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Electron-induced Chemistry: Preliminary Comparative Studies of Hydrogen Production from Water, Methanol and Diethyl Ether.

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Abstract

Binary, layered ices comprising of benzene (C₆H₆) on water (H₂O), on methanol (CH₃OH) and on diethyl ether (CH₃CH₂OCH₂CH₃) have been irradiated with 250 eV electrons. Molecular hydrogen (H₂) production is observed by quadrupole mass spectrometry to be competitive with (in the case of H₂O), and dominate over (in the case of the organic substrates), C₆H₆ desorption. While very preliminary, these results suggest that chemical change (in the form of dehydrogenation) induced by interaction of organic-rich icy solids with ionising particle radiation may significantly contribute to hydrogen recycling in cold dense environments.

Keywords

Icy grains, molecular clouds, non-thermal desorption, electron-induced chemistry, water ice, solid methanol, solid diethyl ether

Introduction

Solid water is highly abundant in astrophysical environments being one of the main components if not the dominant species in icy mantles coating interstellar dust grains,¹ comets² and in icy planetary bodies such as Europa^{3,4} where exposure to ionising radiation is a significant promoter of physical and chemical change. Laboratory studies have reported on the effect of electrons, ions and electromagnetic radiation on the physics and the chemistry of H₂O ices; highlighting the species produced and the mechanisms by which these species are formed;⁵⁻⁸ phase changes;⁹⁻¹² and desorption of neutral or ionic species during the irradiation.^{13,14}

In astronomical environments, H₂O is always found in the presence of other species. Hence, increasing attention is being paid to understanding the processes taking place after photolysis and radiolysis of other simple pure molecular solids, such as carbon monoxide (CO), ammonia (NH₃), methanol (CH₃OH), acetonitrile (CH₃CN), and their mixtures with H₂O and each other at cryogenic temperatures.¹⁵⁻²⁵ The results clearly point to a significant role for ion, electron and photon induced chemistry in the formation of complex organic molecules (COMs) in these environments.²⁶⁻³⁰ Illustrative is the work of Mason and co-workers on electron bombardment of thin CH₃OH films at 14 K;³¹ wherein the reaction products and their yields seem to be independent of the primary electron energy suggesting that the observed electron-induced chemistry (EIC) is linked to the production of low energy secondary excitations within the ice. The authors conclude with the hypothesis that these secondary excitations might represent a common underpinning for irradiation phenomena.

Layered ices are a convenient system to investigate how the aforementioned excitations behave in the interfacial or seldedge regions of a thin film in comparison to the bulk.^{32,33} In

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3 such regard, Akin et al. have studied the electron-promoted desorption (EPD) of molecular
4 products from multilayer films of amorphous solid water (ASW) capped with sub-monolayer
5 quantities of CH₃OH at 50 K.³⁴ They have shown that the EIC in H₂O films is quenched by
6 the CH₃OH adlayers consistent with reactions occurring at the ASW/vacuum interface rather
7 than in the bulk. In this context, we have previously studied C₆H₆ desorption from H₂O,
8 CH₃OH and CH₃CH₂OCH₂CH₃ surfaces when irradiated with 250 eV electrons^{35,36} These
9 systems were chosen in order to understand the role of hydrogen bonding in transporting
10 electronic excitation within the solid state to the vacuum interface promoting physicochem-
11 ical change. In essence, we have reduced the degree of hydrogen bonding in the substrate
12 film and possibly between C₆H₆ and the substrate by substituting the hydrogen atom (H)
13 for an alkyl group, while potentially retaining the electronic excited states localised around
14 the O-atom that might ultimately lead to efficient electron promoted desorption (EPD) of
15 C₆H₆ from solid H₂O. This is not observed for the organic-based substrates (CH₃OH and
16 CH₃CH₂OCH₂CH₃), where EPD is a minor process.
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32 This leads us to ask what other processes are favoured over C₆H₆ desorption? How do
33 these processes relate to the different chemical nature of the three binary ices? In order
34 to assess these open questions, we present electron irradiation experiments of binary ices
35 comprising sub-monolayer quantities of C₆H₆ on top of H₂O/CH₃OH/CH₃CH₂OCH₂CH₃
36 and compare EPD versus our preliminary observations on electron-induced H₂ formation.
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45 Experimental

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48 The experiments discussed here were performed in a stainless steel UHV chamber with a base
49 pressure in the chamber of $2 < 10^{-10}$ Torr at room temperature as it has been described in
50 detail elsewhere.^{37,38} The substrate is a polished stainless steel disk cooled by thermal contact
51 with a liquid nitrogen reservoir giving a base temperature of 109 ± 2 K. The substrate was
52 resistively heated up to 600 K for 15 minutes to remove volatile contaminants before cooling
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prior to conducting experiments each day.

