LOW-ENERGY ELECTRON DRIVEN PROCESSES IN ICES: SYNTHESIS REACTIONS AND SURFACE FUNCTIONALIZATION

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Abstract. *Low-energy electrons, and subexcitation energy electrons in particular, have the ability to induce efficiently chemical modifications within condensed molecular films and at substrate surfaces. By taking advantage of the Dissociative Electron Attachment (DEA) process, which leads to selective bond cleavages, the induced reactivity can be controlled solely by the electron energy. Two illustrative examples of induced reactivity and substrate functionalization achieved by low-energy electron processing of condensed molecules studied by means of High Resolution Electron Energy Loss Spectroscopy (HREELS) are reviewed, and special interest is given to the possibility of proposing overall reaction mechanisms. The resonant decarboxylation reaction in condensed films of trifluoroacetic acid CF_3COOH induced by electrons at ~1 eV involves the formation of the transient species $[CF_3COOH]^{\#-}$ and the further formation of CO_2 by a concerted mechanism. Diamond substrate functionalization by CH_2CN organic groups through C_{diam}—C and C_{diam}—N bonds is performed by 2 eV electron irradiation of condensed acetonitrile CH_3CN and involves reactants formed by DEA, that are neutral radicals H· and molecular anions $[H_2CCN]^-$.*
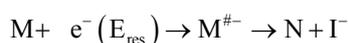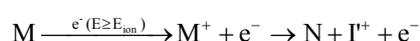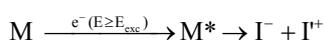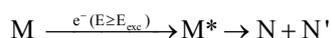
Key words: *Dissociative Electron Attachment, Electron Induced Reactivity, Selectivity, Functionalization, Diamond, High Resolution Electron Energy Loss Spectroscopy*

INTRODUCTION

Low-energy electrons ($E_i < 30$ eV) play a major role in different applications and techniques such as plasma chemistry [1], radiation chemistry and biology [2,3], electron / ion beam [4-7], and photon [8,9] 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 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 (equations (1)-(3)) and at lower energy ($0 < E_i < 20$ eV) dissociative electron attachment (DEA) (equation (4)). 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 [10-14].

$$M \xrightarrow{\quad e^- (E \geq E_{exc}) \quad} M^* \rightarrow N + N'$$

$$M \xrightarrow{\quad e^- (E \geq E_{exc}) \quad} M^* \rightarrow I^- + I'^+$$

$$M \xrightarrow{\quad e^- (E \geq E_{ion}) \quad} M^+ + e^- \rightarrow N + I'^+ + e^-$$

$$M + e^- \left(E_{res} \right) \rightarrow M^{\#-} \rightarrow N + I^-$$

Low-energy electrons ($E < E_{exc}$, called subexcitation energy electrons in the following) are then capable of chemical selectivity [15-17] in contrast to high-energy electrons, for which a large number of non-resonant dissociative channels are open. In this contribution, we review two examples, which are illustrative of the high efficiency of subexcitation electrons to induce chemical modification within condensed molecular films and at substrate surfaces. Molecular films are vapor deposited on an inert hydrogenated diamond substrate cooled down to about 30 K. These films can be regarded as assemblies of physisorbed molecules, whose interaction with the inert substrate is mainly of the Van der Waals type. Moreover in the preparation conditions the obtained films are amorphous [18], and no reaction with the hydrogenated diamond substrate is observed prior to electron irradiation. The films are irradiated using low-energy electrons of tunable energy (0-20 eV) and dose (10^{15}-10^{16} e/mm^2). Reactive species and fragments are created and can further react with each other, with neighboring molecules, and with the substrate surface if they are created in its vicinity. The result of the electron writing procedure is probed by high resolution electron energy loss spectroscopy (HREELS), a very surface sensitive vibrational spectroscopy [19].

