6-14-1998

H2 Formation on Interstellar Grains in Different Physical Regimes

Gianfranco Vidali
Syracuse University

Ofer Biham
The Hebrew University of Jerusalem

Itay Furman
The Hebrew University of Jerusalem

N. Katz
The Hebrew University of Jerusalem

Valerio Pirronello
Universita di Catania

Recommended Citation

Vidali, Gianfranco; Biham, Ofer; Furman, Itay; Katz, N.; and Pirronello, Valerio, "H2 Formation on Interstellar Grains in Different Physical Regimes" (1998). *Physics*. 511.
https://surface.syr.edu/phy/511

Mon. Not. R. Astron. Soc. **000**, 000–000 (0000) Printed 1 February 2008 (MN LaTeX style file v1.4)

H_2 Formation on Interstellar Grains in Different Physical Regimes

O. Biham,[1] I. Furman,[1] N. Katz,[1] V. Pirronello,[2] and G. Vidali[3]
[1] *Racah Institute of Physics, The Hebrew University of Jerusalem, Jerusalem 91904, Israel*
[2] *Istituto di Fisica, Universita' di Catania, Catania, Sicily, Italy*
[3] *Department of Physics, Syracuse University, Syracuse, NY 13244*

1 February 2008

ABSTRACT

An analysis of the kinetics of H_2 formation on interstellar dust grains is presented using rate equations. It is shown that semi-empirical expressions that appeared in the literature represent two different physical regimes. In particular, it is shown that the expression given by Hollenbach, Werner & Salpeter [ApJ, 163, 165 (1971)] applies when high flux, or high mobility, of H atoms on the surface of a grain, makes it very unlikely that H atoms evaporate before they meet each other and recombine. The expression of Pirronello et al. [ApJ, 483, L131 (1997)] – deduced on the basis of accurate measurements on realistic dust analogue – applies to the opposite regime (low coverage and low mobility). The implications of this analysis for the understanding of the processes dominating in the Interstellar Medium are discussed.

Key words: ISM:abundances – ISM:molecules – ISM:atoms – atomic processes – molecular processes

1 INTRODUCTION

The problem of the formation of molecular hydrogen, the most important species in the universe, is a fundamental open question in astrophysics (Duley & Williams 1984). It was recognised long ago (Gould & Salpeter 1963) that H_2 cannot form in the gas phase in the Interstellar Medium (ISM) efficiently enough to account for its abundance. It was proposed that dust grains act as catalysts allowing the protomolecule to quickly release the 4.5 eV of excess energy (in a time comparable to the vibration period of the highly vibrationally excited state in which it is formed). Briefly stated, the problem is as follows. An H atom approaching the surface of a grain has a probability ξ (sticking coefficient) to become trapped. The adsorbed H atom (adatom) will spend an average time $t_{\rm H}$ (residence time) before leaving the surface. If during the residence time the H adatom encounters another H adatom (which has just landed on the surface or was already trapped in a deeper adsorption site), an H_2 molecule will form with a certain probability. Given the fact that, until recently, there were no experiments done in conditions relevant to the ISM, and that little is known of the chemical composition and morphology of dust grains, it is not surprising that quite different models co-existed. This is an area, as many others in astrophysics and astrochemistry, in which by far more theoretical papers have been written [Gould & Salpeter (1963); Williams (1968); Hollenbach & Salpeter (1970; 1971); Hollenbach, Werner & Salpeter (1971); Smoluchowski (1981; 1983); Aronowitz & Chang (1985); Duley & Williams (1986); Buch & Zhang (1991); Sandford & Allamandola (1993)] than experiments have been done.

A milestone has been certainly set by Hollenbach & Salpeter (1970; 1971), who treated sticking and accommodation of H atoms in a semiclassical way, while the mobility was treated quantum mechanically. They concluded that tunneling between adsorption sites, even at 10K, would have assured the required mobility. Hollenbach et al. (1971) obtained for the steady state production rate of molecular hydrogen per unit volume the simple expression:

$$R_{\rm H_2} = \frac{1}{2} n_{\rm H} v_{\rm H} \sigma \xi \eta n_{\rm g}, \qquad (1)$$

where $n_{\rm H}$ and $v_{\rm H}$ are the number density and the speed of H atoms in the gas phase respectively, σ the average cross-sectional area of a grain, $n_{\rm g}$ is the number density of dust grains, and η is the probability that two H adatoms on the surface meet and recombine to form H_2. Note that in the original formulation by Hollenbach et al. (1971) $R_{\rm H_2} = (1/2) n_{\rm H} v_{\rm H} \sigma \gamma n_{\rm g}$, where γ is the fraction of H atoms striking the grain that eventually form a molecule, namely, $\gamma = \xi\eta$. Eq. (1) states that, for $\eta = 1$, whenever two H atoms are adsorbed on a grain, a H_2 molecule is formed.

