Photocatalytic reactions at the graphite/ice interface

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We have studied the photodissociation of water molecules at the ice/graphite interface in the presence of submonolayer amounts of potassium. The ice films were grown at cryogenic temperatures and ultrahigh vacuum conditions. They are transparent for 240–900 nm photons, but the strong light absorption in the uppermost layers of the graphite substrate generates energetic charge carriers that may drive photoreactions at the interface. Similar schemes have been demonstrated and investigated before in the monolayer regime, without an ice layer (D. Chakarov, M. Gleeson and B. Kasemo, *J. Chem. Phys.*, 2001, **115**, 9477). Here, using ice films of tens of monolayer thickness and with different morphologies, we have investigated the confinement effects due to the ice layer, and the ice permeability for reaction products.

Introduction

Studies of photon interaction with systems made up of water adsorbed on surfaces with or without coadsorbates is of potential interest for diverse areas, such as atmospheric and interstellar chemistry or for photo-electrochemical (solar) H_2 production. The latter is considered a promising method of hydrogen generation as a renewable energy source.[2] In principle, a significant fraction of visible light has enough energy to split H_2O into hydrogen and oxygen. However, water itself is transparent in the visible and does not absorb this energy. The combination of a light harvesting system and a H_2O splitting system is thus necessary. Usually, wide-band semiconductors, such as TiO_2 (unfortunately having limited light absorption in the visible) have been tried for this purpose.[3] We are exploring a different substrate, namely graphite covered with small amounts of alkali atoms, not primarily because it might be an interesting system for H_2 production, but because it is an interesting model system for photoreactions at surfaces. The electronic structure of this substrate has a semi-metallic character, allowing photo-excitation of electron–hole pairs at wavelengths where such transitions are forbidden in pure water and ice. Attachment of photo-generated electrons from graphite to defects in amorphous ice adlayers has been demonstrated to induce a re-ordering of the surface ice film, from amorphous to more crystalline.[4] In the case of H_2O coadsorption with alkali metals on graphite, a hot-photoelectron attachment (to the K 4*s* derived LUMO level) has been invoked by two of us to explain the photo induced splitting of H_2O and subsequent reactions. Here hydrogen was the main product, with a number of minority products (CH_4, CO). This scheme can be seen either as a photoinduced hydrogen production scheme or a photochemical carbon gasification scheme.[1]

Depending on the substrate's nature and temperature and by choosing the deposition rate it is possible to grow ice layers with either (poly)crystalline or amorphous structure,[5] and it is also possible to influence the morphology (*e.g.*, dense or porous films). These forms of deposited ice are optically transparent for near UV/visible photons, but have different permeability and trapping properties for hydrogen, oxygen and carbon oxides.[6] We use these differences to construct a model system with different degrees of confinement of the reaction products as they are formed, as schematically shown in Fig. 1. The aim is to explore the confinement effects of ice films with a different structure and compare the results with previous data on the K + H_2O/graphite system but without a confining ice film.

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Experimental

The experiments were performed in home-built, stainless steel UHV chambers, turbo pumped down to a base pressure in the low 10^{-10} mbar range. Details on the experimental chambers have been published elsewhere.[7,8] For detection and direct monitoring of the photodesorbing products we used quadrupole mass spectrometers (MS, Balzers and Hiden Analytical). The ice films were deposited using directed, water vapor inlets in the form of a quartz tube, held at RT, with dimensions and distance from the sample allowing deposition of an ice film of uniform coverage/thickness. Pure water was obtained by repeated pumping and heating cycles on a container with deionized and degassed MilliQ© water. The coverage and desorption rates were calibrated by using background exposures at a given water pressure and assuming sticking coefficient of one. One monolayer (ML) of H_2O ice is defined as 1.15×10^{15} molecules cm^{-2} (corresponding to the standard definition of a H_2O bilayer) and results in an exposure of 2.4 Langmuir (L) (1 L = 10^{-6} Torr). Calibration of H_2O coverages was obtained through comparison of the thermal desorption signals from films obtained by background and directional exposures. Potassium was deposited from a SAES getter source at a typical rate of 0.025 ML s^{-1} (1 ML, or $\theta = 1$ corresponds to 5.2×10^{14} atoms cm^{-2}).[9] Potassium is known to adsorb in a 2D overlayer on graphite at $\theta \leq 1$. At $\theta < 0.3$,