In this paper we will emphasize that reaction mechanisms can be proposed when working with subexcitation energy electrons, since they have the ability to induce selective bond cleavages via DEA. Therefore the formation of the primary reactive species is controlled and hence the set of subsequent chemical modifications within the film and at the substrate surface is guided. Resonances are most often studied in the gas phase by measuring yields of anions [3,15,16,20,21] or excited neutral fragments [22]. In a molecular film the extra electron will be generally localized on an individual molecule, the interaction can therefore be regarded as taking place on a molecular site. However compared to their gas phase counterparts the energies of the condensed phase resonances are lowered due to the electronic polarization of the medium [23,24].

After a brief experimental part, the electron induced decarboxylation at subexcitation energy taking place in condensed films of pure trifluoroacetic acid CF_3COOH will be

presented [25,26]. The resonant regime is well localized around ~1 eV and involves the formation of a TNI [CF$_3$COOH]$^{\#}$ followed by a concerted mechanism leading to carbon dioxide (CO$_2$) formation. The second illustrative example deals with functionalization of diamond surfaces by CH$_2$CN organic groups through C$_{diam}$—C and C$_{diam}$—N bonds, following 2 eV electron irradiation of condensed acetonitrile CH$_3$CN. This selective reaction is initiated by DEA on CH$_3$CN, leading to a neutral radical H$^{\bullet}$ and a molecular anion [H$_2$CCN]$^{-}$ as fragments [27].

EXPERIMENTAL METHOD

The experiments were performed in an ultra-high vacuum chamber (base pressure below 5 x 10^{-11} Torr) equipped with a liquid helium flow cryostat, an electron gun and a HREEL spectrometer.

The polycrystalline diamond films are deposited on a *p*-type doped silicon substrate by a standard microwave chemical vapor deposition (mw-CVD) method using conditions described elsewhere and the full hydrogenation of the sample was performed in-situ by exposing the bare diamond films to activated hydrogen [28,29]. These hydrogenated diamond films are chemically inert [30], thus preventing contribution of reactive/catalytic processes involving the physisorbed layers of deposited molecules. Pure ice films, which are typically 4 monolayers (ML) thick for induced synthesis and 2 ML thick for induced functionalization, were deposited onto the passivated substrate, fitted on the end of the He cryostat and cooled down to 30 ± 5 K, by exposing it to pure gas (pressure typically of 1 x 10^{-8} Torr during 400 s for a 4 L dose).

The samples are irradiated using an electron gun, which supplies, depending on electron energy, a current of 2-40 μA on an average area estimated to ~2 mm^2, with a resolution of about 300 meV. Exposures of typically 10^{15}-10^{16} electrons/mm^2 (uncertainty estimated to 50%) were used for ice processing, corresponding to electron fluxes roughly estimated to 0.5-15 electrons/s per molecule and total doses of about 100-1000 electrons per molecule.

Chemical modifications are probed by HREEL vibrational spectroscopy directly at 30 ± 5 K or at room temperature after annealing to 400 K, depending if induced reactivity or substrate functionalization is considered. In HREELS, electrons with a given energy (usually in the range below 10 eV) are focused on a target and the backscattered electrons are collected as a function of their energy. Spectra present peaks, which are the fingerprints of the vibrational modes of localized functional groups belonging to particular molecules [19]. The HREEL spectrometer consists of a double monochromator and a single analyzer (model IB 500 by Omicron). The presented energy loss spectra were obtained at an incident electron energy of 5 eV, in the specular geometry with an incident direction of 55 degrees with respect to the surface normal and an overall resolution of 6 meV, measured as the full width at half maximum of the elastic peak.

DECARBOXYLATION OF TRIFLUOROACETIC ACID

Low-energy electrons have attracted considerable interest in the last few years due to their potential to induce specific chemical reactions in pure ices condensed at cryogenic temperature. For instance it has been shown that electron irradiation leads to the

formation of ozone (O_3) in condensed oxygen (O_2) [31] and of chlorine (Cl_2) in chlorofluoroalkanes [32,33]. In both cases a resonant process involving electrons of subexcitation energies was established to take place, and in the case of dichlorotetrafluoroethane 1,2-$C_2F_4Cl_2$ Balog and coworkers even observed the complete conversion of a condensed film by electron processing at 1 eV. Recently electron induced decarboxylation of small organic acids RCOOH (R = H, CH_3 and CF_3), was studied and a resonant regime was in particular evidenced in the subexcitation energy region. This will be demonstrated in the following on the example of trifluoroacetic acid CF_3COOH.