From the experimental point of view, besides some pioneering work in the early '60s (King & Wise 1963) and '70s (Schutte et al. 1976), only very recently the problem has been investigated again (Pirronello et al. 1997a; Pirronello et al. 1997b). Pirronello et al. performed their measurements in an ultra high-vacuum (UHV) chamber (typical experimental pressures were in the 10^{-10} torr) irradiating the sample, maintained at temperatures between 5K and 15K, with H and D atoms from two different triple differentially pumped lines (D atoms were used to obtain a better signal to noise ratio). For the very first time they used as a substrate a natural "olivine" (a Mg, Fe silicate) slab (mechanically polished until shiny), that has to be considered with good reasons a better analogue of interstellar dust than any model surface. A quadrupole mass spectrometer detected the amount of HD formed on the cold substrate. Measurements were performed both during and after irradiation with H and D atoms. In the latter case, a Temperature Programmed Desorption (TPD) experiment was carried out in which the temperature of the sample is quickly ramped to over 30 K to desorb all weakly adsorbed species.

The main results obtained by Pirronello et al. (1997a; 1997b) are: (a) In the temperature range of interest for interstellar applications (between 10K and 15K), the formation rates deduced from their experimental data are up to one order of magnitude lower than those calculated by Hollenbach & Salpeter (1970; 1971) and Hollenbach et al. (1971); (b) According to their desorption spectra, hydrogen, that is adsorbed as atomic, becomes mobile only around 10 K, even at the high coverage regime [see Fig. 2 in Pirronello et al. (1997b)]. Thus, at the lowest temperatures (less than about 10 K) tunneling alone does not provide enough mobility to H adatoms. Instead, they find that thermal activation is required. A possible scenario is that thermal energy is necessary to raise H adatoms inside the adsorption well to an energy level from which tunneling can become effective; (c) According to a careful analysis of the kinetics of HD desorption spectra during TPDs, different regimes can be recognised during H_2 formation, depending on the values of certain parameters discussed below. This analysis has led to the proposal of the following expression for the steady state formation rate of H_2,

$$R_{\mathrm{H}_2} = \frac{1}{2}(n_{\mathrm{H}} v_{\mathrm{H}} \sigma \xi t_{\mathrm{H}})^2 n_{\mathrm{g}} \tilde{N}^{-2} \nu f(T, a, \delta E) \gamma\prime, \tag{2}$$

where $\tilde{N}^2$ is the average number of hops an adatom needs to make to encounter another adatom while performing a random walk, and $\nu f(T, a, \delta E)$ describes the hopping rate of adatoms due to both thermal activation and tunneling. Here, ν is a characteristic attempt rate, T is the grain temperature, while a and δE are width and height of the energy barrier, respectively. $\gamma\prime$ is the probability that two H adatoms recombine after encountering. In this expression the rate of H_2 formation is proportional to the square of the effective incoming H flux ($n_{\mathrm{H}} v_{\mathrm{H}} \sigma \xi$) on the grain surface, and is built on a purely phenomenological basis to interpret the experimental data on desorption kinetics.

In Eq. (1), that has been used by Hollenbach et al. (1971) and others in their chemical models, the recombination rate is linearly proportional to the effective incoming H flux. In this note it is shown that rate equations yield Eqs. (1) and (2), as two distinct limiting cases of the H recombination rate.

2 THE CALCULATIONS

For simplicity we will consider the H_2 production rate on a single grain; the total production rate per unit volume can be obtained by multiplying it by n_{g}, the number density of dust grains. The number of H adatoms on the surface N_1, and that of H_2 molecules N_2, as a function of time is given by the rate equations

$$\begin{aligned} \dot{N}_1 &= F - p_1 N_1 - 2\alpha {N_1}^2 && \text{(3a)} \\ \dot{N}_2 &= \alpha {N_1}^2 - p_2 N_2 && \text{(3b)} \end{aligned}$$

where F is the rate of adsorption of H atoms on the grain, α is the rate of H_2 recombination (given by the product of the diffusion coefficient and the recombination probability), p_1 and p_2 are the desorption rates for H and H_2, respectively. The first term in Eq. (3a) represents the growth of the H population due to the incoming flux; the second term is the decrease in the H population due to the desorption of H adatoms; and the third term represents the rate at which H adatoms are lost due to the recombination process. In Eq. (3b) the first term represents the rate of creation of H_2 molecules. It is related to the last term in Eq. (3a) through a factor 1/2 because two H adatoms are needed to form one H_2 molecule. The second term in Eq. (3b) is the desorption rate of H_2 molecules and is equal to the desired production rate $R_{\mathrm{H}_2} = p_2 N_2$, of H_2 molecules released to the gas phase. Note that according to this formulation $F = n_{\mathrm{H}} v_{\mathrm{H}} \sigma \xi$, $p_1 = 1/t_{\mathrm{H}}$ and $\alpha = \tilde{N}^{-2} \nu f(T, a, \delta E) \gamma\prime$.