Layered ices were obtained by sequential background deposition using two independent manifolds for C₆H₆ (Fluka 99.5% pure), and for de-ionised H₂O, CH₃OH (Sigma-Aldrich, HPLC grade 99.9% pure), or CH₃CH₂OCH₂CH₃ (Sigma-Aldrich, Chromasolv grade 99.9% pure). All the chemicals were stored in separate glass vials and were further purified by several freeze-pump-thaw cycles before use. Exposure is reported in Langmuir (1L = 10⁻⁶ Torr s). Film thickness, *d*, can be estimated from (Eq. 1):

$$d = \frac{SPt}{\sqrt{2\pi mk_B T}} \frac{1}{\rho_s} = \frac{Z_W t}{\rho_s} \quad (1)$$

where *S* is the sticking coefficient assumed to be 1, *P* is the ion gauge pressure reading corrected for using appropriate relative sensitivities,^{36,39-42} *t* is the time of exposure, *k_B* is the Boltzmann constant, *T* is the temperature for the dosed molecules, *Z_W* is the bombardment rate (the incident flux), and *m* is the molecular mass. The molecular volume density, *ρ_s*, was assumed to be 2.74 × 10²² molecule cm⁻³, 1.91 × 10²² molecule cm⁻³, 5.80 × 10²¹ molecule cm⁻³ and 8.57 × 10²¹ molecule cm⁻³ for H₂O, CH₃OH, CH₃CH₂OCH₂CH₃^a, and C₆H₆ respectively.⁴³⁻⁴⁸

Desorption of molecular species during electron irradiation at 250 eV was followed by a crossed-beam source, quadrupole mass spectrometer (VG Microtech PC300D, further modified by European Spectrometry Systems) with a homemade line-of-sight tube facing the front of the sample. Sample irradiation was performed using an electron gun (Kimball Physics, ELG-2) incident at ca. 30° with respect to the substrate normal and over an area of 1 mm². The resulting average electron flux was (9 ± 2) × 10¹³ electron cm⁻² s⁻¹. Our previous work on the same ices,³⁶ consistent with the experimental conditions reported herein, showed that in all the systems investigated, the solid films have an overall thickness (> 12 nm) greater than the calculated electron maximum penetration depth (7-9 nm).

^aDensity of the liquid phase, Sigma-Aldrich

Results and discussion

The upper panels of Figure 1 report the electron-promoted desorption (EPD) of C_6H_6 from solid H_2O , CH_3OH and $CH_3CH_2OCH_2CH_3$ surfaces.

