The formation of interstellar H$_2$ on amorphous silicate grains

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Summary. A mechanism by which H$_2$ is formed on interstellar amorphous silicate grains is proposed. The mechanism differs from previous proposals in the method of stabilization of the reacting complex, in which the stabilization energy is transferred to a surface band. The reaction to form H$_2$ is promoted by H atom quantum mechanical tunnelling. The model predicts that the H$_2$ on formation is ejected into the gas kinetically and vibrationally excited but rotationally cool. Subsequent collisions thermalize the kinetic energy and populate the rotational levels. The consequences of these predictions for the observed H$_2$ excitation, for interstellar chemistry, and for H$_2$ re-formation behind fast shocks are briefly explored.

1 Introduction

Molecular hydrogen is observed to be widespread in the diffuse interstellar medium and is inferred to be the major form of hydrogen in dense clouds. It is the seminal molecule on which the formation of all other molecules depends. It provides in its rotation–vibration spectrum a cooling mechanism for shock- or radiation-heated clouds. Considerable uncertainty, however, attends the H$_2$ formation mechanism. It is widely recognized that two-body gas-phase mechanisms involving electrons or protons as catalysts: H(e, $h\nu$)H$^-$(H, e)H$_2$ and H(H$^+$, $h\nu$)H$_2^+$(H, H$^+$)H$_2$ – are ineffective except in special circumstances where the level of ionization is unusually high. Three-body reactions: 3H$\rightarrow$H$_2$+H – are ineffective at number densities n(H)<10^{11} cm^{-3} and do not contribute significantly in the interstellar medium. Therefore, it is now accepted that H$_2$ is formed at the surfaces of interstellar grains, in an efficient process in which nearly every H atom arriving at the grain surface leaves as part of an H$_2$ molecule (see e.g. Duley & Williams 1984).

Although some progress in investigating this process was made in terms of grain temperature restrictions, active-site binding energy, etc. (e.g. Gould & Salpeter 1963; Stecher & Williams 1965; Hollenbach & Salpeter 1970, 1971; Barlow & Silk 1976; Duley & Williams 1984), a detailed investigation of the surface process has had to wait until the nature of the grain surface was reasonably well understood. In this paper, we adopt a conventional amorphous and disordered silicate model for the grains. Recent laboratory work shows that this material has sites of low

coordination similar to those sites occurring on oxide surfaces (see Duley, Millar & Williams 1978). We describe in detail how these sites act to catalyse H_2 formation and how the formation process leads to a strong prediction concerning the v'', J'' state of the H_2 molecules liberated from grains. Earlier work in describing the product state of H_2 on formation has been limited to Monte Carlo modelling of classical atoms on either a rigid (Hunter & Watson 1978) or classical (Leonas & Pjarnpuu 1981) lattice. These models make conflicting predictions. It is our contention that the true nature of the surface must be considered, and that the quantum mechanical nature of the H atoms cannot be neglected.

2 Amorphous silicates

Although a perfect silicate lattice is a covalent structure, a surface is a major defect in this structure resulting in the creation of low coordination sites. It was shown some time ago (Duley *et al.* 1978) that oxygen ions at specific low coordination sites on oxide surfaces give rise to an absorption around 4.6 eV which was capable of explaining the interstellar extinction peak at 220 nm. The carrier of this 220 nm feature is conventionally identified with graphite grains, but the alternative identification of the carrier with oxide or silicate grains is supported by the lack of correlation between carbon depletion and the 220 nm strength found by Millar (1979) and Duley (1985). More recently, 220 nm absorption from amorphous silicates has been demonstrated in the laboratory (Steel & Duley 1985, unpublished work). As for the oxide case, the carrier appears to be a surface species of low coordination, most likely OH^- surface groups. Such hydroxylated structures are expected to be common on oxides and amorphous silicates in the interstellar medium (Jones, Williams & Duley 1984) because of the preponderance of atomic H. Very small grains (radius ~ 10 nm) are inevitably the most disordered as they have the largest surface to bulk ratio and the surfaces of such grains are expected to be covered by OH^- sites. It is important to realize that this population of small grains, which is known to be present because of the steep rise in the far-UV extinction, contribute a large fraction of the total grain surface area per unit volume of the interstellar medium (Duley & Williams 1984). The observed lack of correlation between far-UV extinction and 220 nm absorption is explained in this model by the fact that the former is due to a bulk effect and the latter is a surface effect. Variations in grain size and environment from place to place negate any expected correlations between these observed quantities.

Because of the high surface coverage by OH^- sites, individual vibrational resonances will form a surface band, whose energy is given by $\hbar\omega \simeq 0.4$ eV, the energy of the OH stretching vibration. The width of this surface band, ΔE, will be typical of that of infrared vibrational resonances, i.e. $\Delta E \simeq 0.1$ eV. Such OH^- sites, many of which will be adjacent to lattice vacancies, are plausible locations for H_2 formation.

