Hydrogen molecules in the cosmos

David A Williams presents his Presidential Address for 1999, given to the RAS on 12 February this year.

I have had an interest in molecular hydrogen throughout my research career, even before I became an astrophysicist, so it seems appropriate to devote this Presidential Address to the role of H_2 in astronomy. The last three decades have been a period of wonderful discoveries involving astronomical molecules, but back in the 1960s, when I began research, astronomical H_2 was still a matter only of speculation. Since then it has become apparent that H_2 is abundant in the universe, that its emissions trace a variety of situations, and that it has an active role to play in the cycle of matter from diffuse gas to dense objects.

Molecular hydrogen in interstellar space was first discovered in 1970 by Carruthers in a rocket observation of Lyman band absorption at wavelengths between 100 and 110 nm of starlight from ξPer by a diffuse interstellar cloud. This was the first of a series of important observations of H_2 in space (table 1). In parallel with these observational developments were programmes of laboratory and theoretical development in which many scientists have played a role. This activity includes laboratory investigations of spectroscopy and of reaction kinetics, and theoretical studies of H_2 chemistry and excitation in many kinds of astronomical situation. Dalgarno and his colleagues at Harvard have been pre-eminent in making both fundamental studies of H_2 and modelling its response in the interstellar medium.

All of this activity assumes that H_2 is actually important in astronomy. Table 2 lists a number of reasons why this is so, including the significant fact that much of the mass of non-stellar baryonic matter in the universe is in the form of molecular hydrogen, and shows that H_2 touches every kind of system in the universe. Obviously, then, I must be selective! In this Address, I want to explore several of the important roles of H_2: in the early universe, where H_2 has an active controlling role; in near-stellar environments, where H_2 is an informative tracer of a wide range of physical conditions; and in star formation, where H_2 fuels a chemistry to provide other molecular coolants that permit gravitational collapse. Finally, I shall describe new laboratory and theoretical work on the surface chemistry on dust that is believed to be the main formation route for interstellar H_2 in the Galaxy.

It is less than 30 years since molecular hydrogen was first identified in a non-terrestrial source. Since then, many wonderful discoveries concerning cosmic H_2 have been made, in observations, experiments, and theory. It has become evident that H_2 is found in many astronomical environments and almost all types of astronomical object. Molecular hydrogen had an important role in promoting baryonic structure in the early universe. It is most abundant in interstellar molecular clouds in the Milky Way and other galaxies. These clouds provide the reservoir of mass from which new stars are formed. The impact of stars on their environments often creates conditions in which H_2 can be excited and for which H_2 emission is an effective tracer. Examples of all these phenomena are given in this article.

Molecular hydrogen in the early universe

In this section, I shall argue that astrochemistry pre-dated the formation of galaxies, and was influential in causing structure to develop in the baryonic matter. That structure ultimately produced the galaxies (cf. Lepp and Stancil 1998).

Early chemistry

In the Standard Big Bang Nucleosynthesis Model, the universe became cool enough for helium nuclei and electrons to combine at a redshift z of about 2500 (about 10^5 years post-Big Bang) and for hydrogen neutralization at a redshift of 1300 ($\sim 3\times10^5$ years post-Big Bang), assuming that the cosmological density parameter Ω_0 is unity, and Hubble's constant, H_0, is 50 km s^{-1} Mpc^{-1}. Since hydrogen was the most abundant element, the universe went through a phase transition from almost entirely ionized to mostly neutral, at this epoch; matter and radiation were therefore decoupled.

Once some neutral atoms were present, chemistry – in the real sense, i.e. involving molecules – began. At the earliest stages, the presence of neutral helium and ionized hydrogen allowed the formation of molecular ions such as He_2^+, HeH^+ and HeD^+ through radiative association. However, the abundances of these molecules were never high enough to play an important role, nor to trace these early stages. Once neutral hydrogen was available, then other molecules, including H_2^+, HD^+, H_2 and HD, were able to form, and the abundance of H_2 was high enough for it to influence the development of structure in the early universe. Lithium recombination occurred from about $z=450$, but its relative abundance is so small ($Li/H \simeq 10^{-10}$) that lithium chemistry is unimportant for the present discussion.

All the chemical reaction schemes were initiated by radiative processes, such as

$$H + e^- \rightarrow H^- + h\nu$$

and

$$H + H^+ \rightarrow H_2^+ + h\nu$$

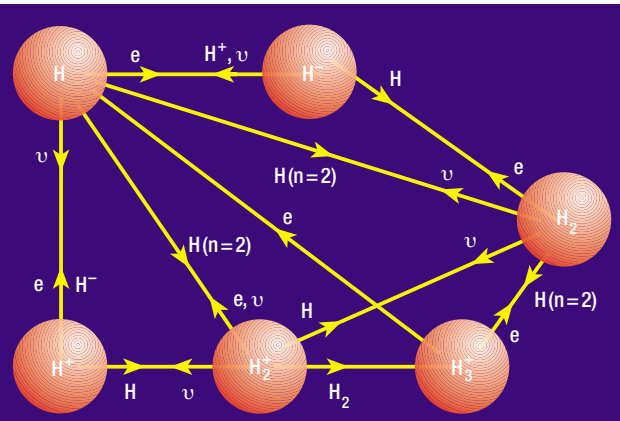
which could be followed by ion–molecule exchange reactions, such as

