Photon stimulated ion desorption from polyatomic molecules in the VUV: C_2H_4 - graphite

LETTER TO THE EDITOR

Photon stimulated ion desorption from polyatomic molecules in the VUV: C_2H_4–graphite

J M Coquel†, T Almeida Gasche†‡, J Wilkes†§, C M Friedrich‖, C L A Lamont§, M A MacDonald¶, R E Palmer† and A M C Moutinho††

† Nanoscale Physics Research Laboratory, School of Physics and Space Research, University of Birmingham, Birmingham B15 2TT, UK
‡ Departamento de Química, Instituto Tecnológico e Nuclear, Estrada Nacional 10, 2686 Sacavem Codex, Portugal
§ School of Applied Sciences, University of Huddersfield, Huddersfield HD1 3DH, UK
‖ Cavendish Laboratory, University of Cambridge, Madingley Road, Cambridge CB3 0HE, UK
¶ CLRC, Daresbury Laboratory, Warrington WA4 4AD, UK
†† GIDS, Departamento de Física, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2825 Monte da Caparica, Portugal

Abstract. We have investigated photon stimulated ion desorption from C_2H_4 physisorbed on highly oriented pyrolytic graphite using VUV synchrotron radiation in the energy range 13–40 eV. In contrast with gas phase photodissociation measurements, only H^+ ions are detected. This result is attributed to the image potential barrier to desorption from the surface and the unequal distribution of kinetic energy amongst the molecular photofragments. The yield of desorbed H^+ ions shows a threshold at 20.5 eV and a resonance at 24 eV and appears to be enhanced in the monolayer regime. This behaviour differs significantly from that of the gas phase, and is attributed to selective quenching of excited molecular electronic states on the surface and to chemical reactions between specific molecular dissociated fragments and the substrate.

The study of ethylene adsorption on solid surfaces is of particular interest because of the importance of hydrocarbon adsorption in various heterogeneously catalysed chemical processes [1–3].

In the last few years an increasing number of studies aimed at understanding the photochemistry of adsorbed molecules have been reported, most recently in the VUV region of the spectrum where completely new behaviour has been observed [4–8]. These studies have set out to investigate the mechanisms occurring when small, e.g. diatomic, molecules are adsorbed on surfaces. The work presented in this letter is the first investigation of VUV photodissociation of a polyatomic molecule, ethylene physisorbed on graphite.

