

## H<sub>2</sub> formation in space: a negative ion route?

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**Abstract.** A new proposal is put forward for the formation of H<sub>2</sub> from H atoms in the interstellar medium based on the conjecture that efficient production of H<sup>-</sup> may take place at the surface of dust grains via attachment of weakly bound surface electrons. Subsequent gas phase associative detachment of H and H<sup>-</sup> forms H<sub>2</sub>.

The model is shown to be compatible with known properties of the interstellar medium in low and high density photodissociation regions and in the interior of dark clouds. Observation of H<sub>2</sub> IR emission in diffuse and dark clouds with the VLT and perhaps also of H<sup>-</sup> absorption, using the Far Ultraviolet Spectroscopic Explorer (FUSE), would provide useful tests of the model. The chief source of uncertainty in this proposal lies in the lack of data for binding energies of electrons to grains and thus in the feasibility of the H<sup>-</sup> surface formation process.

**Key words:** ISM: clouds – ISM: molecules – ISM: reflection nebulae – infrared: ISM: lines and bands

### 1. Introduction

The mechanism by which molecular hydrogen forms in the interstellar medium (ISM) is not firmly established. This creates considerable uncertainty in chemical models, for example for photodissociation regions (PDRs) in which the balance between destruction of H<sub>2</sub> through photodissociation and the formation of H<sub>2</sub> is a key factor (see Hollenbach & Tielens 1999).

Dust grains conventionally provide surfaces for the formation of H<sub>2</sub> from atomic hydrogen (e.g. Hollenbach & Salpeter 1970, 1971; Duley and Williams 1984). However, recent experimental investigations show that the range of grain temperatures for efficient H<sub>2</sub> formation is very limited on candidate grain surfaces, that is, amorphous carbon and olivine (Pirronello et al. 1997a,b, 1999; Biham et al. 1998; Katz et al. 1999). Indeed Katz et al. 1999 conclude that olivine cannot provide a suitable surface for H<sub>2</sub> formation under interstellar conditions. Amorphous carbon gives efficient production for surfaces at temperatures only between 9 K and 13 K, with an efficiency dropping sharply to zero at either limit. For comparison, grain temperatures in dense PDRs, for example, are typically several tens of degrees K (e.g. NGC7023: Whitcomb et al. 1981; Carey 1991).

Detailed simulations are required to evaluate the implications of these new experimental data. Evidently they constitute a serious problem for the conventional H<sub>2</sub> formation process as a general mechanism in the ISM. This raises the question of whether there may be two (or more) means by which H<sub>2</sub> forms in the ISM. For example in the warm PDR in Ophiucus, Boulanger et al. 2000 suggest reactions of H atoms with large protonated molecules or very small dust grains as a source of H<sub>2</sub>.

In the early Universe, the gas phase reaction of H<sup>-</sup> with H, first mentioned in connection with the Sun (Dalgarno 1999) is an important source of H<sub>2</sub> (e.g. Pagel 1959; McDowell 1961; Hirasawa et al. 1969; Takeda et al. 1969; Puy et al. 1993; Lepp & Stancil 1998; Galli & Palla 1998; Babb & Kirkby 1998). Formation of H<sub>2</sub> proceeds through radiative association



followed by associative detachment



Radiative association is the rate limiting step and is too slow to reproduce the rate of H<sub>2</sub> formation required in the ISM by observations (Jura 1975).

The essential feature of the current work is that the gas phase formation of H<sup>-</sup> by radiative association may be replaced by a process in which thermal hydrogen atoms attach an electron located on the surface of dust grains. This may provide a more efficient route for the formation of H<sup>-</sup>. Subsequently reaction (2) forms H<sub>2</sub> in the gas phase. There are insufficient experimental data to determine the feasibility of the surface formation of H<sup>-</sup>. The present work therefore seeks to show that the suggested mechanism is viable, in that it does not conflict with any well-established knowledge of the nature of the ISM.

A central issue is that the binding energy, relative to vacuum, of electrons attaching on the surface of grains is unknown. The energy of the conduction band relative to the vacuum level remains undetermined for olivines or for ices (adsorbed onto the surface of grains), noting that electrons adsorbing on the surface of insulators will enter into the conduction band. MgO may give an indication for bulk olivines, with a conduction band lying  $\sim 1$  eV below the vacuum level (Deutscher et al. 1999).