$$H^- + H \rightarrow H_2 + e^-$$

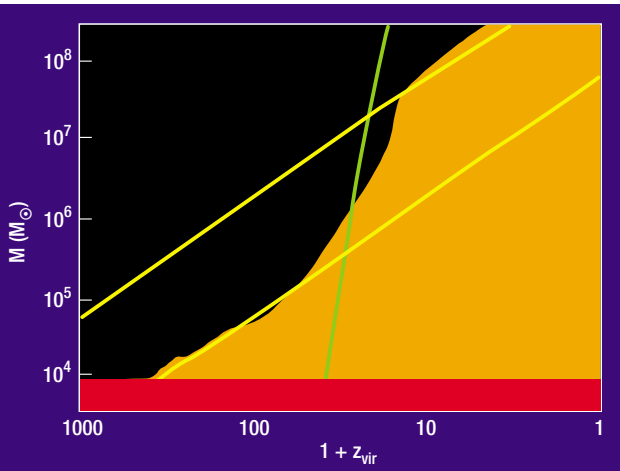
and

$$H_2^+ + H \rightarrow H_2 + H^+$$

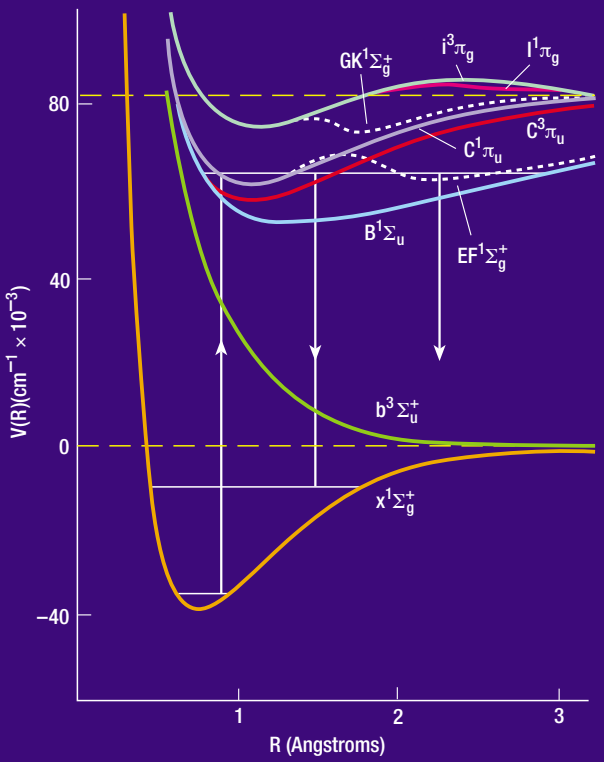
The full network of reactions was fairly complex (see figure 1) and as the conditions changed in the expansion of the universe, different reactions and products were emphasized. However, the abundances of the main molecular species were always rather low. At $z \simeq 10^3$, the fractional abundance of H_2 was about 10^{-12}, with the abundances of HD and H_2^+ about 5 and 7 orders of magnitude smaller. By $z \simeq 10^2$, fractional abundances were close to



1 The important reactions involved in the formation and destruction of H_2 in the early universe are summarized in this diagram (adapted from Dalgarno and Lepp 1996; Lepp and Stancil 1998).



2 The minimum total mass needed to collapse in the early universe, as a function of the redshift at which virialization occurs. The calculation assumes $\Omega = 1$, the baryon fraction is 0.06, and $H_0 = 50$ km s^{-1} Mpc^{-1}. Only lumps whose parameters are in the black region can collapse. The green line indicates peaks in the standard Cold Dark Matter model. The yellow lines are for $T_{vir} = 10^3, 10^4$ K (Tegmark *et al.* 1997).



3 Absorption in the Lyman B-X and Werner C-X bands of H_2 from the $v'' = 0$ level is followed by relaxation into either bound or free states of the ground electronic states, X. The former populates vibration-rotation states of X, while the latter destroy H_2 (cf. Stecher and Williams 1967). Collisional excitation between vibration-rotation levels can also occur. Molecules may also be formed in excited internal states (cf. Duley and Williams 1993).

Table 1: Key observations of cosmic H_2

Observation	Reference	Source
Lyman band absorption B–X	Carruthers 1970	Rocket UV
Lyman and Werner band absorption B–X, C–X	Spitzer *et al.* 1974	Copernicus satellite UV survey
Vibration-rotation emission 1–0	Gautier *et al.* 1976 Treffers *et al.* 1976	Ground-based observation
Line and continuum emission B–X, C–X	Jordan *et al.* 1977 Brown *et al.* 1981 Witt *et al.* 1989	Rocket UV IUE satellite IUE satellite
Pure vibration absorption by trapped H_2 on dust	Sandford *et al.* 1993	Ground-based observation

Table 2: Why is H_2 important?

- H_2 is the most abundant molecule in the universe
- A significant fraction of non-stellar baryonic matter in spiral galaxies is in H_2
- H_2 is an important coolant of diffuse gas from temperatures $\lesssim 10^4$ K down to temperatures $\simeq 100$ K
- H_2 cooling influenced structure formation in the early universe
- H_2 infrared emission traces warm gas, collisionally and/or radiatively excited
- H_2 promotes all interstellar chemistry

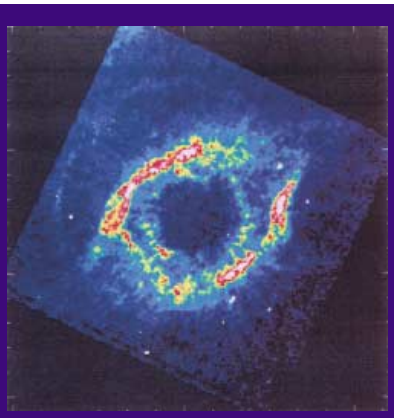
the limiting values of 10^{-6} for H_2, and 10^{-9} for HD. All other molecules were very much less abundant. Thus, by $z \sim 10$, the interesting era for structure development, about one part in a million of hydrogen was in H_2. Was this trace amount of H_2 significant?

