# H$_2$ Formation on Interstellar Dust Grains
# The Viewpoints of Theory, Experiments, Models and Observations

Cazaux, Stephanie

**Important note**
To cite this publication, please use the final published version (if applicable).
Please check the document version above.

# H$_2$ Formation on Interstellar Dust Grains: The Viewpoints of Theory, Experiments, Models and Observations

**Stephanie Cazaux**

**Abstract** Molecular hydrogen (H$_2$) is the most abundant molecule in the Universe. Its formation involves catalytic reactions occurring on the surface of interstellar dust grains, but also involving polycyclic aromatic hydrocarbons (PAHs). Experiments and theoretical calculations have been performed to determine the processes governing the formation of H$_2$ on dust and involving PAHs. These studies were recently brought in a review paper (Wakelam et al. 2017), from which this contribution is based.

**Keywords** Molecular hydrogen · ISM · Molecules

## 1 Observing H$_2$ in the Universe

Molecular hydrogen is the most abundant molecule in the Universe. In diffuse molecular clouds, it is the first molecule to form (Snow and McCall 2006) while in Photo-Dissociation Regions (PDRs; see A.G.G.M. Tielens in this volume), which are predominantly neutral regions bathed in far-ultraviolet light, H$_2$ can be dissociated by ultraviolet radiation, and therefore an efficient route for molecular formation must be present (Jura 1974) to compensate this loss. Furthermore, H$_2$, either in its neutral or ionized form, controls the chemistry in the interstellar medium (ISM). In dense clouds where UV penetration is greatly reduced, most of the hydrogen is in molecular form, and most of the H$_2$ in the Universe resides in these dense clouds. It has been recognized for a long time that under ISM conditions H$_2$ cannot be formed efficiently enough in the gas phase to explain its abundance and that interstellar dust grains act as catalysts for the formation of H$_2$ (Hollenbach and Salpeter 1971; Jura 1974). It is now well established that H$_2$ formation occurs via catalytic reactions on surfaces of

S. Cazaux (✉)

Faculty of Aerospace Engineering, Delft University of Technology, Kluyverweg 1, 2629 HS Delft, The Netherlands
e-mail: s.m.cazaux@tudelft.nl

University of Leiden, P.O. Box 9513, 2300 RA Leiden, The Netherlands

interstellar dust grains. The observationally determined $H_2$ formation rate coefficient in the diffuse ISM, $R(H_2) = 3 - 4 \times 10^{-17}$ cm$^3$ s$^{-1}$ (Gry et al. 2002), appears to be rather invariant. Nevertheless, considerably higher $H_2$ formation rates have been derived at high gas temperatures in PDRs (Habart et al. 2005).

## 2  Processes for $H_2$ Formation on Dust Grains

The various processes involved in the formation of $H_2$ can be decomposed in several key physical processes summarized in Fig. 1. Atoms and molecules stick on the surface either in physisorbed (van der Waals) or chemisorbed (covalent bond) sites, and can diffuse through thermal hopping (solid lines) or quantum tunneling (dashed red lines). The formation of $H_2$ can then occur either via the Langmuir-Hinshelwood (LH) mechanism, in which atoms from the gas phase first become accommodated on the surface and then, via diffusion, can encounter each other and react, or via Eley-Rideal (ER) reaction, in which an incoming atom interacts directly with an atom on the surface. To quantify the different adsorption energies of H and $H_2$ as well as the formation rate of $H_2$ via the ER or LH mechanism on different types



**Fig. 1** Different processes involved in the formation of $H_2$ on dust grains. HA is the hot atom mechanism: an atom coming from the gas phase has additional energy which increases the diffusion
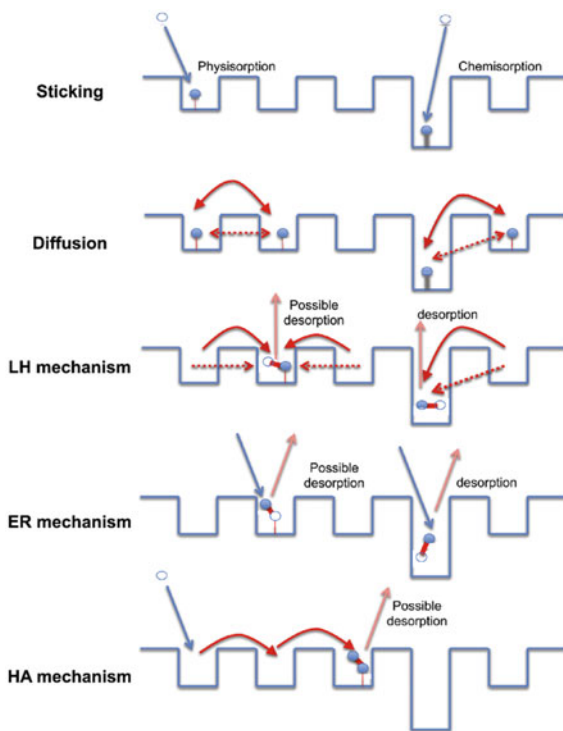
of surfaces, experiments and ab-initio calculations have been performed in the last decades (see references in Wakelam et al. 2017). Several types of surfaces have been studied such as crystalline or amorphous silicates, carbonaceous surfaces, graphite and crystalline and amorphous ices. For each of these surfaces, the sticking of H atoms, binding energies of H in physisorbed and chemisorbed sites, the diffusion barriers from sites to sites but also barriers to enter chemisorbed sites have been discussed (Wakelam et al. 2017). For water ice note that chemisorption sites are not present, so the atoms are limited to physisorbed sites.