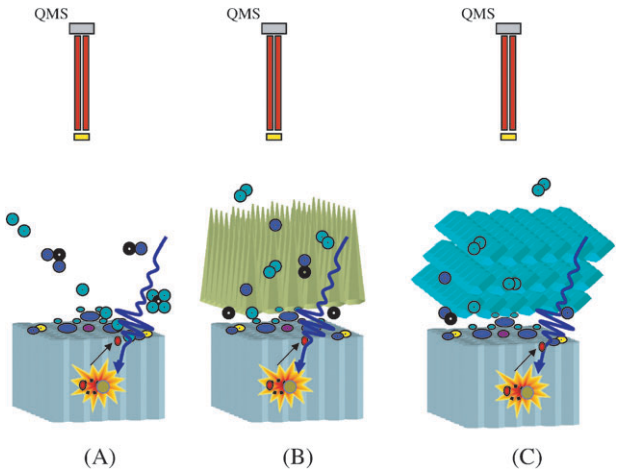

Fig. 1 Cartoon presentation of the experimental systems. In case (A) water and potassium (purple) are coadsorbed on the graphite (0001) plane and irradiated with light. The photon absorption and excitation of electron–hole pairs take place in graphite, at or close to the interface. Hot electrons with sufficient energy can attach to the K 4*s* derived LUMO level of the hydrated K^+–$(H_2O)_n$ adsorbate complex, and thereby induce the K + H_2O + $C_{substrate}$ reactions, forming volatile H_2, CO and CO_2. The reaction products and intermediates are free to leave the substrate, if they posses enough energy to overcome the desorption barrier. In case (B) the same catalytically active species are confined at the graphite/ice interface by an amorphous ice film (beige spikes). The reaction products are spatially restricted, but partly mobile trough voids and defects in the ice film. In case (C) the ice film is (poly)crystalline (bluish green) with expected further restriction on the products mobility and probability to desorb. Molecules in the figure are made up of carbon (black), hydrogen (green), and oxygen (blue).

which were the coverage range used here, potassium adatoms exist in a diluted, partly ionized single phase, with substantial charge transfer to the substrate, leading to work function decrease by 2.1 eV.[9] Coadsorption of the K adatoms/ions with water leads to partial depolarization and detachment of the K adatoms from the surface, as deduced from calculations.[10] This K + nH_2O complex has many similarities with a hydrated ion.[10,11]

The graphite sample was a 12 × 6 × 1 mm piece of highly oriented pyrolytic graphite (HOPG) grade XYA (Union Carbide Co), exposing the basal (0001) plane. It could be resistively heated up to 1300 K and subsequently cooled down to ~40 or to ~95 K (within ~15 min) by contact with the cold finger of a closed cycle He cryostat or circulating liquid nitrogen through the holder. For details on the graphite cleaning and submonolayer H_2O adsorption on graphite, see ref. 12.

Irradiation was performed in either pulsed or continuous (cw) mode. As a photon source we used a Nd : YAG laser pumped OPO (Continuum) system, tunable in the range 225–705 nm and providing ~5 ns long pulses, or a short arc lamp system (PI) in combination with a monochromator or band pass filters. The photon fluxes on the sample, using both sources, were kept well below the threshold intensities for measurable thermal effects (see ref. 13 for a discussion of this point).

Results and discussion

Fig. 2 shows quadrupole mass spectrometer traces of several masses during irradiation of a sample covered with 0.25 ML