Early structure

Molecular hydrogen has a vibration-rotation energy level structure that enables the molecule to act as a coolant down to relatively low temperatures. Collisions between H atoms and H_2 molecules in the pre-galactic gas populated the H_2 internal energy levels, from which the molecule ultimately radiated, thereby cooling the gas. The importance of suppressing a temperature rise during collapse can be seen from the expression for the Jeans mass, the baryonic mass above which a self-gravitating cloud is unstable to collapse:

$$M_J \simeq 2 \times 10^5 M_\odot (T/100)^{3/2} n^{-1/2}$$

where T is the gas temperature (K) and n is the number density cm^{-3}. For the recombination era, therefore, $M_J \simeq 10^5$–$10^6 M_\odot$, comparable with the masses of globular clusters observed in the Milky Way and other galaxies. Consequently, Peebles and Dicke (1968) suggested



4 The ISO LW2 image of the Helix Nebula (Cox *et al.* 1998).

that globular clusters were the first objects to form. These considerations indicated that a more detailed study was needed, and there have been many studies in which the microscopic processes were accounted for, in various degrees of detail, since the early work of Couchman and Rees (1986).

Recently, Haiman *et al.* (1996b) have carried out hydrodynamical modelling of the 1-D collapse of pre-galactic spherical gas clouds including chemistry of H_2 formation and H_2 cooling. These simulations indicate that bound objects of baryonic masses 10^2–10^3 $M_\odot$ may have formed, and could have been the progenitors of the postulated Population III stars.

In the expanding universe, the cooling timescale must be shorter than the Hubble time, otherwise structure cannot form. Figure 2 indicates how the total mass of the collapsed region depended on the virialization redshift for a universe of cold dark matter with baryonic fractional mass of 0.06. The details of this figure depend rather sensitively on the H_2 cooling function, which is not precisely known at present. However, the diagram does show that relatively small objects were able to collapse at early times, and conversely – suggesting a "bottom-up" universe, i.e. one in which larger units formed from the aggregation of smaller units.

Later developments

Population III stars would have affected subsequent evolution, not only through the injection of heavy elements into the intergalactic medium (IGM), but also through their UV radiation and winds. The UV radiation re-ionized the IGM (which had been neutral since the recombination era) and this promoted more H_2 formation (see figure 1). A simulation by Ostriker and Gnedin (1996) shows how a burst of Population III star formation, initiated by H_2 cooling, re-ionized the IGM and suppressed further star formation by $z = 12$. Cooling in the IGM initially by H-atom lines and subsequently by H_2 initiated a second burst of star formation of stars with increased metallicity, the Population II stars.

This is not quite the end of the story as far as H_2 in the early universe is concerned. Shocks from cloud–cloud collisions, or from explosions of the earliest objects, caused compression of gas, and cooling led to even higher densities with increased H_2 fractional abundances. A number of models incorporating these processes have been explored. The gas, initially ionized and hot (~10^4 K) cooled at first by inverse Compton scattering, then by Lyman α emission, and finally (below 7000 K) by H_2 emission. Kang and Shapiro (1992) have shown that the H_2 fraction in the cooling shells (formed through the H^- and H_2^+ reactions as in the early universe) can rise to about 10^{-3}, enabling the shells to cool to 100 K. While a high radiation field could inhibit this process, at later stages ($z = 2$–4), the effect of quasar UV radiation has been found to enhance ionization, H_2 production and cooling (Haiman *et al.* 1996a).

Thus, it appears that H_2 was an important agent in promoting baryonic structure in the early universe. Is there any hope of H_2 radiation also being a tracer of these times? Lepp and Shull (1984) have argued that large amounts of gravitational potential energy must be radiated away from collapsing objects at high redshift, and that since there was no dust, the radiation was not degraded. However, such radiation has not yet been detected.

Molecular hydrogen as a tracer of galactic events

The infrared spectrum of H_2 is rich in lines arising from transitions in its vibration-rotation and pure rotation energy levels. The study of these lines has been remarkably productive in elucidating the physical conditions in a variety of astronomical situations. In this section, I discuss briefly several examples where observations of H_2 lines help our understanding of the physical nature of the regions, and I also describe a couple of examples that we do not understand at all! In none of these examples is H_2 controlling the region's development. It is purely a tracer

Much of the interest in these observations lies in determining the means by which the excited energy levels of H_2 are populated (see figure 3). Do collisions dominate, or is radiative pumping the main mechanism? Or does the formation mechanism of H_2 produce molecules in excited states? There is a traditional unwillingness by astronomers to invoke an active role for interstellar dust, but as we shall see below it seems inescapable that H_2 molecules are formed on dust in excited states.