In the bulk of the conducting material graphite, the bottom of the conduction band is located at the Fermi level and the

binding energy of electrons relative to vacuum is given by the work function of 4.5 eV (see Boettger 1997). However grains are likely to have been processed, for example by high energy particle bombardment in J-type or C-type shocks (Tielens et al. 1994; Flower & Pineau des Forêts 1995; Field et al. 1997). In laboratory experiments to make diamond-like carbon, carbon films are generally formed by impact of C (and C<sup>+</sup>), with inclusion of up to 30% H, with particle energies of  $\sim 100$  eV. For carbon, this corresponds to a velocity of  $\sim 40$  km s<sup>-1</sup> which is fortuitously similar to impact velocities encountered in C-type shocks. Material so formed has conduction bands which lie very little below the vacuum level, or indeed lie above the vacuum level (see for example Himpfel et al. 1979; Silva et al. 1998; Robertson 1998; Diederich et al. 1999). Hence processed graphitic material in space may bind adsorbed electrons very weakly, providing an exothermic channel for H<sup>-</sup> formation. Expressed in electrostatic terms (Jackson 1962; Draine & Sutin 1987), processed graphitic surfaces display a very weak attractive image force retaining electrons on the surface. The properties of olivines following particle bombardment are unknown but a determination of the conduction band energies relative to vacuum would clearly be of interest.

For the purposes of the present work we assume that surface electrons are bound by an energy less than the electron affinity of H (0.75 eV) less the binding energy of H to the surface, 32 meV and 57 meV respectively for olivine and amorphous carbon (Katz et al. 1999). The latter energy should be included if a Hinshelwood mechanism operates (see below).

## 2. H<sub>2</sub> formation

The present proposal introduces a reservoir of electrons stored in negative ions, primarily H<sup>-</sup>. We show in Sect. 2.1 that this reservoir represents a negligible perturbation to the distribution of charge within the gas. We also consider other processes, such as photodetachment, which may compete with associative detachment in removing H<sup>-</sup>. In Sect. 2.2, the mobility of electrons on a grain surface is discussed. In the concluding remarks in Sect. 3, experimental, theoretical and observational aspects of the model are mentioned.

The surface formation of H<sup>-</sup> may take place through either a Rideal-Eley mechanism, a Hinshelwood mechanism or a combination. In a Rideal-Eley mechanism, a gas phase H atom removes an electron directly from a grain surface. This is appropriate if there are abundant electrons on the grain surface (see Sect. 2.2). A mechanism may also be envisaged whereby an electron encounters the grain and attaches to an adsorbed H atom via a Rideal-Eley process. This may operate if there is extensive coverage of H, for example on a cold grain. In a Hinshelwood mechanism, a gas phase H atom adsorbs on the surface and then forms H<sup>-</sup> through diffusive exploration of the surface by H and electrons. The Hinshelwood mechanism is very similar to the standard H + H formation process, but here one adsorbed H atom is replaced by an electron on the surface.

It is not evident that a surface adsorbed H atom reacting with a surface adsorbed electron would necessarily lead to

evaporation of the resultant H<sup>-</sup>. If the assumption of a negligible image force, as suggested above for electrons, may be extended to H<sup>-</sup>, then H<sup>-</sup> would not be retained on the surface electrostatically. However H<sup>-</sup> may become bound to the surface by chemical forces. H<sup>-</sup> on the surface (however bound) could for example react with a surface-mobile H, perhaps enhancing the efficiency of H+H recombination on a grain surface. In addition if a grain is overall positively charged, for example in a diffuse region, then H<sup>-</sup> would require some kinetic energy to escape the surface. For example an energy of 14 meV (170 K) would be required to escape a grain of radius 0.1  $\mu$ m with a single positive charge. Retention of H<sup>-</sup> on the surface is not considered further in the present work for lack of appropriate data.

### 2.1. Abundances of H<sup>-</sup>

The formation rate of molecular hydrogen in the standard model is given by a rate of hydrogen atoms adsorbing on grains, multiplied by an efficiency for conversion of adsorbed H atoms into H<sub>2</sub> via a surface chemical reaction. The formation rate in the present case is given in a very similar manner, again by a rate of H atoms striking grains, but now multiplied by an efficiency for conversion of H into gas phase H<sup>-</sup> through attachment of an electron at the surface. The rate of reaction of H<sup>-</sup> in the gas phase with H atoms to form H<sub>2</sub> is effectively instantaneous on the timescale of production of H<sup>-</sup> by collision with grains. The relative efficiency of the standard surface and negative ion mechanisms is given simply by the relative efficiency of conversion of H atoms into H<sub>2</sub> at the surface and the efficiency of H<sup>-</sup> production at the surface.