The mechanisms that can occur in surface photochemical processes can be divided into 'direct' and 'indirect' processes. In the former, the photon reacts directly with the molecule. In an indirect process, typically driven by photoelectrons, the photons can either be absorbed by the substrate or in the molecular film itself. In both cases electrons are produced, which can react with the adsorbed molecules. The specific mechanisms leading to ion desorption are threefold: dipolar dissociation, dissociative ionization and dissociative attachment [4, 9, 10]. In the case of the C_2H_4 molecule, the probability of direct dipolar dissociation and consequent production of negative ions is quite small in comparison with the other mechanisms [11]. As such, the direct photoion yield is dominated by dissociative ionization which only produces positively charged photofragments.
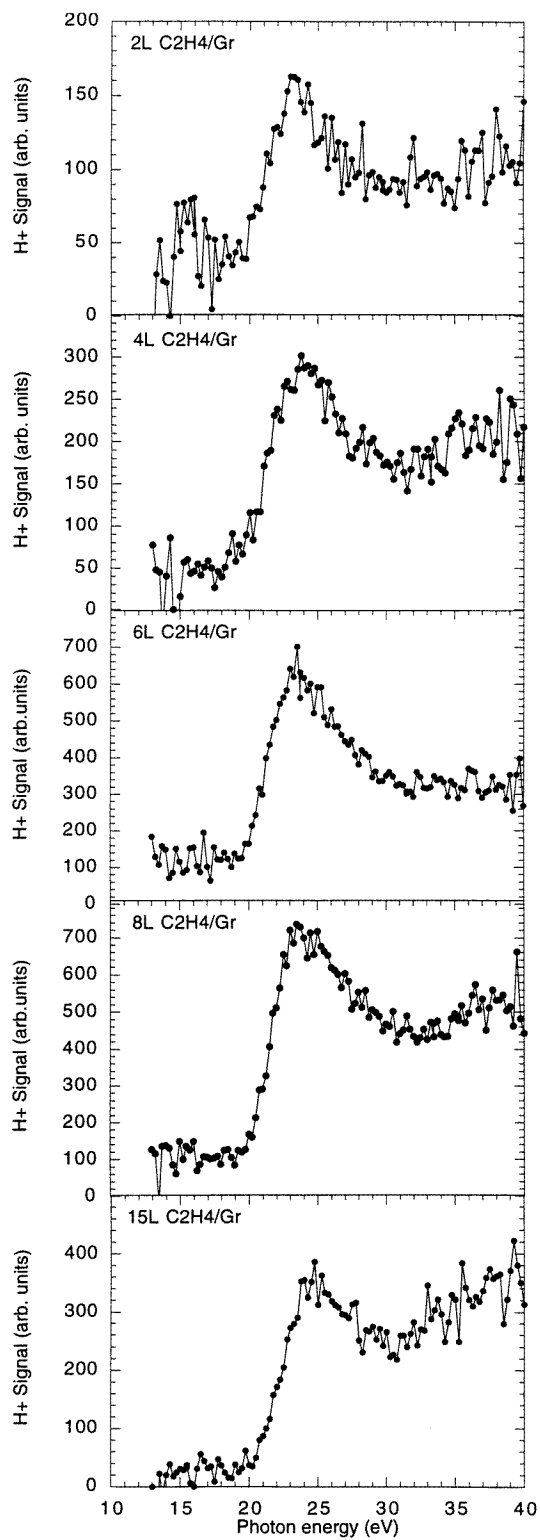
Figure 1. The normalized H^+ ion yield recorded as a function of the photon energy for different coverages of C_2H_4–graphite: 2, 4, 6, 8 and 15 L.

In the gas phase, several different positive ion photofragments are observed from C_2H_4 [11–13]. The predominant ions are $C_2H_4^+$, $C_2H_3^+$ and $C_2H_2^+$. The threshold energies for the production of these ions are 10, 13.3 and 13.1 eV, respectively. The other ions observed, in order of decreasing intensity, are C_2H^+, CH_2^+, H^+, CH^+, CH_3^+, C_2^+, C^+ and H_2^+ [12].
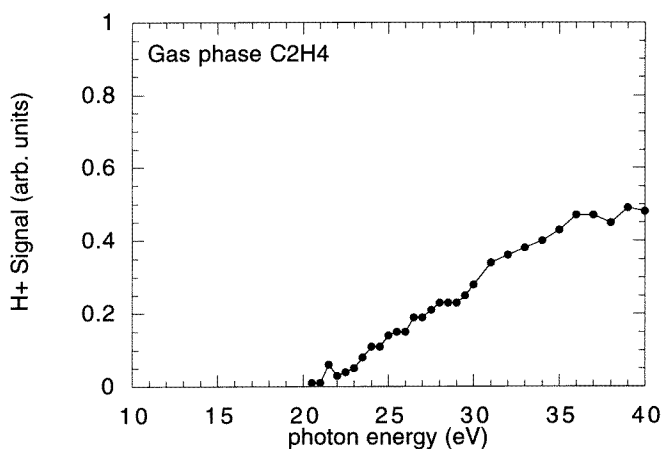
Figure 2. The photodissociation yield of H^+ ions from gas phase C_2H_4 measured as a function of the photon energy.
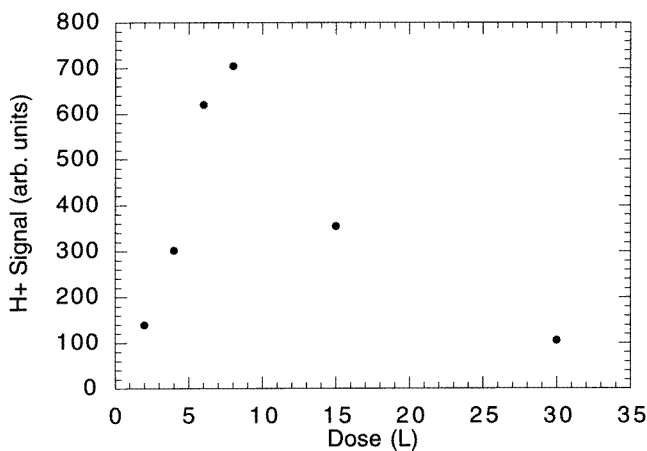
Figure 3. The coverage dependence of the C_2H_4–graphite H^+ signal, taken at a photon energy of 24 eV.

