

1: The UCL H₂ and HD work in the context of related recombination experiments on relevant surfaces

● **Experiment of Vidali and colleagues**, Syracuse, New York (Biham *et al.* 1998, Katz *et al.* 1999, Manico *et al.* 2001, Perets *et al.* 2005, Pirronello *et al.* 1997a, 1997b, 1999, 2000, Roser *et al.* 2002, 2003, Vidali *et al.* 1998, 2004a, 2004b): HD formation from cool H and D beams on surfaces of olivine, amorphous carbon, and water ice at 5–20 K; a period of dosing is followed by temperature programmed desorption (TPD). HD is detected both during the dosing, to detect “promptly” formed HD, and after the dosing to study “delayed” formation. Efficiencies of both processes are measured.

Results for amorphous carbon surfaces:
 (i) “Prompt” formation efficiency is fairly flat over the range of surface temperature 5–20 K.
 (ii) “Delayed” formation efficiency falls from 0.5 to 0.1 over a similar temperature range.
 (iii) Nascent molecules have low translational energy and there is significant energy transfer to the surface.

Comparison with the UCL experiments:
 (i) Agreement that surface morphology significantly affects molecular hydrogen formation.
 (ii) The UCL surface is non-porous, so nascent molecules do not thermalize in pores; hence, a high “prompt” fraction is expected with high internal (ro-vibrational) energy (as detected in the UCL experiment).
 (iii) The UCL experimental upper limit of 1 eV on translational energy is in accord with these experimental measurements of low translational energy.

● **Experiments of Hornekaer and colleagues**, University of Odense and University of

Aarhus, Denmark (Hornekaer *et al.* 2003, Hornekaer *et al.* 2005, 2006): HD formation on both amorphous and non-porous water-ice surfaces studied by TPD, and on graphite surfaces studied by scanning tunnelling microscopy.

Results:

- (i) Nascent molecules are fully thermalized on porous amorphous water-ice.
- (ii) Nascent molecules are rapidly desorbed from non-porous surfaces, and internal excitation is expected.
- (iii) Two distinct dimer adsorption structures are possible for chemisorbed H atoms on graphite, and recombination is only possible for one of these states.

Comparison with the UCL experiments:

- (i) Detection in the UCL experiment of ro-vibrational excitation in nascent molecules is consistent with the interpretation that molecules do not fully thermalize with non-porous surfaces.

● **Experiment of Baurichter and colleagues**, University of Odense (unpublished): HD formation on graphite by dosing with H and D beams, followed by TPD.

Results for graphite:

- (i) Detection of “delayed” fraction is weak, implying the “prompt” channel is dominant.

Comparison with the UCL experiments:

- (i) Results are consistent and confirm that the nature of the surface (porous/non-porous) is important.

● **Experiments of Zecho and colleagues**, MPI Garching and University of Bayreuth (Guttler *et al.* 2004a, 2004b, 2004c, Zecho *et al.* 2002a, 2002b, 2003, 2004): Reactions of hot

(2000 K) H and D atoms, which have enough energy to chemisorb on graphite.

Results for graphite surface:

- (i) Sticking coefficients determined for chemisorbing H and D atoms. Confirmation of barrier to chemisorption.
- (ii) Recombination of chemisorbed atoms on the surface is relatively insensitive to the level of defects on the surface, indicating that chemisorption occurs mainly at the planar surface of the graphite.

Comparison with the UCL experiments:

- (i) Implication is that the UCL experiments measure the reactions of physisorbed atoms, although reactions at chemisorbed sites involving defects on the surface cannot be excluded.

● **Experiments of Govers and colleagues**, University of Waterloo (Govers 2005, Govers *et al.* 1980, Marengo *et al.* 1972): Pioneering experiments studying H₂ (D₂) adsorption/desorption and H, D atom recombination on a cryodeposit on a liquid helium cooled bolometer.

Results for “ice” surface:

- (i) Sticking probability and accommodation coefficient determined as a function of coverage.
- (ii) Recombination observed to be efficient down to 4 K. Recombination desorbs other H₂ molecules from the surface. Nascent H₂ is ro-vibrationally excited.

Comparison with the UCL experiments:

- (i) Agrees with observation of ro-vibrational excitation. “Prompt” recombination reactions are important down to very low temperatures.

detected HD molecules formed in $v=1$ and $v=2$ when the target temperature is 15 K (Creighan *et al.* 2006). Recently recorded experimental data also clearly show the formation of HD in $v=3$ and $v=4$ from a 15 K HOPG surface. Qualitative indications are that the relative number densities of nascent H₂ molecules in the $v=1$ and $v=2$ states are comparable (Creighan *et al.* 2006). A similar situation exists for the formation of HD. It is important to note that the experimental REMPI signals are proportional to the number density of the molecules in the ro-vibronic state being probed. Obviously, to transform these densities into relative fluxes we need the velocity of the molecules. Other experimental measurements indicate that these molecular products possess a low translational energy, an energy comparable with the surface temperature. Therefore, if we assume that the molecules in the different vibrational states have the same translational

TABLE 2: CHARACTERISTIC TEMPERATURES FOR HD AND H₂

Fitted rotational temperatures $T_{\text{Rot}}(v'')$ for the $v''=1$ and $v''=2$ states of HD formed on HOPG at a surface temperature T_{Surf} .

Product	T_{Surf}/K	$T_{\text{Rot}}(v''=1)/\text{K}$	$T_{\text{Rot}}(v''=2)/\text{K}$
H ₂	15	–	364 ± 37
H ₂	23	314 ± 9	309 ± 41
HD	15	246 ± 24	282 ± 31

temperature, our experimental results indicate that the product fluxes in the $v''=1$ and $v''=2$ vibrational states are similar. Preliminary indications are that the product fluxes in $v''=3$ and $v''=4$, for the formation of HD, are, if anything, larger than for $v''=1$ and $v''=2$.

The rotational populations in the vibrational

states of HD and H₂ we detect (figure 6) are reasonably well modelled as Boltzmann distributions with the characteristic temperatures listed in table 2 (Creighan *et al.* 2006). Note that these rotational temperatures are much greater than the surface temperature. Indeed, for recombination on metals it is often, but not always (Kubiak *et al.* 1985), observed that such rotational distributions are approximately Boltzmann, sometimes with a rotational temperature that is higher than the temperature of the surface (Murphy and Hodgson 1996, Schroter *et al.* 1991, Winkler 1998, Zacharias 1988). The rotational temperatures we observe for HD formed on a 15 K HOPG surface in both $v''=1$ and $v''=2$ are very similar to those we observe for H₂ at all the surface temperatures investigated. Our results do not show any clear evidence of the isotope effects predicted for these processes in some theoretical studies (Meijer *et al.* 2003). However, it is again