The rate of formation of H<sub>2</sub> per cm<sup>3</sup> may be expressed as  $k.N.n(H)$ , where N is the total number density ( $= n(H) + 2n(H_2)$ ) in the medium,  $n(H)$  is the number density of H atoms and  $k$  is an effective second order rate coefficient. If a typical average grain population is assumed with radius 0.1  $\mu$ m, density 3 g cm<sup>-3</sup>, grain to gas mass ratio = 10<sup>-2</sup>, then at temperature T,  $k$  may be estimated to be  $\sim 6.6 \times 10^{-18} T^{1/2}$  cm<sup>3</sup> s<sup>-1</sup> for unit electron attachment efficiency of H at the surface.

The effective second order rate coefficient  $k$  has a value, given unit surface attachment efficiency, which is the same as that associated with the standard mechanism of H<sub>2</sub> formation, which also assumes unit efficiency at the surface. This arises since the rate of H<sub>2</sub> formation is effectively first order in the H atom concentration in both cases and the rate determining step is the flux of H to the surface. Since  $k \sim 1-3 \times 10^{-17}$  cm<sup>3</sup> s<sup>-1</sup> is the value required to match observations (Jura 1975), the present proposal suffers the same constraint as the standard model, that the efficiency of the surface process be high.

The steady-state gas phase abundance of H<sup>-</sup> implied by the model may be estimated by considering the formation and destruction pathways and is given by

$$n(H^-) = k.N.n(H) / (k^{(-)}n(H) + k^{ph} + k^{(+)}n(I^+) + k^{add}) \quad (3)$$

where  $k^{(-)}$  is the rate coefficient for the reaction of H with H<sup>-</sup>, reaction (2), with a value of  $1.3 \times 10^{-9}$  cm<sup>3</sup> s<sup>-1</sup> (Schmeltekopf

et al. 1967).  $k^{ph}$  is the rate coefficient for photodetachment, integrated over all wavelengths, with a value of  $3.4 \times 10^{-8} \text{ s}^{-1}$  for the unshielded ISM (Rawlings et al. 1988).  $k^{(+)}$  is the rate coefficient for removal of H<sup>-</sup> through reaction with all positive ion species, number density  $n(I^+)$ , with a value of  $4 \times 10^{-6} T^{-1/2} \text{ cm}^3 \text{ s}^{-1}$ , assumed insensitive to the nature of the positive ion (Dalgarno & McCray 1973).  $k^{add}$  refers to additional processes which are considered separately below and are found to contribute negligibly to H<sup>-</sup> destruction under the various conditions under which H<sub>2</sub> formation takes place.

Three different environments are considered, the interior of a dark cloud, the diffuse region at the borders of such a cloud and a dense photodissociation region (PDR). The number density of H and of positive ions may be specified as follows. Turning first to a dark cloud, the equilibrium density of H atoms is given approximately by the cosmic ray ionizing flux, expressed as a frequency,  $\zeta/10^{-17} \text{ cm}^{-3}$  (e.g. Le Bourlot et al. 1995) and is thus independent of total number density. A figure of between 1 and  $5 \text{ cm}^{-3}$  may therefore be appropriate. Measurements of  $n(\text{H})$  have however been made in the dark cloud L134 (van der Werf et al. 1988) which show a considerably larger value lying between 30 and  $40 \text{ cm}^{-3}$ . The authors suggested that this may indicate incomplete H to H<sub>2</sub> conversion and that this may in fact be typical of a dark cloud. We adopt the observational figure of (say)  $30 \text{ cm}^{-3}$  and a temperature of 10 K. The number density of positive ions may be estimated, following Oppenheimer & Dalgarno 1974, from  $[I^+] \sim 3.4 \times 10^{-5} N^{2/3} \delta^{1/3}$ , where the prevalent ion may be assumed to be Na<sup>+</sup>.  $\delta$  is the factor of elemental depletion, assumed to be 0.1. Using L134 as an example, the core has a density of  $1.2 \times 10^4 \text{ cm}^{-3}$  (van der Werf et al. 1988) and the degree of ionization is correspondingly  $\sim 7 \times 10^{-7}$ , suggesting a total ion concentration of  $\sim 8 \times 10^{-3} \text{ cm}^{-3}$ . In a dark cloud, the photo-detachment rate coefficient in Eq. 3 is unimportant since the flux of radiation generated within a dark cloud through cosmic ray events yields a negligible radiation field for photodetachment (Le Bourlot et al. 1995). Ignoring for the present  $k^{add}$ , Eq. 3 yields a number density of H<sup>-</sup> of  $\sim 1.5 \times 10^{-4} \text{ cm}^{-3}$ . Thus the charge carried by H<sup>-</sup> in these regions is  $\sim 2\%$  of the total.