Neither photon nor electron stimulated studies of physisorbed C_2H_4 have previously been reported.

In this paper, we will describe a PSD study of C_2H_4 physisorbed on graphite. During these experiments, the only photofragment observed was H^+. This selectivity is interpreted in terms of the image potential barrier to ion desorption and the distribution of kinetic energy amongst the molecular photofragments. The formation of this ion occurs via dissociative ionization. The cross-section differs significantly from that of the free molecule, and appears
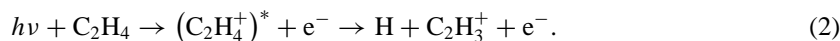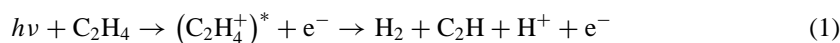
to be enhanced in the monolayer regime: this is attributed to selective quenching of excited molecular electronic states on the surface and to chemical reactions between molecular photofragments and the substrate.

The measurements were performed at beam line 3.1 of the Daresbury Synchrotron Radiation Source. The experimental details are described elsewhere [14]. The incident photon beam impinged on the surface at an angle of $45°$ to the normal. The highly oriented pyrolytic graphite (HOPG) sample was cleaved in air prior to insertion in the vacuum system and was cleaned *in situ* by electron bombardment heating to 820 K. The sample was cooled to $\sim$40 K using a liquid helium cryostat. The ions emitted from the sample were detected using a pulse counting quadrupole mass spectrometer (Hiden Analytical Ltd). Corrections for the background signal due to stray electrons was made by subtracting the signal detected at mass 2. During the measurements the temperature was held constant and the pressure was about 10^{-10} Torr.

The experiments measured the photon induced ion yield as a function of photon energy after different exposures of ethylene to the surface. The exposures studied were in the range 2–30 L. On the basis of comparison with detailed studies of physisorbed O_2 [7], and after correcting for the appropriate ion gauge sensitivity, we estimate that one monolayer corresponds to an exposure of approximately 8 L.

The only ion (positive or negative) detected in our desorption studies was H^+. Figure 1 shows the H^+ signal as a function of photon energy obtained when the graphite sample was exposed to various doses of C_2H_4; figure 2 shows the yield of H^+ from gas phase C_2H_4 [12]. In all the experimental spectra, the measured ion yield shows no appreciable intensity before an initial threshold at 20.5 eV. After this energy, the signal displays a sharp increase showing a maximum at around 24 eV. At higher energy, a decrease in the signal is observed which ceases for some coverages at $\sim$28 eV. Above this energy, a non-resonant increase is observed. The ratio of intensity between the 24 eV resonance and the non-resonant feature is significantly altered as a function of coverage. Moreover, the H^+ signal at all energies grows with increasing coverage and then falls away again, as shown in figure 3.

Of particular interest in connection with these studies of a polyatomic adsorbate is the dramatic difference in the relative yields of different photofragments compared with the gas phase. We believe that kinetic energy considerations can explain the fact that only the H^+ ion is observed. Consider, by way of illustration, the thermodynamic energy thresholds for the formation of H^+ and $C_2H_3^+$ (the principal molecular photofragment in the gas phase), which are determined by the following fragmentation schemes:

$$h\nu + C_2H_4 \rightarrow \left(C_2H_4^+\right)^* + e^- \rightarrow H_2 + C_2H + H^+ + e^- \tag{1}$$

$$h\nu + C_2H_4 \rightarrow \left(C_2H_4^+\right)^* + e^- \rightarrow H + C_2H_3^+ + e^-. \tag{2}$$

The thermodynamic threshold energy in the gas phase for H^+ is $\sim$20.5 eV and that for $C_2H_3^+$ $\sim$13 eV [12]. These thermodynamic thresholds correspond, by definition, to the production of ions with zero kinetic energy. In practice, of course, the observation of photofragmentation from a photon energy corresponding to the thermodynamic threshold energy depends upon the existence of an appropriate photoabsorption transition in the molecule. For H^+ and $C_2H_3^+$, the observed thresholds are in good agreement with the thermodynamic thresholds.