The energy loss spectrum of a 4 ML film of pure CF_3COOH is shown in Fig. 1(a). The mode assignment of the observed losses was done in accordance with published data [34] and is presented in more detail elsewhere [26]. The films and their surfaces consist of molecular networks coupled by hydrogen bonds (O--H—O bridges) [35].

Briefly, the spectrum is dominated by a loss at 150 meV attributed to the overlapping contributions of stretching $\nu(CF_3)$ modes and the bending $\delta(COH)$ mode. The acidic functional group –COOH gives rise to the losses located at 180 meV, 219 meV, and 369 meV, respectively attributed to $\nu(C—O)$, $\nu(C=O)$ and $\nu(OH)$, the latter frequency being strongly shifted towards low energy losses as expected for hydrogen bonded OH groups. Furthermore a collection of peaks is observed in the range of 20-120 meV, which is attributed to CF_3 related bending modes and to skeleton modes of the molecule.
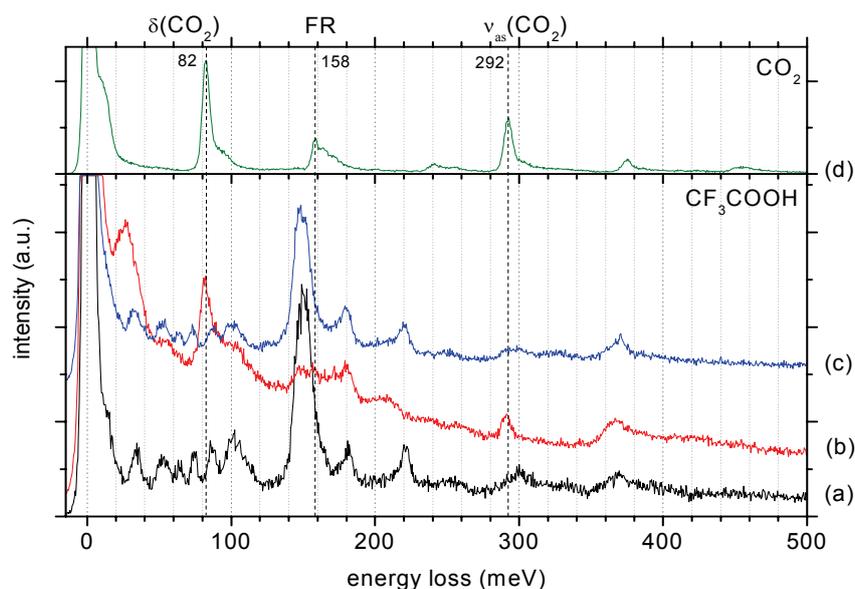

Fig. 1. Energy loss spectra of 4 ML CF_3COOH films before (a) and after electron irradiation either at 1 eV (b) or 2.5 eV (c) (1.3 x 10^{16} e/mm^2). The energy loss spectrum of a multilayer film (8 ML) of carbon dioxide CO_2 (d) is given for comparison in the upper panel. The losses at 82 and 292 meV are respectively attributed to the bending $\delta(CO_2)$ and asymmetric stretching $\nu_{as}(CO_2)$ modes, and the feature peaking at 158 meV is ascribed to the Fermi Resonance (FR).