Excited H_2 in a planetary nebula

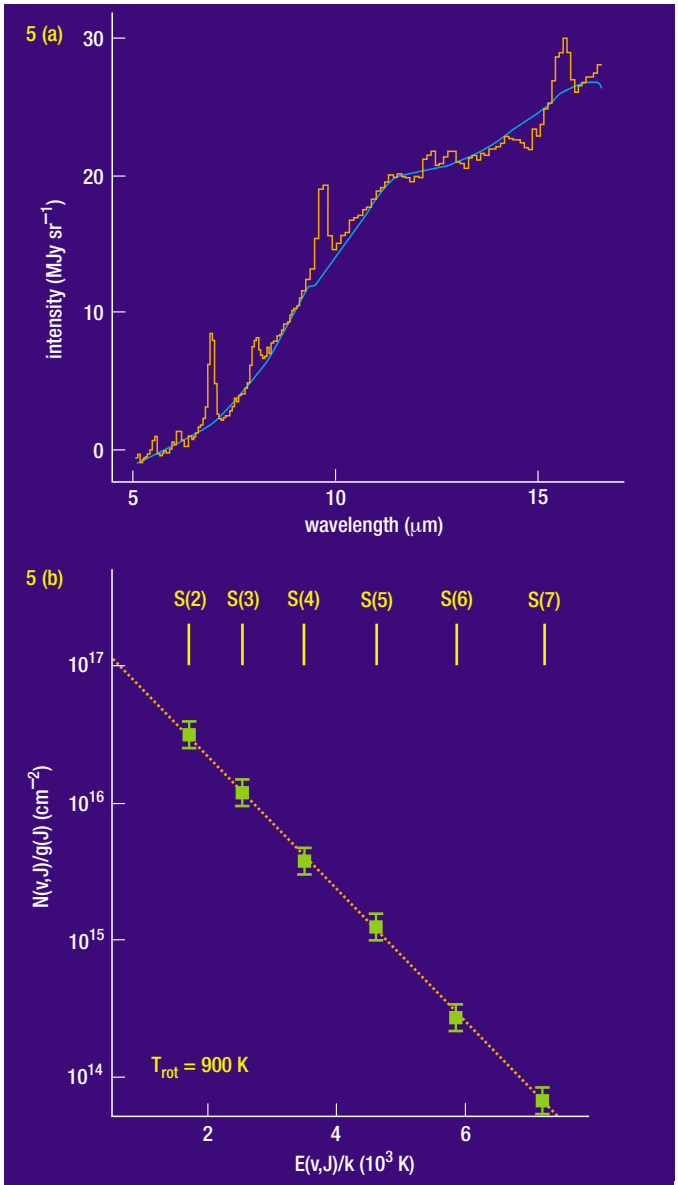
Planetary nebulae are visually beautiful, and have a complex and interesting physics and chemistry (Howe and Williams 1998). The Helix is one of the nearest (about 160 pc distant; Cahn *et al.* 1992) and appears as a double ring both optically (Walsh and Meaburn 1987) and in the molecular envelope (Young *et al.* 1997). The envelope consists of many dense blobs which can be associated with the cometary globules seen at optical wavelengths. The globules have been detected in CO lines, and the chemistry in them is in steady state (Howe, Hartquist and Williams 1994).

Recent imaging and spectroscopy of the Helix have been made by instruments on board the Infrared Space Observatory (ISO) (Cox *et al.* 1998). The image from filter LW2 (around 6.9 μm) shows a similar structure to the optical and molecular images, of globules, filaments, and wisps of gas (see figure 4) and the spectrum of the region 5–16.6 μm shows a series of pure rotational H_2 lines S(7)–S(2) on a continuum that is well fitted by the zodiacal light. The lines indicate H_2 rotational excitation up to at least $J = 9$, and the excitation diagram shows that these levels are all populated in a hot gas at a single temperature of 900 K, and the density must be in excess of 10^5 H_2 cm^{-3} (figure 5). Radiative pumping can play no significant part; in fact, from the geometry and knowledge of the central star, radiation is not expected to play any role.

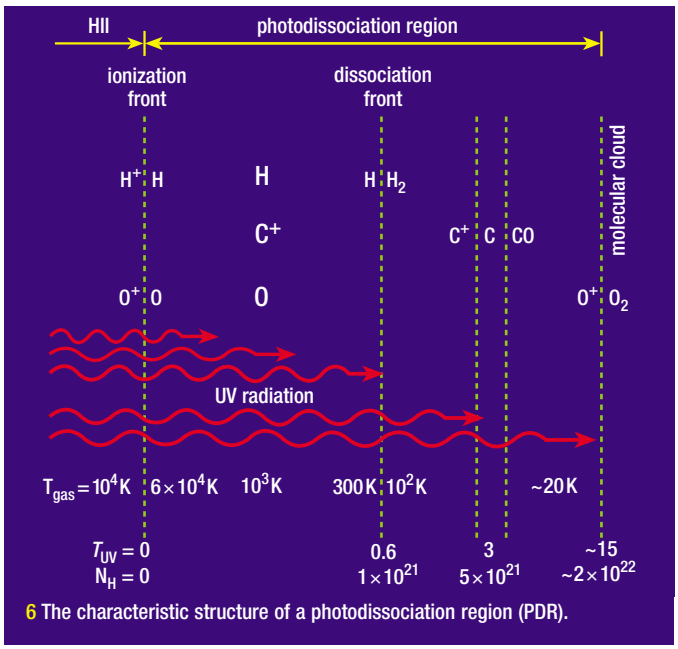
What is the origin of the warm H_2 gas? It seems likely that shock excitation is responsible, and that we are seeing the effect of the well-known (to theoreticians) interacting winds model (Kahn 1983; Kwok 1983). In this, a fast stellar wind sets up a double shock structure; the outer shock is driven through the pre-existing AGB wind. From the H_2 spectrum the mass loss rate and velocity of the stellar wind can be derived, and are found to be 3×10^{-8} $M_\odot$ yr^{-1} and 1000 km s^{-1} respectively. Thus, observations of H_2 rotational emission have constrained the central white dwarf properties.