We believe that H^+ but not $C_2H_3^+$ is observed in the photon energy range studied from C_2H_4–graphite because the kinetic energy of the $C_2H_3^+$ ion is not sufficient to overcome the image/polarization potential barrier, due to the substrate–condensed film, which is of the order of 1 eV [17]. With this barrier, and assuming the conservation of momentum between the fragments produced in the photodissociation process, the thermodynamic threshold

energy for H$^+$ desorption should be about 21.5 eV (since the H$^+$ particle is light). The case of the heavier C$_2$H$_3^+$ fragment, produced according to (2), is different: here the ratio of the kinetic energies between the two fragments (H/C$_2$H$_3^+$) is 27 (their mass ratio). As such the thermodynamic threshold energy for C$_2$H$_3^+$ desorption should be approximately 41 eV, a dramatic increase with respect to the gas phase threshold and outside the range of photon energy in the present experiment.

Figure 2 shows the yield of H$^+$ as a function of photon energy from gas phase C$_2$H$_4$ and allows comparison with the surface data. As can be seen, the experimental threshold energies for H$^+$ production in the gas phase and on the surface are similar although the overall shapes of the spectra are quite different, at least until around 28 eV. In particular, a resonance is observed at 24 eV for the C$_2$H$_4$ adsorbed on graphite.

In summary, the main features of the experimental surface spectra (for all dosages) are a threshold energy at 20.5 eV, a resonance at 24 eV and a non-resonant increase at energies higher than 28 eV. The appearance of a resonance at 24 eV is indicative of a direct photodissociation process (photoelectron driven processes tend to show threshold behaviour), yet this feature is not observed for gas phase C$_2$H$_4$. We believe the appearance of this resonance may arise from the selective quenching of some of the electronic states of the molecule (at higher energy) when it is adsorbed. Such behaviour has been observed for NO adsorbed on different rare gas surfaces [15], where the quenching of some states was accompanied by a relative enhancement in the intensity of other peaks. Indeed, matrix studies suggest several effects can occur when a molecule is adsorbed (even in the case of physisorption) at the surface, leading, for example, to energy shifts in Rydberg, ionic and valence states and also to the formation of new intermolecular ionic states or to a change in character of an electronic state, e.g. from predominantly Rydberg to primarily valence in character [16]. The types of effect that can be observed in a system are extremely dependent both on the type of surface and also on the molecule which is adsorbed. In the present case, selective quenching of higher-lying excited states of the C$_2$H$_4$ molecule (above about 25 eV) would account for the resonance observed at around 24 eV.

The enhancement of the H$^+$ yield in the monolayer regime, compared with the multilayer (figure 3), is intriguing. As already indicated, the resonance at 24 eV suggests a direct photodissociation mechanism, which would rule out light absorption in the substrate in the cause of the enhanced yield in the monolayer.

Experiments by Dixon-Warren *et al* [18] on the photodesorption of Cl$^-$ ions from R–Cl species (R = CCl$_3$, CHCl$_2$ and CH$_2$Cl) adsorbed on Ag(111) observed an enhancement in the yield of Cl$^-$ ions at the monolayer coverage which they attributed to the chemical reaction between the remaining R photofragments and the surface. In this scheme, some of the energy released by the surface reaction appears as kinetic energy of the desorbed Cl$^-$ fragment. We suggest that a similar mechanism may lie behind the enhanced H$^+$ yield from a monolayer C$_2$H$_4$–graphite; this would require a chemical reaction between one of the remaining C$_2$H$_4$ fragments and the graphite surface. The radicals produced by the photodissociation event seem likely candidates, e.g., in equation (1), the C$_2$H radical.