We will now consider the steady state conditions, where $\dot{N}_1 = \dot{N}_2 \equiv 0$. In this case N_1 can be extracted from Eq. (3a), giving rise to $N_1 = [-p_1 + (p_1^2 + 8\alpha F)^{1/2}]/(4\alpha)$, where the unphysical negative solution is discarded. The steady state condition and Eq. (3b) imply $R_{\mathrm{H}_2} = p_2 N_2 = \alpha N_1^2$. By substituting the expression for N_1 into this equality we find an exact formula for the H_2 production rate of a single grain

$$R_{\mathrm{H}_2} = \frac{p_1^2 - p_1 (p_1^2 + 8\alpha F)^{1/2} + 4\alpha F}{8\alpha}. \tag{4}$$

Note that the H_2 desorption rate p_2, does not affect the steady state production rate R_{H_2}. However, it will affect the number of H_2 molecules on the grain N_2 in the steady state. We now evaluate expression (4) in two limiting cases. The first case is when the adatom desorption rate is negligible compared to their recombination rate on the surface. This is the limit of ${p_1}^2 \ll \alpha F$. We can neglect the first two terms in the numerator on the right hand side of Eq. (4), finding

$$R_{\mathrm{H}_2} = \frac{1}{2} F; \qquad {p_1}^2 \ll \alpha F, \tag{5}$$

namely, all H atoms that attach to the surface recombine and desorb as H_2 molecules. In the other limit, ${p_1}^2 \gg \alpha F$, adatom desorption is important and we expect the production rate R_{H_2} to be dependent on p_1. Indeed, expanding the square root in Eq. (4) according to $(1+x)^{1/2} \simeq 1 + x/2 - x^2/8$ with $x = (8\alpha F)/{p_1}^2$, we obtain:

$$R_{\mathrm{H}_2} = \frac{\alpha}{{p_1}^2} F^2; \qquad {p_1}^2 \gg \alpha F. \tag{6}$$

The important result of Eqs. (5) and (6), which is the focus of this note, is that the production rate R_{H_2} can be *either linear or quadratic* in the adsorption rate F of H atoms, depending on the conditions stated above. Eq. (6) also predicts the dependence of R_{H_2} on the recombination rate α and the adatom desorption rate p_1 when the latter is significant.

To make contact with Eqs. (1) and (2) we substitute $F = n_H v_H \sigma \xi$, $p_1 = 1/t_H$ and $\alpha = \tilde{N}^{-2} \nu f(T, a, \delta E)\gamma\prime$, and multiply the result by n_g, the grain density. Thus, Eq. (5) is transformed into Eq. (1) apart from a factor η which is in fact equal to unity at the conditions studied by Hollenbach et al. (1971). Similarly, Eq. (6) is identical to Eq. (2), apart from a factor of 1/2 that arises due to a different definition of α.

3 DISCUSSION

It has been shown analytically that the expressions to calculate the H_2 formation rate given in Eqs. (1) and (2) are correct in two different regimes. Eq. (1), introduced by Hollenbach et al. (1971) almost thirty years ago, holds when high flux, or high mobility of H adatoms, makes it very unlikely that H adatoms evaporate before they recombine. Specifically, it is the appropriate expression to use when $\alpha F \gg {p_1}^2$. The assumption of a high mobility has been experimentally proven (Pirronello et al. 1997a; Pirronello et al. 1997b) to be inappropriate for the case in which a more realistic grain analogue surface is used rather than a monocrystalline one. Experimental data suggest that H adatoms have limited mobility and, in the low coverage regime, H_2 is not readily formed at the lowest temperature. Such a result had been already obtained theoretically by Smoluchowski (1981). In his calculations of H_2 formation on amorphous water, he obtained that the onset temperature for mobility and recombination was about 18K, a value significantly higher than 10 K measured by Pirronello et al. for olivine. In dense, cold clouds, Smoluchowski's value would be too high and would make H recombination too infrequent. The expression given in Eq. (2) introduced by Pirronello et al. (1997b), can be applied in the opposite limit or whenever the physical conditions maintain a low flux or low mobility of H adatoms, with respect to their desorption rate.

4 IMPLICATIONS FOR THE INTERSTELLAR MEDIUM

The results on the rate of formation of molecular hydrogen obtained experimentally (Pirronello et al. 1997a; Pirronello et al. 1997b), and also shown to hold on theoretical grounds in this communication, can be used to speculate on how this fundamental process might proceed during the dynamical evolution of an interstellar cloud.

