Electronic Supplementary Information (ESI):

Electrons, Excitons and Hydrogen Bonding: Electron-promoted Desorption from Molecular Ice Surfaces †

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1 CASINO calculations

The electron trajectories were simulated using the CASINO code^{1,2} for an electron beam at 250 eV, incident at 30° consistent with the experimental conditions. Calculations were performed by simulating a number of electrons which was equivalent to the beam fluence (electron per unit of surface) in 700 s multiplied by the beam area. However, using both the actual area of the electron beam spot at the surface (1 mm²) and the corresponding average experimental electron flux $(9 \times 10^{13} \text{ electron cm}^{-2} \text{ s}^{-1})$ would be computationally too expensive. Therefore, we have run the calculations employing a smaller area, having radius of 3 nm, that significantly lowers the total number of trajectories calculated, while being consistent with the experimental conditions at least locally, over a surface area of ca. 28 nm². It is important to stress that preliminary benchmark calculations show that the distribution of electrons within the film as a function of the ices depth appear to be independent on the beam area. In fact, the choice of simulating a specific number of electrons is purely arbitrary and has the only advantage of allowing a visualisation of the trajectories in a small section of the film and not scattered over macroscopic lengths.

Solid densities were assumed to be: 2.74×10^{22} molecule cm⁻³ for H₂O,³⁻⁶ 1.91×10^{22} molecule cm⁻³ for CH₃OH,⁷ 5.80×10^{21} molecule cm⁻³ for CH₃CH₂OCH₂CH₃,ⁱ and 8.57×10^{21} molecule cm⁻³ for C₆H₆.⁸ Film thickness was estimated employing eqn (1) as reported in the main article. The key conclusion is that for an electron energy of 250 eV all the systems investigated have an overall larger film thickness than the calculated maximum electron penetration depth.

Figure S1 shows the distributions of electrons within the film as a function of the maximum penetration depth corresponding to those ices employed for the experiments in **Figure 2** of the main article. The results clearly show that all of the incident electrons are stopped within the uppermost 7 - 9 nm of the ices. This is less than the thickness of the thinnest irradiated ice film (> 12 nm). The same conclusion is confirmed by the curves relative to the remaining EPD experiments

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Figure S1: Distributions of primary electrons within the film as a function of the penetration depth during the irradiation with 250 eV electrons of binary-layered ices. These ices are comprised of 5 L of C_6H_6 on solid: (A) $CH_3CH_2OCH_2CH_3$, 500 L, (B) CH_3OH , 200 L, and (C) H_2O , 100 L. The estimated thickness for the three ices is (A) 30.37 nm, (B) 15.37, and (C) 12.17 nm.

(Figure 3 of the main article), which are reported in Figure S2. It is noticeable that the change in thickness due the C_6H_6 adlayer does not significantly affect the distributions for C_6H_6/CH_3OH , and all the curves overlap nicely to one another (see Figure S2a). In contrast, given the higher



Figure S2: Normalised distributions of primary electrons as a function of the penetration depth during the irradiation with 250 eV electrons of binary, layered films comprised of: (a) C_6H_6 on 200 L of solid CH_3OH , or (b) C_6H_6 on 500 L of solid $CH_3CH_2OCH_2CH_3$. C_6H_6 exposures are: 0 L in green, 1 L in red, 5 L in black, 10 L in blue, 20 L in yellow, and 50 L in brown.

density assumed for C_6H_6 (1.11 g cm⁻³) with respect to solid CH₃CH₂OCH₂CH₃ (0.714 g cm⁻³), the transition from one species to another is marked by a double peak structure, as one can see in the plot corresponding to 50 L of C_6H_6 on CH₃CH₂OCH₂CH₃ (**Figure S2b**). In this case, the more C_6H_6 is dosed, the sooner the primary electrons are stopped. This trend is only slightly noticeable for C_6H_6/CH_3OH since the density used for the two solids in the layered ices are similar (1.02 g cm⁻³ for CH₃OH).

We would like to stress that the sources of error that are present in the models employed for the calculations are numerous. For instance, film erosion due to sputtering and electron-induced chemical reactions are not taken into account and ices are unlikely to be perfectly flat. Therefore, these plots should not be regarded as "exact" nor accurate, but only as sensible estimates that allow us to define upper limits for the maximum penetration depth of the primary electrons.

2 Effect of the substrate

In order to test whether the substrate has any effect on the observed EPD of C_6H_6 , we have compared two sets of experiments. In one case 250 L of CH₃OH were deposited directly on the substrate, in the other case a spacer of 100 L of ASW was added between the substrate disk and 200 L of solid CH₃OH. Then these ices were exposed to different doses of C_6H_6 (1 L, 5 L, 10 L, 20 L, and 50 L). The resulting binary and tertiary layered ices were subsequently irradiated with 250 eV electrons. The data show identical C_6H_6 EPD curves for a fixed C_6H_6 dose regardless of the presence of the ASW spacer and regardless of the CH₃OH film thickness. This strongly suggests that using 250 L of CH₃OH guarantees no effect due to the substrate in our experiments.

Concerning the ices containing solid $CH_3CH_2OCH_2CH_3$ it was decided to employ relatively large doses of $CH_3CH_2OCH_2CH_3$ (500 L), as for the case of CH_3OH , in order to 1) neglect the effect of the substrate on the EPD measurements, 2) and in order to guarantee a film which is thick enough (30.2 nm) to minimise the accretion of non-volatiles due to the electron-induced chemistry at the disk interface, which appears to be enhanced for C-rich ices.

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