In the photon energy range of interest, there a number of different thermodynamic thresholds for the (direct) photodissociation of C$_2$H$_4$ leading to the production of H$^+$, and these different pathways correspond to the generation of different sets of photofragments, of which equation (1) is only one example. The existence of these different photodissociation channels may also contribute to the perturbation of the gas phase photodissociation cross-section, because different chemical fragments are produced at different photon energies. Indeed, it is clear from figure 1 that the resonance at 24 eV becomes less apparent in the multilayer regime, and that at higher coverage the H$^+$ yield as a function of photon energy

becomes more similar to that of the gas phase.

In summary, we have reported studies concerning the mechanism of photodissociation of C_2H_4 physisorbed on graphite, using synchrotron radiation in the energy range 13–40 eV. Only H^+ ion desorption was observed because conservation of momentum in the photofragmentation of this polyatomic molecule means that no other ion has enough kinetic energy to overcome the image potential barrier to desorption.

The features observed in the H^+ yield are assigned to direct molecular photoexcitation. The appearance of a resonance at 24 eV, which is not observed for gas phase C_2H_4 itself, is attributed to the selective quenching of higher-lying excited electronic states of the molecule in the condensed film.

The yield of H^+ ions is found to be enhanced in the low-coverage regime. We believe that this behaviour may arise from a chemical reaction between the neutral fragments of molecular fragmentation and the substrate. This effect may also contribute to the enhancement of the resonance at 24 eV with respect to other direct photodissociation channels (producing different chemical fragments).

Finally, we note that the results show how the *excited* electronic states of a physisorbed molecule can be modified in the condensed phase. Although the ground state electronic structure of physisorbed molecules is not significantly perturbed by adsorption [19], our work adds to recent studies [10, 15, 16] which suggests this concept does not hold for all excited states. Further investigations of the dissociation dynamics of adsorbed polyatomic molecules are planned.

References

[1] Cassuto A, Mane M, Jupille J, Tourillon G and Parent Ph 1992 *J. Phys. Chem.* **96** 5987
[2] Heitzinger J M, Gebhard S C and Koel B E 1993 *J. Phys. Chem.* **97** 5327
[3] Albert M, Sneddon L G and Plummer E W 1984 *Surf. Sci.* **147** 12
[4] Palmer R E 1992 *Prog. Surf. Sci.* **41** 51
[5] Bennett R A, Bennett S L, Siller L, MacDonald M A, Palmer R E, Wright H M and Foord J S 1994 *J. Phys.: Condens. Matter* **6** 1955
[6] Bennett S L, Siller L, MacDonald M A, Bennett R A, Palmer R E and Foord J S *Phys. Rev. Lett.* submitted
[7] Bennett S L, Crabtree H M, Siller L, Bennett R A, Friedrich C M, Wilkes J, Lamont C L A, MacDonald M A, Palmer R E and Foord J S *Surf. Sci.* submitted
[8] Friedrich C M, Wilkes J, Palmer R E, Bennett S L, MacDonald M A, Lamont C L A and Foord J S 1995 *Chem. Phys. Lett.* at press
[9] Locht R and Momigny J 1971 *Int. J. Mass Spectrom. Ion. Phys.* **7** 121
[10] Dehmer P M and Chupka W A 1975 *J. Chem. Phys.* **62** 4225
[11] Shiromaru H, Achiba Y, Kimura K and Lee Y T 1987 *J. Phys. Chem.* **91** 17
[12] Ibuki T, Cooper G and Brion C E 1989 *Chem. Phys.* **129** 295
[13] Schiavone J A, Donohue D E and Freund R S 1977 *J. Chem. Phys.* **67** 759
[14] Bennett R A, Sharpe R G, Guest R J, Barnard J C, Palmer R E and MacDonald M A 1992 *Chem. Phys. Lett.* **198** 241
[15] Chergui M, Schwentner N and Bohmer W 1992 *J. Chem. Phys.* **97** 2881
[16] Schwentner N, Bressler C, Lawrence W, Xu J and Chergui M 1994 *Chem. Phys.* **189** 205
[17] Palmer R E 1994 *Surf. Sci.* **307–309** 335
[18] Dixon-Warren St J, Jensen E T and Polanyi J C 1993 *J. Chem. Phys.* **98** 5938
[19] Nilsson A, Palmer R E, Tillborg H, Hernnäs B, Guest R J and Mårtensson N 1992 *Phys. Rev. Lett.* **68** 982