Electron irradiation at an energy of 1 eV leads to major changes in the energy loss spectrum (Fig. 1(b)), in that several modes present in the pure film vanish after irradiation while new modes appear in the spectra. The modes that are strongly decreased in intensity or vanished completely after irradiation are: (i) the loss at 219 meV assigned to $\nu(C=O)$, (ii) the formerly dominant loss at 150 meV mainly attributed to overlapping $\nu(CF_3)$ modes and (iii) all the skeleton and CF_3 related losses in the range 20-120 meV. We can thus conclude that most of the CF_3COOH molecules were destroyed upon irradiation. New losses are observed at 82 and 292 meV, as well as an unresolved feature at 158 meV. By comparison with a spectrum of a pure film of CO_2 (Fig. 1(d)) these new features can be directly associated with electron induced formation of CO_2. Accordingly, the losses at 82 meV and 292 meV are attributed to the fundamental bending $\delta(CO_2)$ and asymmetric stretching $\nu_{as}(CO_2)$ modes of CO_2. Furthermore, a contribution of the Fermi resonance (FR) combining the symmetric stretching mode with the overtone $2\,\delta$ of the bending mode is visible at 158 meV.

This electron induced decarboxylation of trifluoroacetic acid is particularly interesting because it occurs only in a quite narrow energy region. The spectrum obtained after irradiation at 2.5 eV (Fig. 1(c)) using the same electron dose as for 1 eV shows no major changes in comparison to the non-irradiated film, i.e. all the characteristic losses are still observed, including the low energy ones. Thus, no significant chemical modifications were induced in the film by electron irradiation at 2.5 eV.

The initial step for the production of CO_2 is therefore a resonant electron attachment leading to the formation of a TNI $[CF_3COOH]^{\#-}$. The latter can further decompose in an anion and one or more radicals, thereby forming reactive species in the film which may then interact in the medium and form CO_2. Similarly, formic acid and partially deuterated acetic acid show also formation of CO_2 via a low energy resonant process around 1 eV electron energy.

Since the reaction $CF_3COOH + e^- \rightarrow CO_2 + CF_3 + H + e^-$ is endothermic, as well as the reaction leading to the formation of the anion CF_3^- by attachment of the extra electron, we propose a concerted mechanism. This mechanism assumes that the most probable co-product is trifluoromethane CF_3H and the reaction enthalpy can then be evaluated for the gas phase to $\Delta_r H_{(g)} \sim -0.61 / -0.76$ eV, depending on the value taken for the enthalpy of formation of CF_3COOH [36].

$$CF_3COOH + e^- \rightarrow CO_2 + CF_3H + e^-$$
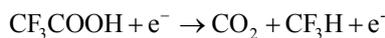
However CF_3H could not be observed, in particular no significant energy loss which could be assigned to one of the dominant CF_3 related modes of CF_3H (observed at 143 meV in the gas phase [36]) could be evidenced in the vibrational spectrum recorded after irradiation at 1 eV (see Fig. 1(b)). The vibrational modes are tabulated for CF_2 at 152, 137-138 and 83 meV, for CF at 114 meV, for F_2 at 162 meV and for HF at 514, 488, 475 meV, depending on the degree of hydrogen bonding [36,37]. There are no indications for these possible small fluorinated fragments and products, which is not understood at the present time.

The remarkable point of electron induced chemistry in CF_3COOH films is that it is possible to selectively control the decarboxylation reaction by tuning the electron energy of irradiation. While at subexcitation energy photons are not operative agents to induce this reaction, 1 eV electrons are remarkably efficient ones.

FUNCTIONALIZATION OF DIAMOND BY CH$_2$CN GROUPS

Functionalization of semi-conductor materials by small organic groups is a fast growing field, in particular due to possible applications in chemical or biological sensors and in molecular electronics [38-42]. Functionalization by small organic groups may serve as a route toward further complex chemical modifications of surfaces. Wet and dry chemistry methods have been developed, some of them being photon or electron initiated. In the case of electron induced functionalization of surfaces, oxidation of Indium phosphide InP(110) [43] has been obtained as a result of electron bombardment of O$_2$ molecules condensed on InP surfaces. The role of O$_2^{-\#}$ resonant state formation was invoked to explain the reaction. Later, fluorination and oxidation of hydrogen passivated silicon substrates have been obtained as a result of electron bombardment of condensed CF$_4$ and H$_2$O films, respectively [44,45]. Electron energy dependences on the functionalization have shown that dissociative electron attachment processes must play a role in the reaction. However, in the different studies, the mechanisms involved in the functionalization processes of InP and Si substrates are not fully understood.