Moving to diffuse photodissociation regions at the borders between a dark molecular cloud and the intercloud medium, there may for example be a total number density of  $500 \text{ cm}^{-3}$ , with about 20% of H-nuclei in the form of H<sub>2</sub> and 80% as H atoms, with a temperature of (say) 300 K. Ionization in this region is dominated by C<sup>+</sup> and may typically be as high as  $10^{-4}$  or more (van Dishoeck 1998). Assuming that the interstellar radiation field is unshielded, Eq. 3 yields a number density of H<sup>-</sup> of  $\sim 4 \times 10^{-5} \text{ cm}^{-3}$ . The charge carried by H<sup>-</sup> in these regions is therefore less than 0.1% of the total. In addition, in the diffuse medium specified here the removal of H<sup>-</sup> by reaction with H to form H<sub>2</sub> is  $\sim 4$  times more rapid than the removal by positive ions, represented by  $k^{(+)n(I^+)$  in Eq. 3.

With regard to the relative importance of reaction of H<sup>-</sup> with H and photodetachment of H<sup>-</sup> in diffuse regions, the photodetachment rate of H<sup>-</sup> and the H<sub>2</sub> formation rate are equal for an H atom concentration of  $25 \text{ cm}^{-3}$ . Passing from the intercloud

medium into a molecular cloud, H:H<sub>2</sub> ratios would reflect the balance between associative detachment, photodetachment of H<sup>-</sup> and photodissociation of H<sub>2</sub> (Jura 1975), with reactions between H<sup>-</sup> and positive ions also playing a role, as indicated above. Visual extinction eventually suppresses both photodissociation, at  $A_v$  of unity, and photodetachment at  $A_v$  of (say) 10 magnitudes. Accurate estimates of the H/H<sub>2</sub> ratio require detailed modeling taking account of density profiles, but it is evident that diffuse clouds are predicted to be surrounded by a halo containing H atoms to a depth of a few tenths to  $\sim 1$  pc. Substantial column densities of H are observed in the direction of clouds such as  $\zeta$ Oph,  $\delta$ Per and  $\xi$ Per (Bohlin et al. 1978; Wagenblast 1992) consistent with both the present and the standard models of H<sub>2</sub> formation.

Turning to dense PDRs associated with reflection nebulae, the proximity of a hot star yields a radiation field which may be several thousand times the average interstellar field. For example in NGC2023, there is a region of vibrationally excited H<sub>2</sub> emission close to the exciting B-star, where the radiation field is  $\sim 5000$  times the average field and the number density has been estimated to be  $\sim 10^5 \text{ cm}^{-3}$  (Field et al. 1998). The gas has a high proportion of H atoms in the emitting region. The photodetachment rate coefficient is  $1.7 \times 10^{-4} \text{ s}^{-1}$  and the pseudo-first order rate coefficient for the formation of H<sub>2</sub> is  $1.3 \times 10^{-4} \text{ s}^{-1}$  for  $n(\text{H}) \sim N$ . Thus the processes of reaction with H atoms to form H<sub>2</sub> or to photodetach compete strongly in such a region. In this connection, the value of  $A_v$  in NGC2023 is only  $\sim 10^{-2}$  at a distance of  $10^{-4}$  pc into the illuminated gas, where most of the H<sub>2</sub> emission is formed. Assuming that the degree of ionization does not exceed a few  $\times 10^{-3}$ , the influence of H<sup>-</sup> removal by positive ions is not important in these regions, noting that the temperature is  $> 500$  K (Lemaire et al. 1999).

Collisional detachment of H<sup>-</sup> with H atoms and with gas phase electrons



are additional mechanisms that may in principle compete with reaction of H<sup>-</sup> with H to form H<sub>2</sub>. Reactions (4) and (5) are represented by  $k^{add}$  in Eq. 3. Reaction (4) however takes place only at higher kinetic energy and can be ignored (Esaulov 1986). Reaction (5) has been studied in detail by Vejby-Christensen et al. 1996 and has a threshold energy of 1.5 eV. Reaction (5) is therefore unlikely to influence the chemistry of H<sup>-</sup> in the present context.