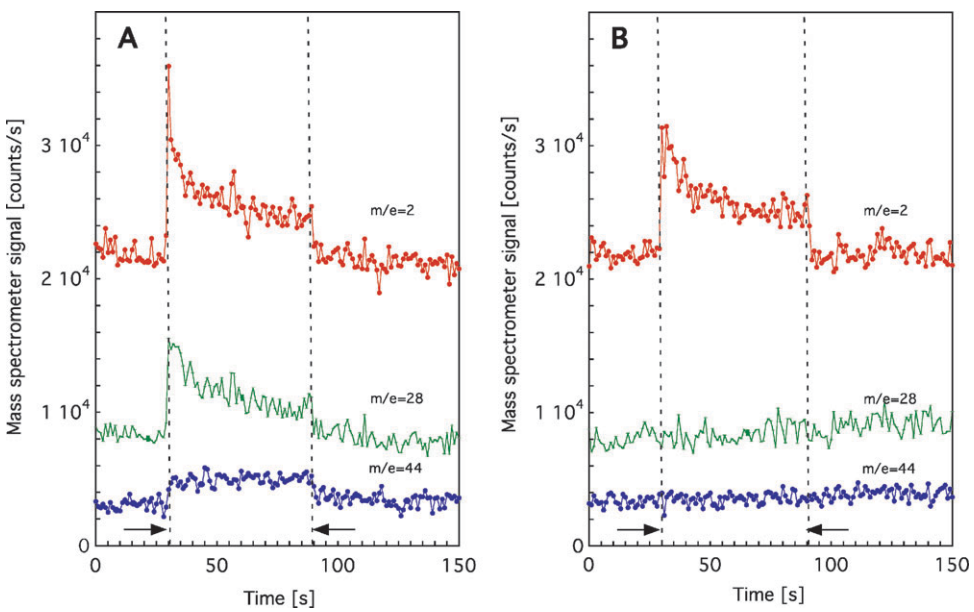

Fig. 2 Mass spectrometer traces of the photodesorbing products, H_2, CO, and CO_2 from K/graphite surface covered with multilayers of ice. The initial coverages and irradiation conditions for the systems on panel A and B are the same, except for the annealing procedure performed before the irradiation. The arrows and the dashed lines indicate the irradiation period. The figure show that crystallization of the ice through annealing led to hindered escape of reaction products other than H_2 during irradiation, which can permeate the crystalline ice. Molecular transport through the amorphous ice is possible because of high concentration of defects and porosity.

potassium and an approximately 38 ML thick H_2O "ice-lid" on top. The sample was prepared by first depositing potassium and then exposing the surface to water vapor for ice growth. (At this low K coverage, K does not react with H_2O to form KOH, but forms instead hydrated ions of K with a water shell.[10,14] The irradiation was performed with 3.5 eV (355 nm) photons in a 10 Hz train of ~5 ns pulses for 60 s. The laser beam was attenuated to 1.8 mJ cm^{-2} per pulse and defocused in order to illuminate the whole sample. The irradiation geometry was fixed with the beam hitting the sample at 30° with respect to the surface normal. The sample is placed in a stagnation chamber in the front of the mass spectrometer in order to collect most of the desorbing species.

The coadsorption of K and water on the graphite surface, at sufficiently low coverage to have K in the ionic state, leads, as mentioned above, to formation of hydration shells around the ionic K at the surface.[10,11] The shells, 2D at low water coverage with three to four molecules sitting around the K atom, evolve into different 3D structures as the size/number of water molecules increases. The water molecules in the shell are strongly perturbed, as evident from the vibrational spectra.[11] The mechanistic picture is that these molecules dissociate/react via resonance electron attachment to the hydrated K^+ ion as discussed in ref. 11 (Fig. 3). Note that these hydrated potassium ions are in a highly metastable state, since the thermodynamic driving force to form KOH is very strong. (If the coverage of potassium exceeds that for the ionic state, direct reaction of potassium to KOH and KO_x occurs.)[15] Also note that alkali metals lead to substantial decrease of the work function, leading to an increase in the fraction of hot (photo)-electrons that can reach the LUMO orbitals of surface adsorbates.[16]

The two panels of Fig. 2 illustrate the main finding of this study: for the same adlayer composition (K + H_2O) and irradiation regime, different photodesorbing products are observed, depending on the properties of the ice-lid. The new findings can be summarized as follow: for ice films with a polycrystalline structure and thicker than ~35 ML only hydrogen diffuses from the interface into vacuum at the photoreaction substrate temperature of 92 K, while the CO and CO_2 remain trapped under or in the ice bulk. The release of the latter products takes place at elevated temperatures, *e.g.* during a TPD ramp. If the ice film is instead amorphous and porous (which is the case when it is deposited at sufficiently low temperatures), desorption of CO_x occurs already at the temperature of 92 K during irradiation.