In the last decade, hydrogenated diamond substrates have raised growing interest due to their remarkable electrical, chemical, thermal and mechanical properties and to their biocompatibility [38,40-42,46,47]. Furthermore, robust, inert and stable synthetic diamond films can be easily grown on microelectronic compatible substrates by microwave chemical vapor deposition (mw-CVD) method [48]. In this section, the electron induced functionalization of diamond at subexcitation energy is presented. The molecule chosen as precursor for substrate functionalization is acetonitrile, because only one selective DEA process takes place when it interacts with subexcitation energy electrons. It leads to the selective breaking of a C—H bond, resulting in the formation of CH$_2$CN$^-$ ion and H$^{\bullet}$ radical as fragments [49]. This process is expected to take place at 2 eV in the condensed phase, once the polarization energy has been taken into account.

A 2 ML film of acetonitrile was condensed on the cooled hydrogenated diamond and then irradiated by 2 eV electrons. The sample was subsequently annealed to 400 K in order to desorb all the physisorbed material, so that only the chemisorbed species would remain on the substrate surface. The HREEL spectra recorded at each step of the electron induced procedure are shown and discussed in detail elsewhere [27]. Significant changes and indications for chemisorption of species containing C=N, C=C, C≡N bonds and/or CH$_2$ groups were observed, while the vibrational signature of hydrogenated diamond were no longer visible. This can be interpreted as resulting from (CH$_2$CN) group chemisorption on the diamond substrate, either through a C$_{diam}$—C or a C$_{diam}$—N covalent bond. These transformations must be initiated and associated with electron dissociation processes in CH$_3$CN layer condensed on hydrogenated diamond since (i) hydrogenated diamond surfaces are known to be chemically very stable, and we have checked that condensation of few ML of CH$_3$CN on this surface followed by desorption at 400 K restore the original HREEL spectrum of the hydrogenated diamond, and (ii) the interaction of 2 eV electrons on the hydrogenated diamond leads only to vibrational excitation, H$^-$ desorption being observed only above 4.5 eV [28].

The overall mechanism represented in Fig. 2 could be proposed:

(1)   DEA process: CH$_3$CN + e$^-$(2eV) $\rightarrow$ [CH$_3$CN]$^{\#-}$ $\rightarrow$ [CH$_2$CN]$^-$ + H$^{\bullet}$.

(2)   Depassivation of the hydrogenated diamond surface via recombinative abstraction of H atoms by H$^{\bullet}$ radicals [50] leading to the release of molecular hydrogen and leaving active dangling bonds on the substrate.

(3)   Simultaneous bonding of H$_2$CCN chains to the diamond substrate by their C or N terminal atoms (the negative charge in the molecular anion being delocalized over the whole molecule) to dangling bonds and electron ejection in vacuum or flowing through the substrate. However, for this step, the reaction of intact CH$_3$CN molecules with dangling bonds cannot be excluded.

The characteristics and selectivity of the DEA process at 2 eV in CH$_3$CN allow efficient covalent attachment of CH$_2$CN chains to diamond substrate, the steps involved in the overall process being understood at the molecular level.
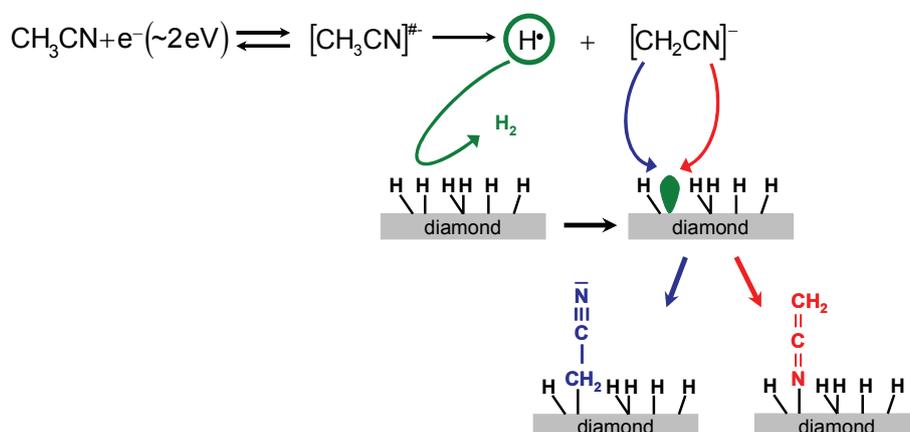