3 The H_2 formation mechanism

The interaction between an H atom and an OH^- surface ion is indicated schematically in Fig. 1. Measurements of the interaction energy are not available, and we have therefore estimated the depth of the potential well on the assumption that the interaction is of a charge-induced dipole, truncated by a steep nuclear repulsion at an internuclear separation equal to the sum of the classical radii of H and O^-. This gives an estimate of 0.4 eV. Unless some of the energy can be removed from the $H \cdot OH^-$ complex in one vibrational period the H atom will merely be scattered and no further interaction occur. Energy removal can occur because of a near resonance between the energy of the surface OH^- band and the $H + OH^-$ excess energy, with the transfer occurring as indicated schematically in Fig. 1. Energy is thus delocalized from the $H - OH^-$ system and the
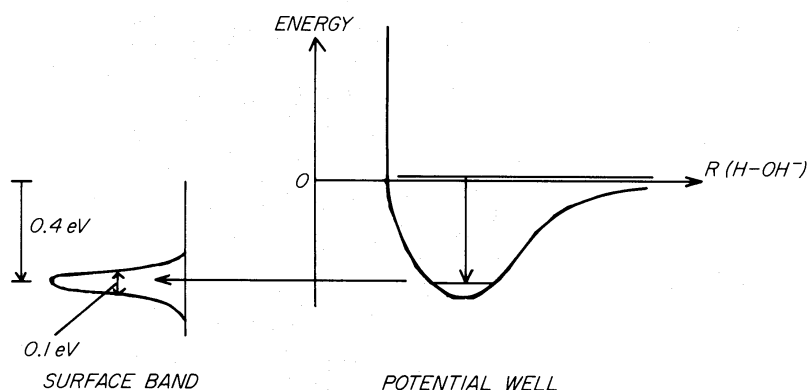
Figure 1. The interaction of H and OH_s^-. At the minimum of the potential energy curve, the interaction energy is about 0.4 eV. This energy can be transferred to (and delocalized in) the surface band arising from the surface oscillators of which the OH_s^- group is a member.
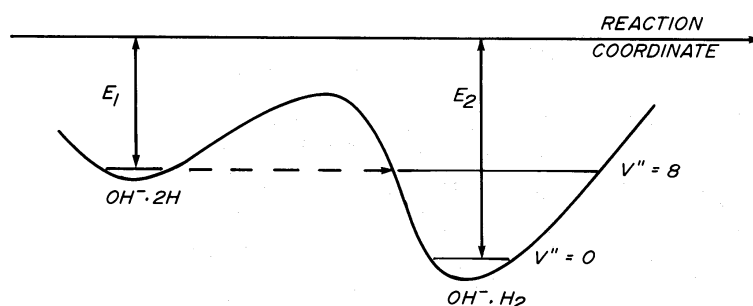
Figure 2. Schematic diagram representing the rearrangement reaction $OH^- \cdot 2H \rightarrow OH^- \cdot H_2$. The energy $E_1 = D(OH^- - H) + D(OH^- \cdot H - H)$. The energy $E_2 = D(OH^- - H_2) + D(H - H)$. The energy appearing internally in H$_2$ is, therefore, $(E_2 - E_1)$, which is about 4 eV (see text). The final v'' state on formation of H$_2$ is then $v'' < 8$.

complex can be stabilized. The overall process can be represented

$$H + OH_s^- \rightarrow (H \cdot OH^-)_s^* \rightarrow H \cdot OH_s^- + h\nu.$$

The incident H atom is now trapped and is retained at the site during thermal fluctuations. Rearrangement reactions within the $OH^- \cdot H$ group via quantum mechanical tunnelling are possible if an exothermic channel exists. However, the OH^- bond energy is probably too large to permit a rearrangement to form H$_2$ (Huber & Herzberg 1979) and the site remains in the form indicated. An additional H-atom may also be bound to the site by a process similar to that illustrated in Fig. 1. The excess energy is again delocalized from the group, so that a new complex is formed

$$OH_s^- \cdot H + H \rightarrow OH_s^- \cdot (2H) + h\nu.$$
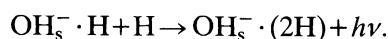
An exothermic rearrangement is now possible (see Fig. 2)

$$OH_s^- \cdot (2H) \rightarrow OH_s^- \cdot H_2^*.$$
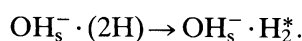
If any barrier exists (as shown in Fig. 2) it is likely to be small. In any case, H atoms are very mobile because of quantum mechanical tunnelling (Leitch-Devlin & Williams 1984), and the time-scale of this rearrangement is very much less than that of any other possible interstellar process.