Molecular hydrogen in PDRs

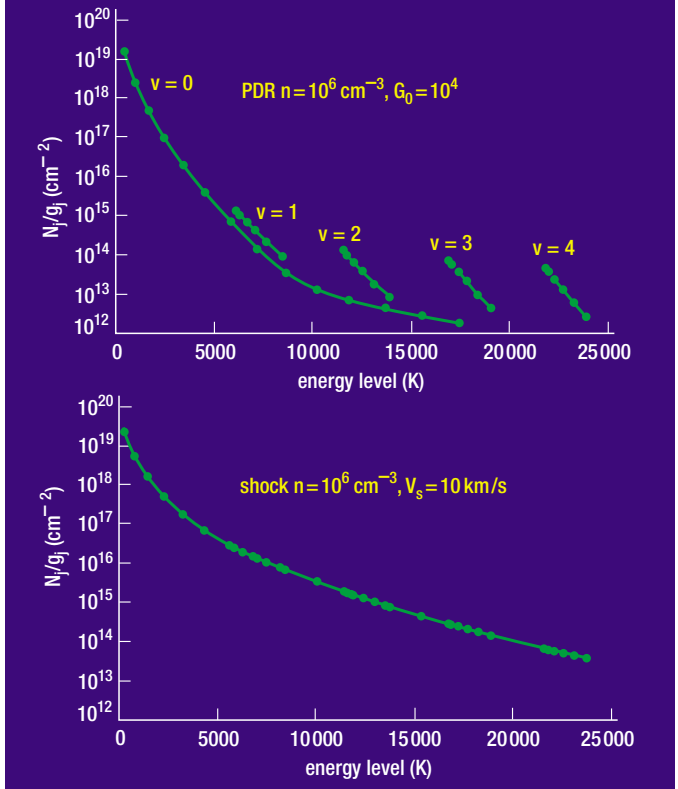
Studies of CO 1-0 emission in giant molecular clouds reveal that the clouds are far from uniform and are clumpy on a scale of a few visual magnitudes; also, it is apparent that the gas is often associated with hot stars. In fact, much of the molecular material in the Galaxy is significantly affected by powerful UV radiation fields that may be thousands of times as intense as the mean interstellar radiation field. These photodissociation regions, or photon dominated regions (PDRs) have a structure indicated schematically in figure 6. The chemical and radiative diagnostics of such structures have been explored extensively (e.g. Hollenbach and Tielens 1997; Sternberg 1998). Where radiation processes are important, predicted excitation diagrams for H_2(v,J) show quite different characteristics from those for a warm collisionally dominated region, such as shocked gas (see



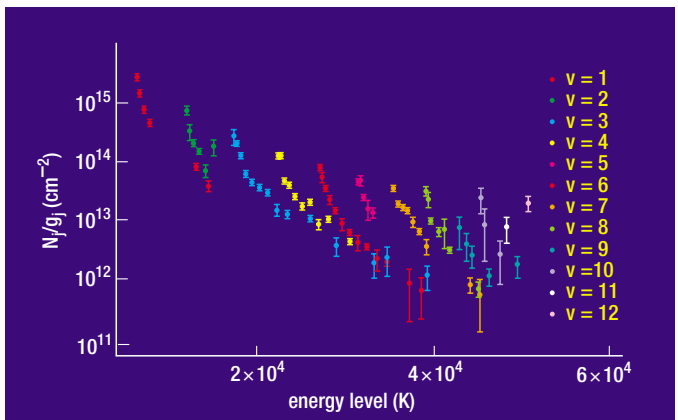
5 (a) The ISO spectrum of the western rim of the Helix Nebula. The orange line shows the zodiacal emission. (b) The H_2 excitation diagram for the data in (a). The dashed line represents a single temperature fit to the data, with $T_{rot} = 900 \pm 50$ K (Cox *et al.* 1998).



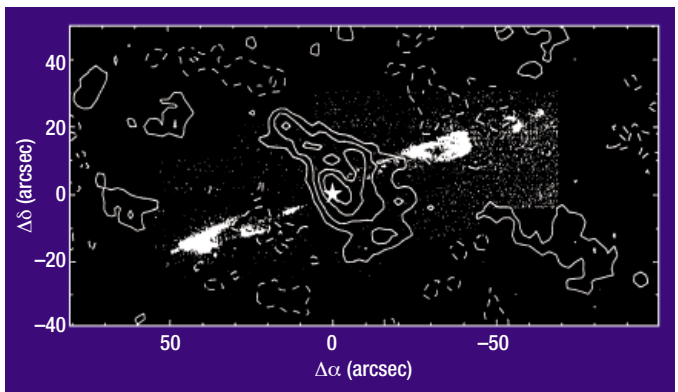
6 The characteristic structure of a photodissociation region (PDR).



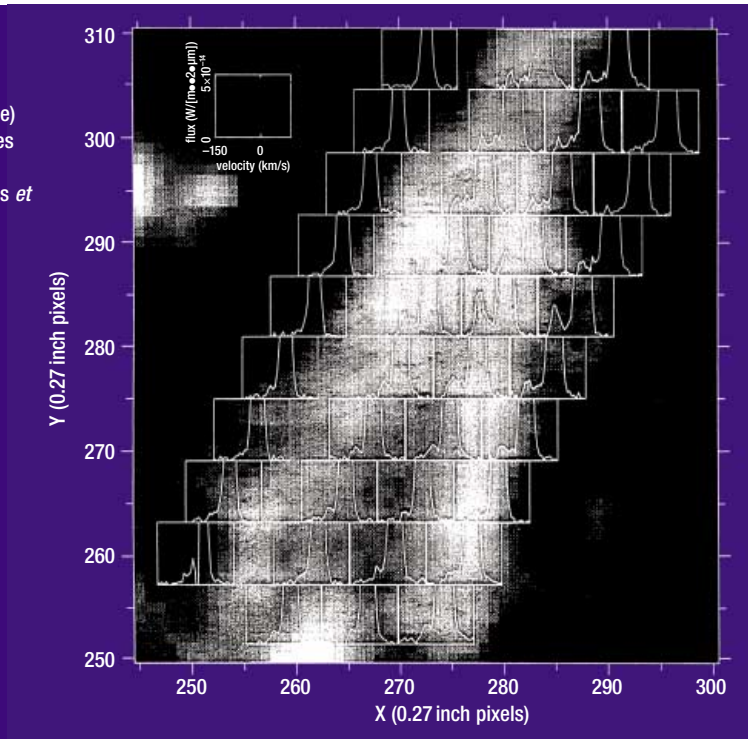
7 Theoretical H_2 excitation diagrams for PDR and a shocked region (Burton 1992).