Associative detachment forms nascent populations of H<sub>2</sub> preferentially in  $v=6,7,8,9$  states (Black et al. 1981; Launay et al. 1991; Cizek et al. 1998). Vibrationally excited H<sub>2</sub> rapidly undergoes dissociative attachment, the reverse of reaction 2 (see Gauyacq 1985). For example H<sub>2</sub>( $v=8$ ) in collision with low energy electrons forms H + H<sup>-</sup> with a rate coefficient between  $10^{-8}$  and  $10^{-9} \text{ cm}^3 \text{ s}^{-1}$ . Vibrational lifetimes for fluorescent emission however lie between  $10^5$  and  $10^6$  s (e.g. Black & Dalgarno 1976) and therefore vibrational relaxation through fluorescence takes place very much more rapidly than dissociative attachment.

## 2.2. The mobility of electrons on grain surfaces

In shielded regions, grains of characteristic size around 0.1  $\mu\text{m}$  will tend to carry one or a few net negative charges (Draine & Sutin 1987 and references therein). If grains are unshielded, for example in diffuse regions, or are subjected to a powerful radiation field, as in dense PDRs, the net charge on grains may become positive rather than negative through photoemission of electrons (Watson 1972; Feuerbacher et al. 1973; Bakes & Tielens 1994). The dynamic equilibrium which maintains the grain charge is essentially unaffected by the efficient circulation of charge between the surface and the gas phase implied by the negative ion route for H<sub>2</sub> formation. The reason is that electrons, removed from the surface as H<sup>-</sup>, are rapidly reintroduced into the gas phase, through reaction of H<sup>-</sup> with H, and therefore remain available for adsorption at grain surfaces. The charge balance with for example net negative charge on the grain is retained unchanged.

When a grain surface has a net charge of (say) 1 electron, does this imply a single electron on the grain or an excess of one electron over the number of positive ions on the grain? The first model would arise from mobile electrons recombining with ions on the surface, and the second from immobile electrons and ions on the surface with charges distributed over the entire surface of a grain (Umebayashi & Nakano 1980). Electron mobility further determines whether surface electrons will migrate to the deepest sites available or remain on more weakly bound sites. Electron mobility also relates to the Hinshelwood surface mechanism, which would be facilitated if rapid surface electron diffusion is possible.

In order to investigate electron mobility, a model is adopted in which favourable adsorption sites are assumed to be separated by some mean distance which is typically very much greater than the surface atom separation (Smoluchowski 1979, 1981). Motion on the surface is achieved by tunneling through the barrier binding the electron to its current site to a nearby available site. The length of the barrier is taken to be the average distance apart of adsorption sites. Thus we estimate below the requisite mean separation of binding sites such that an electron can tunnel from one site to an adjacent site within a specified time through a single tunneling event. Using standard theory of tunneling, the average separation of sites,  $d$ , such that electrons can migrate to an adjacent site within some time,  $t$ , may be expressed as

$$d = (\hbar/(2m_e E_b)^{1/2}) \times \sinh^{-1}[(2\sqrt{2}E_{th}/m_e^{1/2}\pi r)^{1/2}(t/E_b^{1/2})^{1/2}] \quad (6)$$

where  $m_e$  is the electron mass,  $E_b$  is the barrier against tunneling, with a value which is some fraction of the electron surface binding energy,  $E_{th}$  is the thermal energy, given by the grain temperature, and  $r$  is the extension of the surface vibration of the bound electron ( $\sim 1\text{\AA}$ ).

Two values of  $E_b$ , 75 meV and 700 meV, are used for illustration, the upper value chosen as the limit for which surface H<sup>-</sup> formation is exothermic. Positive ions are less mobile than electrons on the surface and, for simplicity, positive ions are in fact assumed immobile. The time  $t$  is the residence time

