = H, CH_3, C_2H_5, CF_3), carbamic acid formation in CO_2:NH_3, HCOOH:NH_3 and CF_3COOH:NH_3 binary ice mixtures, and glycine formation in a CH_3COOD:NH_3 mixture are presented and discussed.

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Contents

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1. Introduction

Low-energy electrons ($E_i < 30$ eV) play a major role in different applications and techniques such as plasma chemistry [1–3], radiation chemistry and biology [4–8], electron and ion beam [9–13], and photon [14,15] induced surface chemistry. Upon interaction with condensed (physisorbed) molecules, electrons drive bond cleavage thus generating a population of very reactive species in the condensed medium. These reactive species may interact either within the volume leading to the synthesis of new molecules or with the substrate surface by forming strong chemical bonds. The former reaction is known as electron induced synthesis and the latter one as electron induced surface functionalization. Bond cleavage may involve neutral or ionic dissociation mechanisms (Eqs. (1)–(3)) and at lower energy ($0 < E_i < 20$ eV) dissociative electron attachment (DEA) (Eq. (5)).

$$M \xrightarrow{e^-(E>E_{exc})} M^* \rightarrow N + N' \quad \text{neutral dissociation} \tag{1}$$

$$\rightarrow I^- + I'^+ \quad \text{dipolar dissociation} \tag{2}$$

$$M \xrightarrow{e^-(E>E_{ion})} M^+ + e^- \rightarrow N + I'^+ + e^- \quad \text{dissociative ionization} \tag{3}$$

DEA implies the formation of a transient negative ion (TNI) or negative ion resonance $M^{\#-}$, which can be viewed as a molecular quantum state embedded in the electron-target continuum [16–24]. The evolution of a TNI can proceed along the dissociative pathway already mentioned (Eq. (5)) but also via autodetachment eventually leaving the molecule in a vibrationally (Eq. (4)) and/or electronically excited state M^*. The latter excited state was observed then to decay by dissociation into neutral fragments (Eq. (6)), and/or dissociative ionization (Eq. (7)).

$$\begin{tikzcd} & M(v,j)+e^- \quad (4) \\ M+e^-(E_{res}) \arrow[r] & M^{\#-} \arrow[u] \arrow[d] \arrow[r] & N+I^- \quad (5) \\ & M^*+e^- \arrow[r] & \begin{cases} N+N'+e^- & (6) \\ I'^{+}+N+2e^- & (7) \end{cases} \end{tikzcd}$$