8 The H_2 excitation diagram obtained for one position in the reflection nebula NGC2023 (McCartney *et al.* 1999).



9 Superposition of a greyscaled image of the HH211 jet taken in H_2 v=1-0 S(1) at 2.122 μm (McCoughrean *et al.* 1994) with contours of NH_3 (1,1) emission (R Bachiller and M Tafalla unpublished), (from Bachiller 1996).



10 H_2 1-0 S(1) emission from HH126-053 in Orion (greyscale) with line profiles at various locations (Tedds *et al.* 1999).

figure 7), and the excitation diagram has become a powerful tool. The single molecule, H_2, may be excited in dozens of rotational and vibrational-rotational lines, providing a wealth of information about collisional and radiative processes.

A very detailed study has been made of H_2 emission in a bright filament of the reflection nebula NGC2023, caused by the proximity of a B1.5 star HD37903 to the edge of the molecular cloud L1630 (McCartney *et al.* 1999). The excitation diagram obtained (figure 8) shows the characteristics of a PDR, with sets of rotational energy levels for each vibrational state being separated. Attempts to fit these (and other) data have been made with some success by Draine and Bertoldi (1996), and in general the geometry of the cloud and its orientation with respect to the star may be inferred from the modelling. The radiation field at the filament must be about 5×10^3 times stronger than the mean interstellar radiation field, and the density in the filament must be about 10^5 H_2 cm^{-3}.

H_2 in stellar jets and outflows

All young stellar objects (YSOs) undergo periods of intense mass loss. The youngest (so-called Class 0 objects) have the greatest rates of mass loss. The outflows are detectable at many wavelengths, from UV to radio (cf. Bachiller 1996) and are observed for YSOs of a wide range of masses and luminosities. The basic picture is of fast, well-collimated, oppositely directed winds, sweeping up ambient gas and creating two cavities, one on each side of the star. Molecular gas (often traced in CO) displaced from these cavities expands into irregular lobes. While this description is broadly satisfactory, there is much that we do not know. What initiates the outflows? Why are the youngest outflows collimated into "jets"? How is the ambient molecular gas entrained? How do narrow jets create a wide cavity? Observations of H_2 have been important in addressing some of these questions.

H_2 emission is expected to occur whenever high-speed stellar jets impact on ambient molecular material, at least for orthogonal shock speeds up to about 50 km s^{-1}. Many studies (cf. Hodapp and Ladd 1995) have shown H_2 emission to arise in the jets that give rise to Herbig–Haro objects, small knots of optical nebulosity. The H_2 emission often has a bow shock morphology, which supports the general picture that a Herbig–Haro object is the post-shock gas heated in a jet–cloud interaction.

H_2 infrared emission can be detected around many YSOs that are still deeply embedded in the dense gas from which they formed, and are optically invisible. For example, in L1448, a Class 0 source with a highly collimated outflow, the H_2 image reveals a well defined bow shock (Bally *et al.* 1993), while the slow moving CO emission (Bachiller *et al.* 1995) reveals a complementary structure centred on the star and delineating the cavity created by the bow shock. In figure 9, the region of the Class 0 source IC 348 – mm in a dense clump traced in NH_3, the H_2 1-0 S(1) emission traces gas that appears to be a "sheath" of mixing layer gas around the true jet (McCaughrean *et al.* 1994). Therefore, H_2 emission is giving information about the transfer of energy and momentum from the jet into the wider outflow. The situation is physically very complex, and requires a numerical hydrodynamical study of the mixing between the jet and the ambient molecular gas, and the chemistry induced. Taylor and Raga (1995) have made a pioneering calculation of this type, and have predicted in particular the H_2 emission from a mixing layer. Noriega-Crespo *et al.* (1996) find that the optical and H_2 morphologies of the HH110 jet agree with the Taylor and Raga predictions. Recent studies (Lim *et al.* 1999) indicate that the physical mixing of the two gases is less pronounced than had previously been thought.

Two H_2 excitation problems

Studies have been made of Orion Peak 1, an intense source of H_2 emission excited by the high-velocity outflow from the infrared source IRc2, using the Short Wavelength Spectrometer on board ISO (Rosenthal *et al.* 1999). A very rich H_2 spectrum of pure rotational lines was obtained from S(1) to S(25). The excitation diagram shows no hint of fluorescence, and the gas may be the hot post-shock material cooling through a range of temperatures.

The observation of the J = 27 pure rotational level is remarkable enough, but the data also indicate that this level is overpopulated by a factor of five, and the authors suggest that a specific mechanism may be populating this level. It does not seem likely that grain surface reactions could contribute specifically to such a level (see "The formation of molecular hydrogen on interstellar dust" below). Rosenthal *et al.* suggest that the H^- route to H_2 may leave the product in a high rotational state.