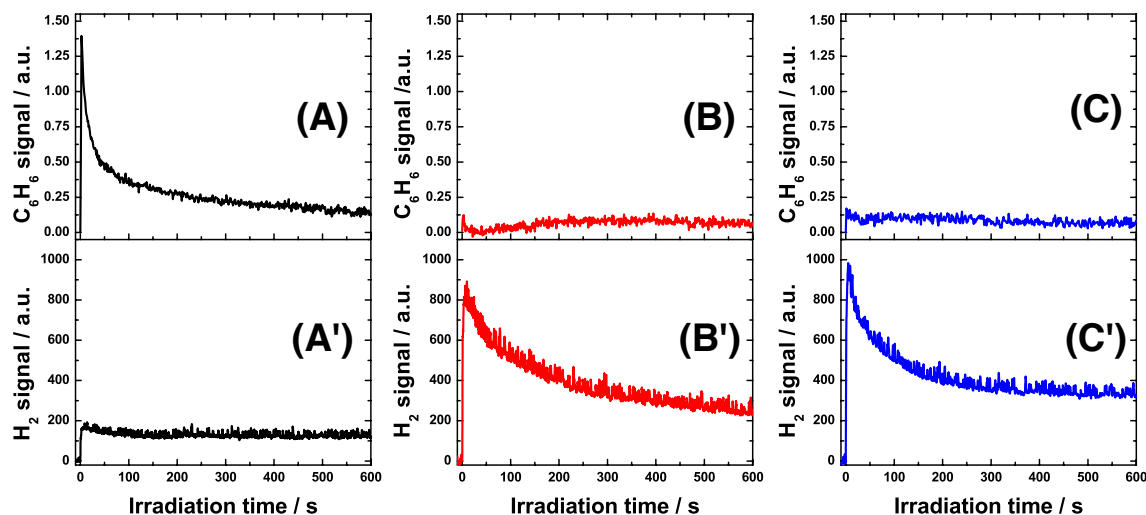


Figure 1: Upper panels: C_6H_6 EPD signal obtained for 5 L (0.2 nm thick in average) of C_6H_6 on a thick ice of ASW, in black (A), of CH_3OH in red (B), and of $CH_3CH_2OCH_2CH_3$, in blue (C). Irradiation starts at $t=0$ s with 250 eV electrons. Lower panels: H_2 formation detected obtained during irradiation of 1 L of C_6H_6 on a thick ice of ASW (150 L; 18 nm) in black (A'), of CH_3OH (250 L; 19 nm) in red (B'), and of $CH_3CH_2OCH_2CH_3$ (500 L; 30 nm) in blue (C'). Irradiation starts at $t=0$ s with 250 eV electrons. The intensities have been scaled by the same factor used for the plots in the upper panels for ease of comparison

As discussed elsewhere,^{35,36,49} these results indicate that non-thermal desorption of the C_6H_6 adsorbate is not significant from the CH_3OH and $CH_3CH_2OCH_2CH_3$ substrates, in contrast to H_2O . It follows that the energy deposited during the irradiation with 250 eV electrons is directed towards other, perhaps more chemical, outcomes. In fact, we noticed that, as soon as the irradiation began, the base pressure inside the chamber increased almost an order of magnitude for a few minutes. In comparison, the base pressure remained almost unchanged while irradiating the C_6H_6 /ASW system or relatively thick films of C_6H_6 (*e.g.* 50 L) regardless the substrate (data not shown). This observation is incompatible with EPD of C_6H_6 , given the low signal-to-noise ratio of the data (Figure 1, panels B and C), and points unequivocally towards different processes occurring on and in CH_3OH and

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4 CH₃CH₂OCH₂CH₃ ices. We would like to stress that a detailed understanding of the reactive
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6 processes involved is beyond the scope of this letter. Simply, we wish to address the following
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8 questions: what is the dominant process occurring upon irradiation of C₆H₆/CH₃OH, and
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10 C₆H₆/CH₃CH₂OCH₂CH₃? Furthermore, if this process is also observable for C₆H₆/ASW,
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12 how does it relate to EPD of C₆H₆?

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14 Preliminary experiments of controlled and slow sublimation of the irradiated ices are
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16 consistent with the detection of complex organic molecules (COMs) as previously identified
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18 by Kaiser and co-workers.^{15,16} These species are likely to be formed also during the irradiation
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20 of CH₃CH₂OCH₂CH₃ films along with many other products given the high reactivity of
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22 ethers. The numerous studies on non-thermal reactions in condensed phases stimulated by
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24 charged particles and energetic photons, particularly those on solid CH₄^{50,51} and H₂O,^{8,14,52}
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26 provide us with the means to readily identify molecular hydrogen (H₂) formation-desorption
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28 as the main process which satisfies two essential requirements: 1) it is relevant to the three
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30 investigated systems; 2) it is in common for all of the binary ices reported in this work.