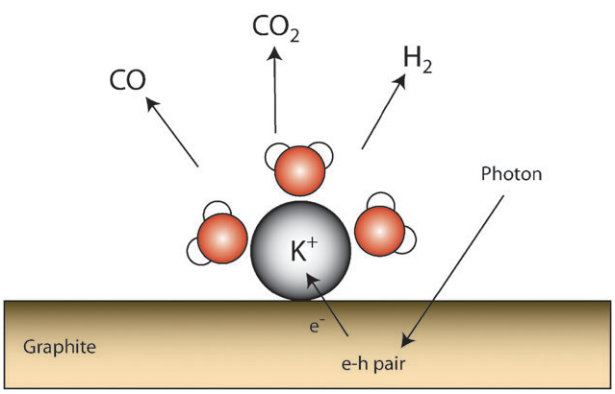

Fig. 3 Mechanistic picture to explain how hot photoexcited electrons in graphite attach to and induce reactions in the hydrated K^+–$(H_2O)_n$ surface complex (from ref. 11).

The spectra in panel **A** are obtained directly after the deposition of the ice film at 92 K on the potassium precovered graphite. This procedure is known to produce ice with a high degree of defects and voids.[5] The irradiation was started at 30 s and terminated at 90 s. In this experiment H_2, CO and CO_2 are seen as desorbing photoreaction products immediately upon irradiation. The $CO:CO_2$ branching ratio is the same compared to what was observed earlier with 1 ML H_2O coadsorbed[1] and no ice film on top. The spectra in panel **B** are from a new potassium and water deposition, but after thermal annealing to 125 K, before the photo-reaction experiment. Referring to previous studies with ice films on different substrates,[17,18] we can conclude that the annealing of the film leads to phase transformation from amorphous to (poly)crystalline ice. The annealing was performed inside the stagnation chamber of the mass spectrometer using a temperature ramp of 1 K s^{-1}. The sample was then kept at 125 K for 3 min and then quickly cooled down to 92 K, where the irradiation was performed. In both cases A and B the strongest signal is associated with hydrogen desorption, as was seen in experiments without an ice lid.[1] Qualitatively, the shapes of the signals resemble those obtained in the latter work. However, the intensities are smaller and no mass 16, previously assigned to methane, was observed. No signals from mass 28 and 44 are seen during the irradiation of the annealed film, in contrast to the case with the un-annealed ice lid or no ice lid.

From these experiments it is clear that only H_2 is able to permeate through the annealed ice layer and desorb during the irradiation, while all other reaction products, such as CO and CO_2, remain trapped. This is confirmed by the post-irradiation TPD spectra. Fig. 4 shows how the CO and CO_2, generated during the irradiation, and trapped under the ice, or in the ice bulk, are released during the temperature ramp. There are two different types of desorption of CO and CO_2 from under the ice film. First, a rapid desorption at the point when amorphous ice crystallize in a 'molecular volcano' event.[6] Secondly, there are molecules desorbing later (at higher temperature) together with the H_2O, possibly coming from molecules trapped inside molecular cages made up by H_2O.

The different formation regions, indicated in Fig. 4 are identified by comparison of spectra obtained without photon irradiation. In brief, we have a low temperature regime where reactions within the hydration shell cause release of H_2, followed by an intermediate T-regime where the main effect is a so-called volcano effect, reported earlier for other systems,[19] and where percolation-like rearrangement and crystallization of the ice layer allow release of already formed products. Note that the rearrangements in the hydrated shell take place at relatively low temperature.

One experimental difficulty with the measurements described here is to detect relatively small amounts of photoreaction products (CO, CO_2) simultaneously with the intense water desorption from multilayers of ice. In an attempt to explore the photon dose dependence and maybe increase the amount of trapped species, we performed the experiments