Orion contains a range of mysteries. When the Orion nebula is imaged in H_2 1-0 S(1) and Fe emission (Allen and Burton 1993) a remarkable structure of "fingers" of emission is apparent. Tedds *et al.* (1999) have examined the tip of the most northerly finger, and measured the profile of the 1-0 S(1) line (figure 10). The line is typically around 150 km s^{-1} wide. If such a velocity distribution is brought about by a shock, then it is at present unclear how H_2 molecules can survive a shock of that strength. In J-type shocks, H_2 is expected to be destroyed for shock velocities around 20 km s^{-1}; in C-type shocks this limit is increased to around 45 km s^{-1}. However, this is far from explaining velocities of ~150 km s^{-1}.

Molecular hydrogen and star formation

Interstellar clouds are mainly H_2, and form the reservoir of mass from which new stars are made. The gravitational collapse of an interstellar cloud to form a star, from a typical density of ~10^3 H_2 cm^{-3} and dimension about a parsec, must increase the density by some 21 orders of magnitude, compressing much of the mass into the size scale of stellar dimensions, ~10^{11} cm. The release of gravitational potential energy during this process is enormous, and this energy must be radiated away.

Initially, the cloud has a temperature ~30 K, not dissimilar to the temperature of Class 0 YSOs (Bachiller 1996) at the end of the collapse. Evidently, the cooling processes are efficient enough to maintain a low temperature throughout the collapse from the interstellar cloud phase (duration $\gtrsim 10^6$ years) Class 0 phase. Of course, the temperature rises rapidly as the YSO moves into the Class I phase.

Gravity must overcome thermal pressure, turbulence and magnetic pressure. The precise understanding of how this is achieved is one of the major challenges of astronomy today.

Although H_2 cannot be the important coolant in such regions, as it is ineffective below ~100 K, nevertheless H_2 plays an important active role in fuelling a chemistry that provides molecular coolants (in addition to dust) that are capable of cooling to the lowest temperatures. Equally importantly, this chemistry also controls the fractional ionization, and thereby the magnetic support given to the cloud. In this section, I shall indicate briefly these roles of H_2 in collapsing clouds (Hartquist *et al.* 1998).

Molecular hydrogen does not react readily with oxygen and carbon atoms; however, it can be transformed into a reactive species, H_3^+, by cosmic rays (c.r.):

$$H_2 + \text{c.r.} \rightarrow H_2^+ + \text{c.r.}$$
$$H_2^+ + H_2 \rightarrow H_3^+ + H$$

The H_3^+ initiates by proton donation a sequence of H-abstractions from H_2, for example

$$H_3^+ + O \rightarrow OH^+ + H_2$$
$$OH^+ + 2H_2 \rightarrow H_3O^+ + 2H$$
$$H_3O^+ + e^- \rightarrow H_2O + H$$

(with similar reactions for other species). The importance of H_2 in this scheme is apparent; not only does it provide the initiating ion, H_3^+, it also fuels the sequence until the ion (in this case H_3O^+) can take up no more hydrogen. Then, a recombination with electrons occurs. The result of this sequence is the formation of H_2O, and also OH; these are two important coolants. A third, CO, can be created from them by other means, e.g.

$$H_2O + C^+ \rightarrow HCO^+ + H$$
$$HCO^+ + e^- \rightarrow CO + H$$

There is another entry to the carbon chemistry, through the slow radiative association of C^+ with H_2

$$H_2 + C^+ \rightarrow CH_2^+ + h\nu$$

following which further H-abstractions from H_2 occur, and ultimately dissociative recombination

$$CH_2^+ + H_2 \rightarrow CH_3^+ + H$$
$$CH_3^+ + e^- \rightarrow CH_2 + H$$

similar to the H_2O sequence.

The recombination of molecular ions such as H_3O^+ and HCO^+ is generally fast, and occurs dissociatively on almost every collision between the molecular ion and electron. Recombination of atomic ions, however, is a radiative process, and much slower. Therefore, the effect of reactions of atomic ions with H_2 or other molecules is to create molecular ions that are destroyed quickly. Hence, the fractional ionization in a molecular cloud is closely linked to the chemistry. Ruffle *et al.* (1998) have shown that the fractional ionization falls rather abruptly within a molecular cloud, for visual extinctions greater than about two magnitudes. This effect has been interpreted as a critical extinction; for clouds that are more heavily extinguished, then the ionization fraction falls (to about 10^{-8}) and the coupling of magnetic fields to the gas is much reduced, (the ambipolar diffusion timescale falls to $\lesssim 10^6$ years), hence collapse may be initiated. The detailed observational study by Williams, Blitz and Stark (1995) of clumps in the Rosette Molecular Cloud, showed that stars were generally present in clumps with the highest CO column densities. See table 3 for a discussion of the timescales of collapse, chemistry, cooling and ambipolar diffusion.

The H_2-fuelled chemistry that occurs in molecular clouds is, therefore, capable of producing efficient coolants that enable the gravitational potential energy released in the collapse to be radiated away; simultaneously, the chemistry suppresses the fractional ionization that enables magnetic effects (including both static support and magnetic waves) to support the cloud.

11 The H_2 experiment at the UCL Centre for Cosmic Chemistry and Physics.

The formation of molecular hydrogen on interstellar dust

As we have seen, molecular hydrogen was formed in the early universe through a sequence of gas phase reactions involving atoms, protons, and electrons. The simple radiative association of two neutral H-atoms did not play a part, as this is strongly forbidden. Three body reactions were also excluded, at least until very high densities [$n(H) \simeq 10^{12}$ cm^{-3}] were achieved in collapsing regions. The fraction of hydrogen converted to molecules in the early universe was generally rather small.