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32 Therefore, we have repeated the three key experiments in Figure 1 and performed 250
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34 eV electron irradiation experiments on binary layered systems comprised of 1 L of C₆H₆
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36 adsorbed on thick ices of ASW, CH₃OH or CH₃CH₂OCH₂CH₃; but this time the aim was
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38 to observe volatile reaction products, particularly H₂ which is formed in large quantities in
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40 all the investigated systems. The lower panels of Figure 1 displays the EIC curves obtained
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42 by plotting the mass spectrometer ion signal at $\frac{m}{z} = 2$ as a function of irradiation time
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44 for C₆H₆/ASW, C₆H₆/CH₃OH and C₆H₆/CH₃CH₂OCH₂CH₃. The most striking aspect
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46 is that the average intensity of the recorded traces is several orders of magnitude larger
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48 than the intensity of the EPD curves. This is particularly evident for C₆H₆/CH₃OH and
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50 C₆H₆/CH₃CH₂OCH₂CH₃ where non-thermal desorption of the adsorbed C₆H₆ is negligible.

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52 The moment irradiation begins, a prompt rise in the recorded traces is noted. The
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54 increase in H₂ signal intensity is larger for CH₃OH and CH₃CH₂OCH₂CH₃ ices and clearly
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56 smaller for ASW in a manner consistent with the qualitative observations on the change in
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the chamber base pressure. Furthermore, it is noticeable from Figure 2 that the curve C'

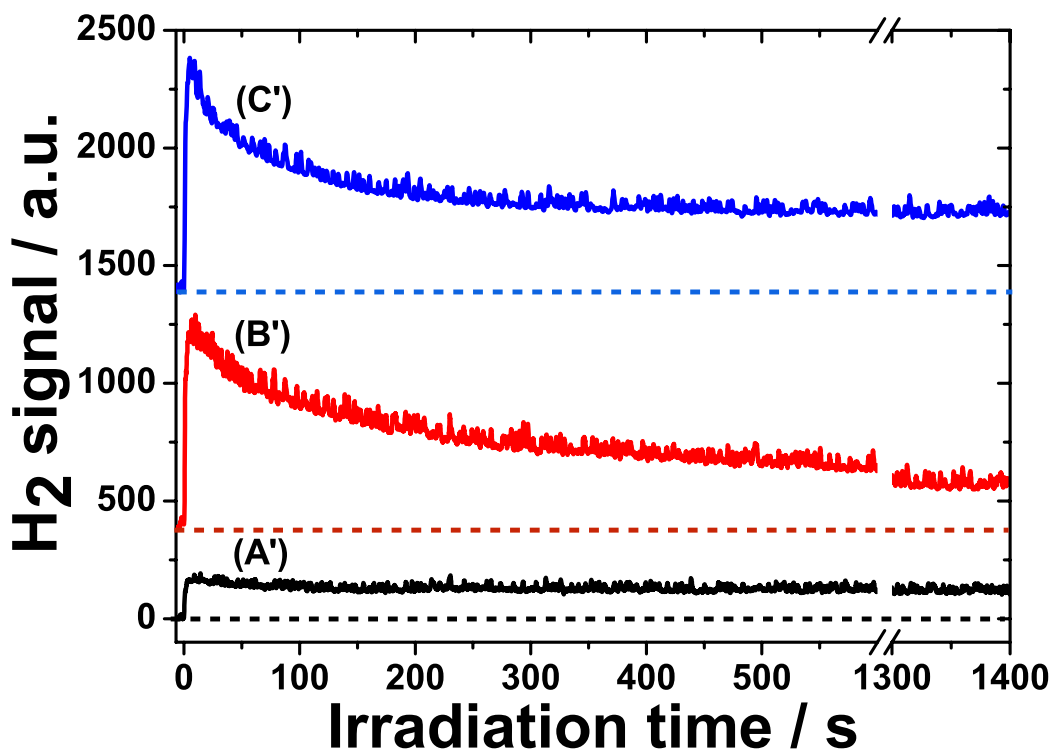


Figure 2: H₂ formation detected obtained during irradiation of 1 L of C₆H₆ on a thick ice of (A') ASW in black (150 L), (B') CH₃OH in red (250 L), and (C') CH₃CH₂OCH₂CH₃ in blue (500 L). These are the same experiments shown in Figure 1, but over a longer time scale. Irradiation starts at t=0 s with 250 eV electrons. EIC traces have been offset for clarity with the dashed lines showing the zero lines for each curve. The intensities have been scaled by the same factor used in Figure 1 for ease of comparison.