The energy E appearing in the excited H$_2$ molecule is

$$E = D(OH^- - H_2) + D(H - H) - D(OH^- - H) - D(OH^- \cdot HH).$$
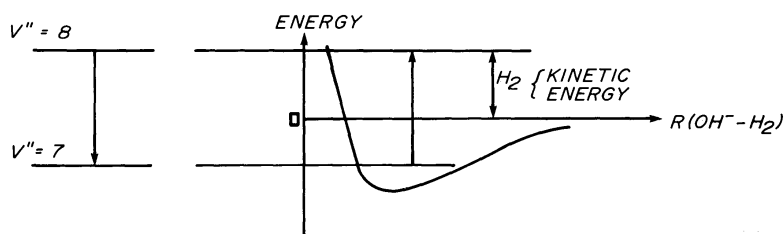
Figure 3. The diagram represents the transfer of one H_2 vibrational quantum to the $OH^- - H_2$ bond, with resultant kinetic energy in the H_2 molecule.

The major contribution to E is from $D(H-H) \simeq 4.5\,\mathrm{eV}$. All other terms are polarization energies (typically $\gtrsim 0.5\,\mathrm{eV}$), and so $E \simeq 4\,\mathrm{eV}$, equivalent to about eight vibrational quanta in the $H-H$ band. As shown in the diagram (Fig. 3), the transfer of one of these quanta into the $OH^- - H_2$ bond will break it, resulting in free H_2 with kinetic energy $h\nu(H_2) - D(OH^- - H_2)$ which we estimate to be about $0.1-0.2\,\mathrm{eV}$. Note, however, that if our estimate of $D(OH^- - H_2)$ is too low, then the transfer of *two* H_2 quanta should release the H_2 and the kinetic energy estimate is then $2h\nu(H_2) - D(OH^- - H_2)$. It is a particular characteristic of this mechanism that the kinetic energy of the released molecules is not Maxwellian but has a discrete value which is however, broadened by the bandwidth of the $OH^- - H_2$ bond (see Fig. 1). Once the H_2 is ejected, the OH_s^- site is immediately available again for H_2 formation.

The rotational state of H_2 immediately on formation may also be determined. The impact parameter for capture of the H atom by the OH^- ion is about $2\,\mathrm{Å}$. If the H atom is thermalized at a temperature $\sim 10\,\mathrm{K}$, then the initial total angular momentum is about (or less than) that in the $J=1$ level. The newly formed molecule cannot, therefore, have high rotational excitation; we expect $J=0$ or $J=1$ on formation.

The model predicts, therefore, that H_2 molecules are ejected from the surface in the following state: kinetic energy $< 0.2\,\mathrm{eV}$, $v'' \leq 7$, $J'' \leq 1$.

The time-scale for collisions with other H_2 molecules or with H atoms in the interstellar gas is $\sim (10^{10}/n)\,\mathrm{s}$, and the time-scale for radiative relaxation between in the vibrational levels is $\sim 10^7\,\mathrm{s}$ (Black & Dalgarno 1976). Collisional processes involving other H_2 molecules will tend to partition any excess vibrational excitation. Both processes reduce the vibrational excitation, and the kinetic energy is converted into rotational excitation. Thus, after several collision times, we expect to find H_2 with thermal kinetic energy, in a vibrational state with $v''=0,1$, and in a rotational state with $J'' < 6$. Collisional relaxation of the $v''=1$ excitation in H_2-H_2 interactions is unfavourable, so the final stage of relaxation occurs radiatively.

4 Discussion

The mechanism described here depends on the delocalization of the energy of stabilization in the initial collision. The requirement is, therefore, for a surface band of appropriate energy and width to accept the stabilization energy. When this stabilization is achieved, there is ample time for the rearrangement to occur. It is clear that OH^- sites are not unique in this respect, and that other types of grains may also have suitable properties. However, the detailed predictions derived on the basis of other grain models (i.e. the resulting v'', J'' states) would be different.