In the interstellar medium of the Galaxy, and other galaxies, much of the hydrogen is molecular. Evidently, a more efficient formation process is required. Along lines of sight where the H_2 abundance is low enough for the absorption to be optically thin, the destruction rate of H_2 by stellar UV radiation can be estimated accurately, and on the assumption of chemical steady state gives a reliable measure of the H_2 formation rate. The gas phase routes are clearly inadequate, and it has been conventional for many years to invoke surface reactions on dust as the formation mechanism. This may seem to be a circular argument! Interstellar dust tends to form in regions that are chemically active, yet – as we have seen above – H_2 is needed for an active chemistry. Which is the chicken, and which the egg? The way out of this dilemma is to recognize that much of the dust is produced in very dense circumstellar environments where three-body (and other) reactions to form H_2 will operate. In the interstellar clouds, however, where most of the hydrogen is H_2, the densities are much lower, and only surface reactions on dust (that has emerged from circumstellar regions) seem capable of generating the observed H_2.

From the dust number density and size distribution inferred from studies of interstellar extinction, one can deduce that the surface formation of H_2 on interstellar dust grains is required to be reasonably efficient; i.e. most H atoms arriving at a grain surface must leave as a part of a molecule. The energy budget has also been an important topic of discussion: how much of the energy released in the formation of H_2 appears as internal excitation, as kinetic energy, or is deposited in the grain itself? The answers to these questions affect the interpretation of H_2 observations and potential

Table 3: Timescales in star-forming regions

Process	Mechanism	Approx. timescale (y)	Timescale for $n_H = 10^4$ cm^{-3}
Collapse	Gravitation	$10^8/n_H^{1/2}$	10^6
Chemistry	Ion–molecule reaction	3×10^5	3×10^5
Cooling	Molecular radiation	$3\times10^9/n_H$	3×10^5
Ambipolar diffusion	Ion-neutral drift	$4\times10^5[X(i)/10^{-8}]$	4×10^5

X(i) is the fractional ionization, $X(i) = n(\text{ions})/n_H$ and is about 10^{-8} in dark interstellar clouds

heating mechanisms of gas and dust.

Early studies of the surface formation process have been largely superseded by huge advances in both experimental and theoretical capabilities. It is now possible to contemplate undertaking fairly realistic studies both in the laboratory and through numerical modelling. The H_2 formation problem has become the focus of a major experimental and theoretical effort at UCL, under the auspices of the UCL Centre for Cosmic Chemistry and Physics. The programme has been generously funded in a rare joint grant from EPSRC and PPARC.

The UCL experiment on H_2 formation

The experiment will be an advance on any recent work in that the reaction efficiency and the total energy budget will be determined simultaneously. A variety of reaction surfaces will be used, ranging from ideal crystalline to more realistic amorphous materials. The initial experiments will concentrate on carbons, though silicates will also be used. The apparatus is illustrated in figure 11. An H-atom source (on the left) provides a beam ($\sim10^{16}$ H cm^{-2} s^{-1}) that is cooled to 10–100 K, and mechanically chopped to give a pulsed H-atom beam (period $\sim10^{-5}$ s). This beam enters the chamber (on the right) and impinges on the substrate maintained at 10 K, and product molecules leaving the surface are ionized by a laser (visible in the foreground) and the ions formed are detected by a time-of-flight mass spectrometer. The background gas will have a pressure $<10^{-10}$ torr. These procedures will result in the determination of the recombination efficiency, the internal (v, J) excitation of the product H_2 and its translational energy.

Our results for the recombination efficiency will be compared with on-going theoretical work, and with experiments conducted by other teams. Pirronello *et al.* (1997a, b) have reported the results of experiments in which HD was formed from H and D atom beams at temperatures in the range 5–15 K on the surfaces of an olivine slab, at a pressure of 10^{-10} torr. The main results of those authors for those experiments were that the formation rate was low compared to earlier predictions (Hollenbach *et al.* 1971) that were in harmony with the observations. Clearly, more experimental study of this problem is required, and results from the UCL experiment should be available later this year.

Theoretical studies of H_2 formation are also underway in the UCL Centre. Preliminary results have been reported by Farebrother, Fisher and Clary (1999) for the formation of H_2 by the (vertical) approach of an H-atom directly on to another H-atom chemically bonded to a (horizontal) piece of graphite lattice (see Williams 1998). The system is extended by periodic boundary conditions. The entire system is treated quantum mechanically using the density functional method. The preliminary results for this direct approach (the Eley–Rideal mechanism) are that there is a barrier-free approach, that the reaction probability is very close to unity, and that the product H_2 has considerable internal excitation, with states v = 3 and 4 being highly populated. With the geometry used in this calculation, no rotational excitation can occur. The calculation is now being generalized to include H-atoms incident on the bound H-atoms at any angle. The diffusion approach (the Langmuir–Hinshelwood mechanism) will also be investigated.

Molecular Dynamics

These preliminary H_2 formation results can also be compared with a major study using the classical Molecular Dynamics approach (Takahashi *et al.* 1999a,b). The surface used in these experiments was amorphous H_2O ice, itself numerically prepared by Molecular Dynamics calculations. Then numerical experiments are performed in which an H atom collides with the ice surface and binds at an appropriate site. Subsequently, a second H atom interacts with the surface, and with the H atom. Many trajectories are explored. Both Eley–Rideal and Langmuir–Hinshelwood types of reaction are observed to occur, with high reaction probability, in these numerical experiments. The H_2 molecules are found to be in highly excited vibrational states, v = 5–8, and less than 5% of the H_2 bond energy appears in the surface.

Conclusions

Molecular hydrogen is not merely a passive reservoir of mass awaiting transformation into stars. It had an active role in promoting structure in the early universe, and by fuelling a chemistry in interstellar clouds it is active in controlling the processes in star formation. Molecular hydrogen is an ideal tracer of warm gas in interstellar and circumstellar regions, with a rich infrared spectrum. ●

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