reaches a plateau around 400 s, and will eventually decrease to zero at very long time of exposure to the beam. In contrast, curve B' slowly but continuously decays during the whole experiment. This difference between the EIC traces can be primarily linked to the higher density of C-H bonds per molecule in the irradiated volume, which can be broken releasing H atoms. A complementary argument would be that a thicker CH₃CH₂OCH₂CH₃ film (*ca.* 30 nm) will result in a long-lived steady state of H₂ formation compared to the thinner CH₃OH ice (*ca.* 19 nm). More studies are required to understand the different decay behaviour of C' and B' at long irradiation times (*e.g.* > 1000 s). Pragmatically, it is clear from curves C' and B' in Figure 2 that there is still a significant amount of H₂ desorption above 1000 s,

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4 hence indicating the presence of an icy film not fully depleted in the irradiation area.

5 Integrating each EIC curve up to 600 s (see Figure 1) allows estimates of the gross yield of
6 H₂ to be made, namely $\Phi_{600}(\text{H}_2\text{O})$, $\Phi_{600}(\text{CH}_3\text{OH})$, and $\Phi_{600}(\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3)$, and permits
7 a semi-quantitative comparison among the three systems. The ratio between the area ob-
8 tained for curves B' and A', $\Phi_{600}(\text{CH}_3\text{OH})/\Phi_{600}(\text{H}_2\text{O})$, gives a value of 2.9 ± 0.3 , while taking
9 into account the H₂ formed in C₆H₆/CH₃CH₂OCH₂CH₃ (curve A') with respect to the anal-
10 ogous system with ASW (curve A'), we obtain a ratio $\Phi_{600}(\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3)/\Phi_{600}(\text{H}_2\text{O})$
11 of 3.2 ± 0.4 . In conclusion, the EIC trace labelled A' provides evidence of less H₂ formation
12 while irradiating C₆H₆/H₂O with 250 eV electrons, and appears to be roughly constant in
13 time after 100 s. In contrast, C' and B' display a significant increase of the signal as soon as
14 the electron beam is turned on, and their exponential decay is still noticeable after 100 s.
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26 In the series experiments represented by Figure 1, irradiation is performed on binary
27 layered ices with 1 L of C₆H₆ as adlayer in order to allow direct comparison with the EPD
28 curves.³⁶ For now we cannot rule out the possibility that the observed EIC traces contain
29 a contribution from both the underlying substrate and from the C₆H₆ adlayer. However,
30 direct dehydrogenation of C₆H₆ can be discarded because we noted a negligible variation
31 of the base pressure (data not shown) during the irradiation of large C₆H₆ doses (*e.g.* >
32 20 L). Moreover, if substrate-mediated dehydrogenation of C₆H₆ were to be important we
33 would expect to see a noticeably more intense signal for the C' trace than for B' curve
34 in the first moments of irradiation because of the larger contact area at the interface for
35 C₆H₆/CH₃CH₂OCH₂CH₃ than for C₆H₆/CH₃OH.⁵³ Therefore, we think that the EIC signal
36 displayed in Figure 1 refers to H₂ production mainly, if not almost exclusively, from the H₂O,
37 CH₃OH and CH₃CH₂OCH₂CH₃ films.
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50 The origins of H₂ from ASW is well-described in our recent publications³⁵ and rests
51 on the extensive work of Kimmel and co-workers.⁵⁴ Briefly, electronic excitations of the O-
52 atom lying in the 8.7-14.5 eV range^{55,56} are compatible with the energy distribution of the
53 secondary electrons produced during the irradiation and result in the formation of excitons in
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3 the ASW film. These long-lived excitons migrate to the C₆H₆ (and vacuum) interface *via* the
4 hydrogen-bonding network in the solid H₂O resulting in electronically excited H₂O molecules.
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6 These, at the C₆H₆ interface, (i) could promote H₂O desorption or bond cleavage leading
7 to H₂ formation and desorption or (ii) could transfer the excitation to the hydrogen-bonded
8 aromatic ring enabling its desorption.
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14 In contrast, the replacement of the H-atoms in the H₂O molecule with alkyl groups, which
15 contain C-atom(s), has a two-fold impact. The degree of H-bonding is significantly reduced
16 in the solid underlying the C₆H₆ which will hinder the excitation transfer from the bulk to
17 the interfaces where desorption can be promoted. The presence the C-atom(s) introduces
18 another electron-rich centre in the molecule that lowers the ionisation potential^{35,36,57,58} by
19 adding an additional spectrum of electronic excitations. This might favour other processes
20 over desorption, channelling the secondary electronic excitations towards reactive routes.
21 This is consistent with 5 keV electron irradiation experiments of pure methane (CH₄) ices at
22 10 K which clearly show that the predominant reaction pathway is the homolytic cleavage of
23 the C-H bond.⁵⁰ The H atoms, free to diffuse in the ice matrix, will subsequently combine to
24 form H₂ which then desorbs. Therefore, the EIC curves in Figure 1, labelled as C' and B' are
25 consistent with the idea that electrons will mainly promote dehydrogenation over physical
26 processes such as EPD for organic-based ices.
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40 It is important to stress that the observed EIC traces are the result of several competitive
41 processes taking place in parallel during the electron irradiation. Hence, their kinetics will
42 be identical. Further work is clearly required to address more fully the nature of the gas
43 phase products from energetic processing of especially ices rich in organic material and to
44 investigate the effect of the ice temperature on the observed processes.
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Conclusions, implications and outlooks