The overall H_2 formation rate by this mechanism will have the form and value of the canonical expression (see, e.g. Duley & Williams 1984). We interpret the relatively high formation efficiency required by the observations as implying that most grains do indeed have surface bands arising from surface oscillators of the kind described here. This is certainly consistent with the constraints from grain optics. However, if the small grain component is absent in some particular
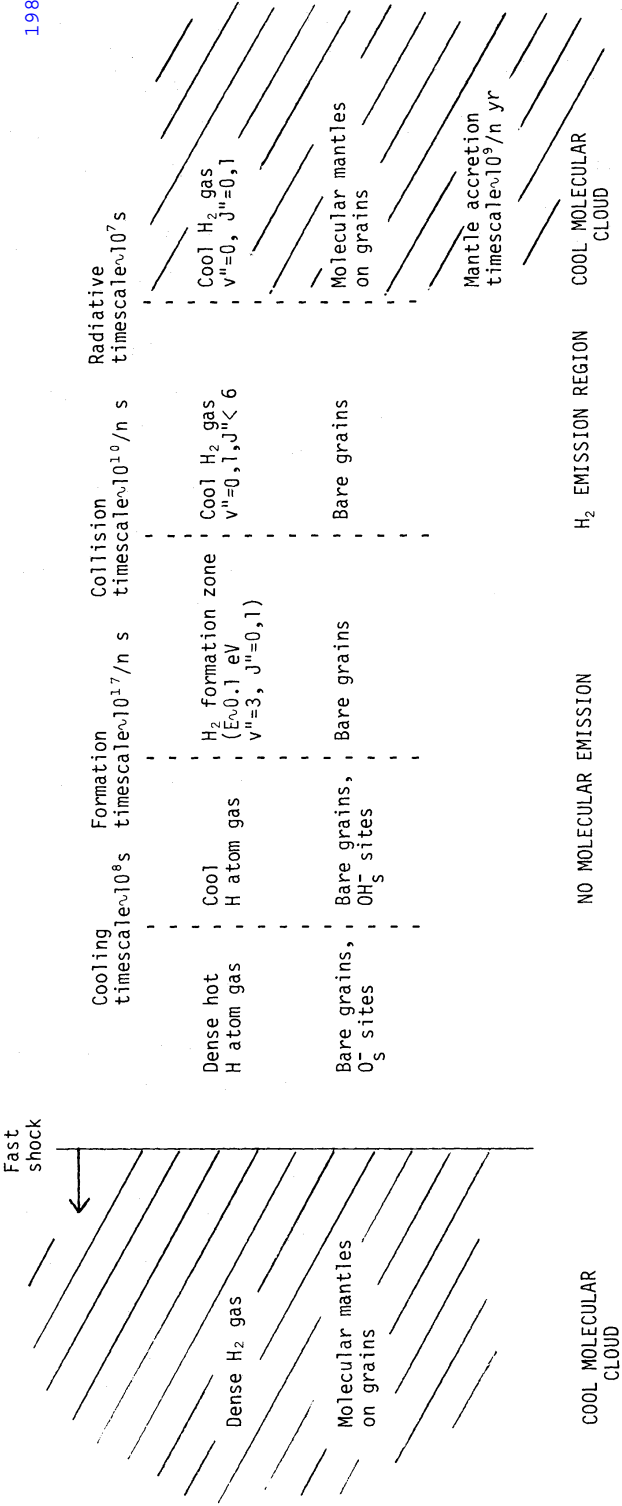
Figure 4. Processes occurring behind a dissociating shock.

sources (as indicated by reduced far-UV extinction) then we may also expect a reduced H_2 formation rate in these regions, with consequent effects on the rest of interstellar gas-phase chemistry.

The mechanism also suggests that formation of H_2 in excited rovibrational states tends to overpopulate the $v''=1$ level, which then radiatively relaxes. This level is also populated by radiative pumping in the Lyman and Werner bands and by collisions in shocked regions. The emission is now widely observed (*cf.* Shull & Beckwith 1982). We note that $H_2(v''=1)$, unlike the ground-state molecule, is chemically reactive with O, C, and C^+. Indeed, the first reaction schemes to be proposed for interstellar ion–molecule chemistry were based on this means of activation (Stecher & Williams 1972; Williams 1974). With the observation of widespread $H_2(v''=1)$ (e.g. in Orion, *cf.* Scoville *et al.* 1982) the effects on the chemistry should be re-examined, as the results may show some differences from conventional ion–molecule schemes which are driven by cosmic ray ionization.

Finally, we consider the situation behind fast ($v_{shock}>45\,\mathrm{km\,s^{-1}}$) H_2 dissociating shocks (see Fig. 4). Behind such a shock the gas consists essentially of atomic H, and any molecular mantles on the grains will have been removed. The grains should now show the O^- surface sites which will be converted to OH^- sites when the gas has cooled. Following this, H_2 formation occurs producing H_2 ($v''\sim1$, $J''\sim6$), which ultimately relaxes radiatively. We note that in this picture the regions between the shock and the H_2 formation zone are too small to be detected in H_2. For example, the region from which no molecular emission occurs has an extent of about $10^{15}\,\mathrm{cm}$, corresponding to less than 1 arcsec for Orion. Thus the appearance is given of H_2 surviving a fast shock, and being detected in the 1–0 emission.

Acknowledgments

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