either of electrons or of positive ions on the surface, and values are not known. Neutralization of positive ions such as C<sup>+</sup> may take place by recombination with valence electrons in the solid (Draine & Sutin 1987) and the residence time  $t$  may then be that of atoms on the surface. Such a process would not be available to ions of lower ionization potential, such as Na<sup>+</sup> on grains in dark clouds. Hence values of residence time,  $t$ , are likely to be strongly dependent on the grain environment. Values of  $d$  are however rather insensitive to the choice of  $t$ , which is characterized here in terms of a surface binding energy of 50 meV (Katz et al. 1999) and two values of grain temperature,  $T_g$ , of 15 K and 50 K. The residence time then becomes  $6 \times 10^4$  s at 15 K and  $10^{-7}$  s at 50 K (Smoluchowski 1979). For  $E_b = 75$  meV,  $T_g = 15$  K and 50 K,  $d = 15$  nm and 11.5 nm respectively. For  $E_b = 700$  meV,  $T_g = 15$  K and 50 K,  $d = 5$  nm and 2 nm respectively. The conclusion that can be drawn is that for a substantial range of conditions an adsorbed electron may be able to interact with an ion (or an atom) if the nearest sites lie between 5 and 10 nm apart. On this basis, a grain of radius 0.1  $\mu\text{m}$ , surface area  $1.3 \times 10^5 \text{ nm}^2$ , may be able to accommodate a steady state surface population of the order of a thousand electrons and ions. If the radius of each site is  $\sim 0.2$  nm, there are about  $10^6$  sites on a typical grain surface. Thus 1 part in  $\sim 10^3$  of surface atoms on the grain may be populated by electrons. This may favour a Hinshelwood mechanism for cold grains. If the distance between adsorption sites is less than the values of  $d$  estimated above, a succession of tunneling events may take place during residence lifetimes. The surface will then tend to be further depleted of electrons and positive ions.

## 3. Concluding remarks

The H<sup>-</sup> model proposed here explains in a natural way why H atoms at number densities of a few tens per  $\text{cm}^3$  in diffuse regions convert to H<sub>2</sub>, through the balance of the H+H<sup>-</sup> pseudo-first order rate coefficient and the photodetachment rate coefficient for H<sup>-</sup>. The mechanism may also function under a very wide range of physical conditions and does not depend on fine tuning of the grain temperature.

There is however considerable uncertainty surrounding the proposal that H<sup>-</sup> may form efficiently at grain surfaces. The following questions arise:

- (i) What are the binding energies of electrons to the surface of insulators and amorphous graphite, including the case for which surfaces have been processed through contact with the interstellar plasma?
- (ii) How mobile are adsorbed electrons on grain surfaces?
- (iii) Do surface-adsorbed electrons react with surface adsorbed molecules and positive ions (Umebayashi & Nakano 1980), and, if so, under what conditions of temperature and number density?
- (iv) Can gas phase negative ions be readily formed by cold atoms and molecules removing electrons from the surface of grains and what is the efficiency of these processes for hydrogen atoms and other species (e.g. O, C etc.)? If other atoms or molecules may form negative ions through

surface attachment, this may have consequences for gas phase chemistry. For example O<sup>-</sup> formation may provide routes to H<sub>2</sub>O, CO<sub>2</sub>, NO etc. through reaction with H<sub>2</sub>, CO and N-atoms (Dalgarno & McCray 1973).

Theory and experiment will be of value in addressing these problems. An estimation of binding energies of electrons at insulator surfaces may be made for example for olivines (Catlow & Price 1990), at any rate for unprocessed material. The formation of H<sup>-</sup> at the surface should then be amenable to theoretical modeling.

The emission spectrum of H<sub>2</sub> arising from formation via H+H<sup>-</sup> has been investigated in some detail by Black et al. 1981. The associative detachment process yields an IR emission spectrum of H<sub>2</sub> which is quite distinct from that of PDRs or shocks, and is dominated by strong, pure rotational transitions of high J in v=1, 2 and 3. This contrasts quite sharply with PDR emission, for example, which tends to be dominated by lower J rovibrational transitions in v=1-0, 2-1 and higher v states (see for example Black & van Dishoeck 1987). Moreover states of H<sub>2</sub> with J > 20 may be generated through associative detachment (Launay et al. 1991). Emission from very high J states has indeed been observed in PDRs in ISO observations (Rosenthal et al. 2000).

Turning to future observational possibilities, estimates show that the K-band (2 μm) spectrum of H<sub>2</sub> emission in the interior of dark clouds and in the diffuse haloes around these clouds may be detectable using the VLT ISAAC instrument (observations scheduled for March 2001). Such a spectrum could show a fingerprint of the associative detachment mechanism of H<sub>2</sub> formation. In addition, absorption of H<sup>-</sup> in the FUV at 1132.071 Å (Balling et al. 2000) in diffuse regions over a pathlength of ~1 pc may have an equivalent width of more than 0.5 mÅ and may therefore be detectable using the Far Ultraviolet Spectroscopic Explorer (FUSE) (J.H.Black: private communication; application submitted to FUSE). The proposal that a negative ion route may contribute to H<sub>2</sub> formation is therefore open to experimental, theoretical and observational studies.

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