EPD of C_6H_6 from solid H_2O , CH_3OH and $CH_3CH_2OCH_2CH_3$ surfaces and the formation of H_2 in systems comprising a C_6H_6 adlayer on solid H_2O , CH_3OH and $CH_3CH_2OCH_2CH_3$ have been investigated. We have demonstrated that the C_6H_6 EPD channel is significantly decreased while the H_2 EIC channel is largely enhanced when ices of carbon-bearing molecules are employed during irradiation with 250 eV electrons. The observation that C_6H_6 desorption is less intense while H_2 formation is enhanced in the absence of H_2O is rather noticeable even given the similarities between the C_6H_6/CH_3OH and C_6H_6/ASW ices.⁵³ H_2 formation and desorption is a common process to the three systems but it is clearly more significant for organic-based ices than in ASW. Ultimately, this striking difference can be addressed by considering the presence of excitations localised around the C-atom *versus* those involving the O-atom with the former favouring reactive routes. Future studies will investigate the nature of the dominant processes occurring during the electron irradiation of organic molecules and how these compare to solid H_2O . This work (i) emphasizes the need to fully understand the distribution of products (branching ratios) of photon- and charged-particle-induced physics and chemistry, (ii) and highlights the importance of looking at the nature of the species leaving the surface and not simply at what remains on and in the ice if we are to incorporate these processes into astrochemical models.

Consistent with the radiolysis of liquids,⁵⁹ if it is true that H/H_2 production is likely to be a major process in photolysis and radiolysis of both simple (*e.g.* water-rich) and complex ices (*e.g.* containing COMs), then it is tempting to question to what extent the formation and desorption of H/H_2 can contribute to hydrogen recycling in various environments. For example, early in dense cloud formation, gaseous H is initially depleted on to grains that catalyse H_2O , NH_3 , and CH_4 formation. Irradiation of these molecules as icy mantles accrue would promote EIC which on one hand yields radicals and enriches the ice in COMs, but on the other seems to return H_2 to the gas phase, leaving residues that will potentially become increasingly unsaturated and with time probably aromatic. Further experiments, at

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3 temperatures as low as 10 K, are required to reinforce these intriguing speculations.
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7 8 Acknowledgement 9

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16 contribution to this work has been done as a private venture and not in the author's capacity
17 as an affiliate of the Jet Propulsion Laboratory, California Institute of Technology.
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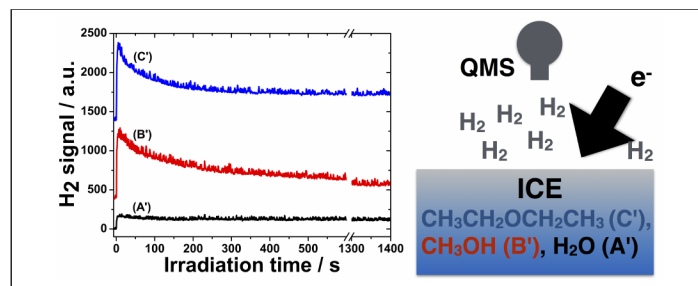
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