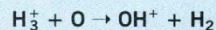
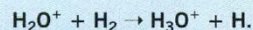
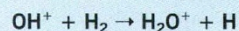


Making molecules

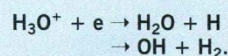
H_3^+ often makes more complicated molecules by beginning with a proton transfer reaction. For example, water, H_2O , and the hydroxyl radical, OH , both result from a string of reactions beginning with:



and continuing to make H_3O^+ via:



The H_3O^+ ion then reacts with an electron to form H_2O or OH :



We believe that most of the complex molecules in interstellar space are made by similar sequences. □

plex molecules (see box) with sequences that begin with the proton-transfer reaction $H_3^+ + X \rightarrow H_2 + XH^+$. Here, X is any chemical species with a greater proton affinity than molecular hydrogen — nearly everything heavier than helium.

That H_3^+ should exist in the interstellar medium was first proposed more than 30 years ago¹. It was first seen in the laboratory⁵ in 1980, and with the spectrum in hand, a number of researchers attempted to find it in interstellar clouds. It was seen in Jupiter⁶, Uranus⁷, Saturn⁸ and possibly in the ejecta of Supernova 1987A (ref. 9), but, being low in abundance and with only a weak emission spectrum, H_3^+ has not been found in interstellar clouds until now.

As an example of how measuring H_3^+ may help us understand the overall chemistry, consider the OH radical. As the box shows, OH is produced by a sequence that starts with atomic oxygen, but it is also removed mostly by reactions with oxygen¹⁰, so its abundance is not sensitive to the atomic oxygen abundance. Instead, it depends on the H_3^+ abundance and the reaction rate coefficients, so simultaneous measurements of H_3^+ and OH could be used to determine the rate coefficients, some of which are highly uncertain. For example, laboratory measurements^{11,12} of the branching ratios in the recombination

of H_3O^+ to H_2O vary from 5 to 33 per cent.

Perhaps the most exciting possibility is the usefulness of H_3^+ as a probe of the ionization rate of interstellar molecules. The formation rate of H_3^+ is directly proportional to the ionization rate times the H_2 abundance, and it is removed primarily by CO — the most abundant of the species that accept a proton from H_3^+ — so measuring the abundances of H_3^+ , H_2 and CO allows a direct calculation of the ionization rate. This is in contrast to the indirect

methods, such as measuring the flux of diffuse γ -rays, which we assume are produced by the same cosmic rays that ionize gas in molecular clouds.

With the detection of H_3^+ , the missing link between ionization and the rest of interstellar chemistry has been found. □

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POLYMERS

When a thick film is thin

Paul Calvert

THE behaviour of polymer films less than a micrometre thick has not long been a concern of polymer science because films and coatings are usually much thicker. But new applications of polymers in electronics have prompted an interest in the properties of these very thin films. They can be strange: a recent paper on a polystyrene¹, published in *Macromolecules*, shows that the diffusion rate in molten films 100 nm thick is half that in bulk polymer, implying that a polymer film effectively becomes 'thin' when it is still many hundreds of atom layers thick, whereas most liquids only show surface effects at thicknesses of one or two atom layers.

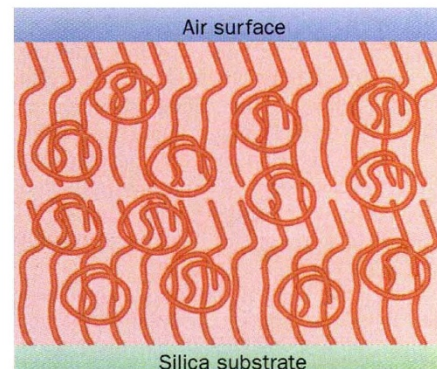
An earlier study explained this as an effect of adsorption². A thin layer of deuterated polystyrene was deposited on a silicon surface and then covered with a thicker layer of normal polystyrene. At 150 °C, the depth profile of deuterium in the film showed that diffusion away from the silicon surface was slower than diffusion away from the air surface. That was attributed to the polymer chains being adsorbed to the silicon so that they only became detached slowly.

In the new experiments¹, Frank *et al.* traced diffusion by attaching a fluorescent dye to polymer chain ends. The film, on a silica substrate, was then bleached in stripes 4 micrometres wide using laser light shone through a mask. As chains diffused into the exposed region from the shadows, the fluorescent signal returned, so diffusion in the plane of the film (rather than away from the surface) could be measured as a function of film thickness. The value was the same as for bulk polymer down to 200 nm, but then diffusion slowed by half as the thickness decreased to 100 nm. This cannot be explained as slow detachment from the surface, so why does it happen?

Long-chain polymers take on a random coil conformation that occupies a sphere. For the chain length in this sample, the radius of gyration is about 3 nm. So if we think of the chains as 3-nm fish in a pond about 100 nm deep, it is hard to see why

their motion should be much affected by the depth. It is possible that the dye units are adsorbing strongly to the substrate, but that would have little evident effect because immobile dye would not be counted.

The critical film thickness, 100–150 nm, is comparable to the fully extended chain length of 120 nm. Without any detailed



Polymer fish in polymer reeds. If a large number of chains are adsorbed at the surfaces, they could hinder the other, coiled chains and explain the slow diffusion observed in some polymer films.

explanation, Frank *et al.* think that somehow the chains are slowed by being unable to straighten fully as they flex between conformations. It could also be that the chains at the silica interface, or at both surfaces, are not coils but are stretched out straight like reeds on the pond bed. Now the remaining coiled 'fish' chains will move slowly through the 'reeds' (see figure). This leaves us with the puzzle of why such a gross distortion of the polymer conformation should occur at these interfaces.

There have already been hints of the long-range influence of polymers at surfaces. Studies in 1984 of polymers adsorbed from solution to mica surfaces showed that attractive forces between the chains went out 50–100 nm, or about three times the radius of gyration of the chain, for both polystyrene in hexane and polyethyleneoxide in water^{3,4}.

But the 'reed' model requires that

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