As is well known, a typical interstellar cloud crosses diffuse and dense stages according to its energy balance with the surroundings. When a cloud loses more energy than it gains from the environment, it contracts; in the opposite limit, it expands. In the evaluation of the rate of formation of molecular hydrogen, the criteria of applicability of Eqs. (1) and (2) will then depend on the particular stage the interstellar cloud is going through. In diffuse clouds conditions favour Eq. (2). This is because of the low flux of H atoms (due to the low gas phase density) and of the relatively high grain temperature (hence low H residence time on the grain surface). If such a diffuse cloud evolves towards a denser stage, the conditions will probably tend to favour Eq. (1) due to the increase of the gas phase density, and to the decrease of the grain temperature. In passing, we note that one must be aware that the processes described above of H_2 formation on bare refractory grains are influenced by at least two other processes, i.e. the decrease of H atom density in the gas phase (due to the ongoing conversion into H_2) and the accretion of an icy mantle. In the latter case, the formation rate of H_2 might be quite different than the one on a sparsely covered silicate surface due to the different depth distributions of adsorption sites and hence the different values of sticking and mobility of H adatoms. It would be very useful to have laboratory measurements of H_2 formation under these conditions.

Finally, when a full dense cloud environment is developed, Eq. (2) should apply again, because of the low density of H in the gas phase and because of the competition between H_2 and H adatoms in occupying available adsorption sites. Moreover, under these conditions, the grain surface may be covered by ice where binding energies for H_2 are slightly larger than for H. In this case, H adatoms will likely be far apart from each other and will have to undergo a long migration before encountering each other, which in turn favours Eq. (2). If we consider evolution from a dense toward a diffuse stage the applicability of Eqs. (1) and (2) will of course take place in the reverse order. Quantitative studies of time dependent chemical models of interstellar clouds have been done under both static conditions (d'Hendecourt, Allamandola & Greenberg1985; Hasegawa & Herbst 1993; Bergin, Langer & Goldsmith 1995), and dynamically evolving conditions (Charnley et al. 1988a; Charnley et al. 1988b; Nejad, Williams & Charnley 1990; Prasad, Heere & Tarafdar 1991; Rawlings et al. 1992; Shalabiea & Greenberg 1995). The qualitative framework we have just given has to be confirmed by quantitatively incorporating it into calculations describing the evolution of an interstellar cloud.

ACKNOWLEDGEMENTS

Helpful discussions with Giulio Manicó are gratefully acknowledged. G. Vidali would like to acknowledge support from NASA Grant NAG5-4998. V. Pirronello would like to acknowledge support from the Italian National Research Council (CNR) grant CN96.00307.02.

REFERENCES

Aronowitz S., Chang S., 1985, ApJ, 293, 243
Bergin E.A., Langer W.D., Goldsmith P.D., 1995, ApJ, 441, 222
Buch V., Zhang Q., 1991, ApJ, 379, 647
Charnley S.B., Dyson J.E., Hartquist T.W., Williams, D.A., 1988a, MNRAS, 231, 269
Charnley S.B., Dyson J.E., Hartquist T.W., Williams, D.A., 1988b, MNRAS, 235, 1257
Duley W.W., Williams D.A., 1984, Interstellar Chemistry, Acad. Press, London
Duley W.W., Williams D.A., 1986, MNRAS, 223, 177
Gould R.J., Salpeter E.E., 1963, ApJ, 138, 393
Hasegawa T., Herbst E., 1993, MNRAS 261, 83
d'Hendecourt L., Allamandola L.J., Greenberg J.M., 1985, A&A, 152, 130
Hollenbach D.J., Salpeter E.E., 1970, J. Chem. Phys., 53, 79

Hollenbach D.J., Salpeter E.E., 1971, ApJ, 163, 155

Hollenbach D.J., Werner M.W., Salpeter E.E., 1971, ApJ, 163, 165

King A.B., Wise H., 1963, J. Phys. Chem., 67, 1163

Nejad L.A.M., Williams D.A., Charnley S.B., 1990, MNRAS, 246, 183

Pirronello V., Liu C., Shen L., Vidali G., 1997a, ApJ, 475, L69

Pirronello V., Biham O., Liu C., Shen L., Vidali G., 1997b, ApJ, 483, L131

Prasad S.S, Heere K.R., Tarafdar S.P. 1991, ApJ, 373, 123

Rawlings J.M.C., Hartquist T.W., Menten K.M., Williams D.A., 1992, MNRAS, 255, 471

Sandford S.A., Allamandola L.J., 1993, ApJ, 409, L65

Schutte A., Bassi D., Tommasini F., Turelli F., Scoles G., Herman L.J.F., 1976, J. Chem. Phys., 64, 4135

Shalabiea O.M., Greenberg J.M., 1995, A&A, 303, 233

Smoluchowski R., 1981, Ap&SS, 75, 353

Smoluchowski R., 1983, J. Phys. Chem., 87, 4229

Williams D.A., 1968, ApJ, 151, 935