Fig. 2. Proposed mechanism for diamond functionalization by electron irradiation at 2 eV of condensed acetonitrile CH$_3$CN. Step 1: DEA process leading to the formation of hydrogen radicals and anions [CH$_2$CN]$^-$. Step 2: Depassivation of the hydrogenated diamond surface via recombinative abstraction of H atoms by H$^{\bullet}$ radicals leading to the release of molecular hydrogen and the creation of active sites on the substrate. Step 3: Simultaneous bonding of H$_2$CCN chains by their C or N terminal atoms on vacant dangling bonds and electron ejection in vacuum or flowing through the substrate.

CONCLUSION

Low-energy electrons and subexcitation energy electrons in particular, have the ability to induce efficiently chemical modifications within condensed molecular films and at substrate surfaces. By taking advantage of the dissociative electron attachment process, which leads to selective bond cleavages, the induced reactivity can be controlled solely

by the electron energy. Two examples were reviewed in order to illustrate how efficient low-energy electron processing of condensed molecular films is to induce decomposition and synthesis reactions within molecular films and functionalization of surfaces. Special interest was given to the possibility of proposing overall reaction mechanisms. The studies were performed by means of High Resolution Electron Energy Loss Spectroscopy. The resonant decarboxylation reaction in condensed films of trifluoroacetic acid CF_3COOH induced by electrons at ~1 eV involves the formation of the transient species $[CF_3COOH]^{\#-}$ and the further formation of CO_2 by a concerted mechanism. Diamond substrate functionalization by CH_2CN organic groups through C_{diam}—C and C_{diam}—N bonds is performed by 2 eV electron irradiation of condensed acetonitrile CH_3CN and involves reactants formed by DEA, neutral radicals $H^{\bullet}$ and molecular anions $[H_2CCN]^-$.

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PROCESI U LEDU INDUKOVANI ELEKTRONIMA NISKE ENERGIJE: REAKCIJE SINTEZE I FUNKCIONALIZACIJA POVRŠINE

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Elektroni niskih energija ispod praga za jonizaciju mogu efikasno prouzrokovati hemijske promene na površini i unutar kondenzovanih molekularnih filmova. Koristeći proces disocijativnog zahvata elektrona, koji uzrokuje selektivno kidanje molekulskih veza, indukovana reaktivnost može

biti kontrolisana samo podešavanjem energije elektrona. Dva ilustrativna primera ovakve indukovane reaktivnosti i funkcionalizacije površine, postignute procesiranjem kondenzovanog molekularnog filma elektronima niske energije i studirana pomoću spektroskopije gubitka energije elektrona visoke rezolucije(HREELS), su prikazana u ovom radu, pri čemu je poseban interes usmeren ka mogućnošću da se predloži opšti mehanizam rekacija. Rezonantna reakcija dekarboksilacije u kondenzovanom filmu trifluor-sirćetne kiseline CF_3COOH prouzrokovana elektronima energije ~1 eV uključuje formiranje prelaznih sistema $[CF_3COOH]^{\#-}$ i dalje formiranje CO_2 usklađenim mehanizmom. Funkcionalizacija dijamantskog supstrata pomoću CH_2CN organskih grupa preko C_{diam}—C i C_{diam}—N veza je postugnuta bombardovanjem kondenzovanog acetonitrila CH_3CN elektronima energije 2 eV, i uključuje reaktante formirane disocijativnim elektronskim zahvatom, neutralne radikale H• i molekularne negativne jone $[H_2CCN]^{-}$.