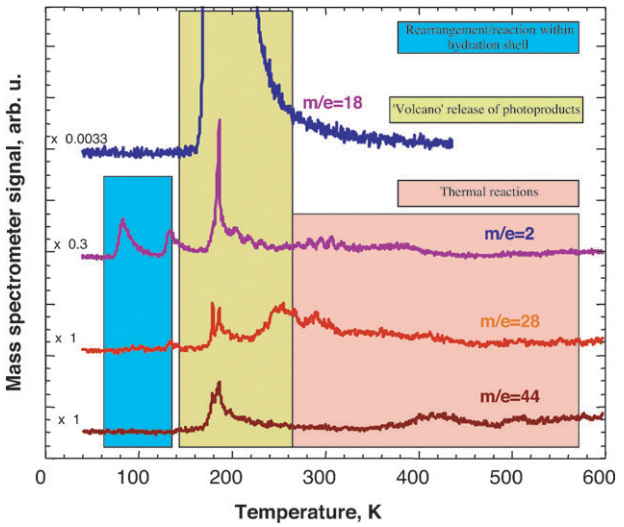

Fig. 4 Thermal desorption spectra from graphite covered with approximately 45 ML of ice coadsorbed with 0.67 ML K at 41 K after cw irradiation with $8.4 \times 10,^{17}$ 289 nm photons. The spectra are obtained with a heating rate of 1 K s^{-1}. CO and CO_2 trapped under ice desorb in two different ways. Firstly, molecules desorb rapidly in a molecular volcano when the amorphous ice crystallizes. After this in the TPD there is desorption of molecules trapped in what is believed to be molecular cages made up of H_2O at the ice–graphite interface and therefore desorb together with the H_2O. The "thermal reactions" region refers to formation and decomposition of KOH.

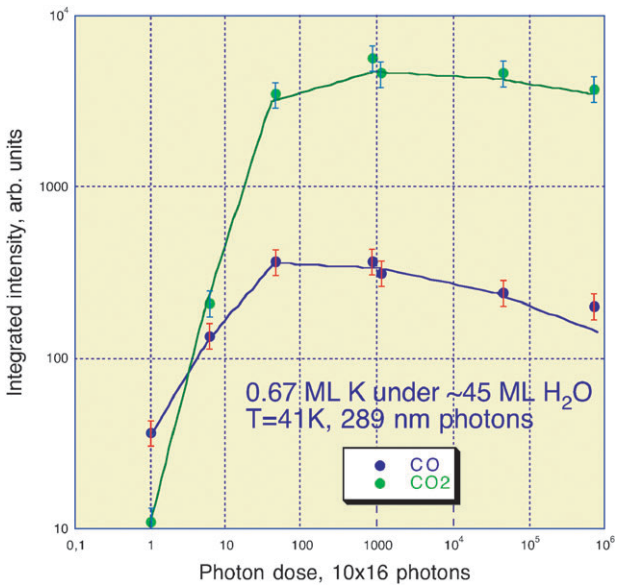

Fig. 5 Photon dose dependence of the amount of accumulated photoreaction products under amorphous ("as deposited") ice film on graphite. The data points are obtained by integration of the respective regions in the TPD spectra similar to those in Fig. 4.

summarized in Fig. 5. Prolonged irradiation of the system leads indeed to an increase in the amount of photogenerated species. However, after irradiation with an accumulated dose of approximately 5×10^{18} photons this amount levels out or even decreases (for CO). With cw irradiation, this dose corresponds to irradiation times longer than 20 min. Similar observations were made with pulsed irradiation. We speculate that the decreased rate of formation of these species (assuming unchanged "leakage" through the ice) is a result of the restricted mobility of the dissociation products implemented by the ice cover.

In conclusion, we have shown that an ice lid on top of a submonolayer coverage of K on graphite, changes the photoreaction behavior of the system, and also depends on the structural state of the ice layer (amorphous or polycrystalline). Our preliminary results on the K/Pt(111) surface confirm this.[20]

Finally, we briefly comment on the possible mechanism behind the formation of photoreaction products from irradiation of the K + $n$$H_2O$ complex. We basically adopt the same picture as used to describe photodesorption of K atoms from submonolayer coverages of potassium on graphite (no H_2O) and generation of photoreaction products from K + $n$$H_2O$ complexes without an ice lid: in the former case hot electrons generated by interband transitions in the graphite substrate have enough energy (above a threshold photon energy) to reach and attach to the 4s derived LUMO level of the adsorbed K ions.[7] In the presence of a water shell the same qualitative picture applies, but now the position of the LUMO orbital is modified by the water. When a photoelectron attaches to the highly metastable K + $n$$H_2O$ complex, it induces a cascade of "downhill"/exothermic reaction steps, the first one most probably being KOH formation, and concomitant hydrogen release (H_2) and reactions with the substrate (CO_x).

Summary

We demonstrated that it is possible to partly hinder the desorption of reaction products generated during photo dissociation of water from a water–alkali coadsorption layer on graphite by covering it with multilayer ice films. While CO and CO_2 were trapped by (poly)crystalline ice, H_2 is able to permeate both amorphous and annealed films. CO and CO_2 were still generated under the ice cover during the irradiation and released later when the ice (re)crystallizes or sublimates. Although not clear, some of the reaction products could have been trapped inside the ice and desorbed later together with the H_2O.

Acknowledgements

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