## 3 Processes for H$_2$ formation involving PAHs

The photodissociation of PAHs upon UV irradiation can lead to the formation of H$_2$. The contribution of this process is discussed by A.G.G.M. Tielens in this volume. Here, we focus on H$_2$ formation via abstraction of H atoms from PAHs. An incident H atom encounters a H from the PAH and generates H$_2$. Such process is not energetically favorable on unfunctionalized PAH molecules, due to high C-H binding energies of 4.8 eV. However, for super hydrogenated PAHs, such reactions are possible and hydrogen addition and abstraction have been demonstrated both experimentally and theoretically (Cazaux et al. 2016; Mennella et al. 2012; Rauls and Hornekaer 2008; Thrower et al. 2012). Addition barriers for PAHs vary, depending on charge state and degree of superhydrogenation (Cazaux et al. 2016; Rauls and Hornekaer 2008). On coronene cations (prototypical PAHs), the first H addition takes place on the periphery of the molecule on an "edge" carbon. This addition has a very small barrier of ∼10 meV. The addition of a second H atom is associated with a barrier of 30 meV (Cazaux et al. 2016). Subsequent H addition reactions have barriers which alternate in magnitude depending whether the PAH is a radical or a close shell system. This makes coronene cations with an odd number of extra H atoms predominant. Some of the barriers, associated with the breaking of the aromaticity of the cations, are as high as 0.1 eV and lead to the predominance of coronene cations with a magic number of H atoms attached (+5, +11 and +17 extra hydrogens). On neutral coronene, the addition of the first H atom is associated with a barrier of 60 meV and takes place on an edge carbon (Rauls and Hornekaer 2008). Subsequent H addition reactions have lower barriers or are even barrierless (Rauls and Hornekaer 2008). However, hydrogenated coronene with an even number of extra hydrogens are more abundant than others, and especially some show stable configurations and magic numbers (+2, +10, +14, +18 and +24 extra hydrogens; Jensen et al. 2019). Experiments on both cationic and neutral PAHs show that H atom beams with energies ranging from 300–2000 K can lead to complete superhydrogenation (one excess H atom per C atom; Skov et al. 2014). H$_2$ formation with PAHs involves barrierless reactions. However, the cross sections for abstraction are lower than for H addition and have been determined via H-D exchange for the neutral coronene (Mennella et al. 2012; Thrower et al. 2012) and coronene cations (Foley et al. 2018). These studies, both concerning neutral and cationic PAHs, show that H$_2$ can form in an efficient

manner on super-hydrogenated PAHs (i.e., PAHHs). However, it has been shown that hydrogenated PAHs lose in an efficient way their extra H with the interactions with photons, which makes the presence of hydrogenated PAHs in space challenging (Boschman et al. 2015; Montillaud et al. 2013; LePage et al. 2009). Recently, it has been shown that H atoms attached to PAHs can diffuse from one carbon atom to another one, a processed called scrambling, which depends on the barrier for diffusion and the binding energy of the H atom in the sites (Castellanos et al. 2018; Wiersma et al. 2020). Such process could increase the stability of hydrogenated PAHs in space and the $H_2$ formation rate involving PAHHs.

## 4  $H_2$ Formation in Space

### 4.1  *Diffuse Clouds*

The main mechanisms which are thought to dominate the formation of $H_2$ in diffuse, translucent and molecular clouds are presented in Fig. 2. For diffuse cloud with low radiation field, dust temperatures are ranging between 15 and 20 K, and physisorbed H atoms can still remain attached to dust grains allowing $H_2$ to form efficiently via the LH mechanism through the reaction of 2 physisorbed H atoms. This formation process is very efficient for dust temperatures lower than 20 K (Cazaux and Tielens 2004; Cuppen and Herbst 2005) and depends on the binding energies of the physisorbed H atoms. For diffuse cloud environments with high radiation field ($\frac{n_H}{G_0} \geq 3 \times 10^{-2}$ cm$^{-3}$, where $G_0$ is the radiation field in Draine's unit LePage et al. 2009), $H_2$ could form involving PAHs or dust grains through the ER mechanism involving chemisorbed H atoms (Boschman et al. 2015) or by photolysis of hydrogenated amorphous carbons (Alata et al. 2014). In translucent clouds, the temperature of dust grains becomes lower than in diffuse clouds (15–18 K) and ices start to form for extinctions larger than $A_V \sim 3$ mag. Since H atoms can only physisorb on ices (no chemisorption possible), $H_2$ formation on icy dust can only involve physisorbed H atoms, and therefore $H_2$ in translucent clouds forms predominantly via the LH mechanism. However, the morphology and porosity of ices set the binding energies of physisorbed H atoms, which determines the efficiency of $H_2$ formation on icy dust. $H_2$ formation in translucent clouds is therefore very sensitive to the characteristics of the ices present in such environments.

### 4.2  *Photo-dissociation Regions*

In PDRs (see A.G. G.M. Tielens in this volume), strong UV fields and gas density variations are observed. Dust in these regions evolves from the edge of the PDR to its center, but also varies from one PDR to another (Rapacioli et al. 2005; Berné et al.
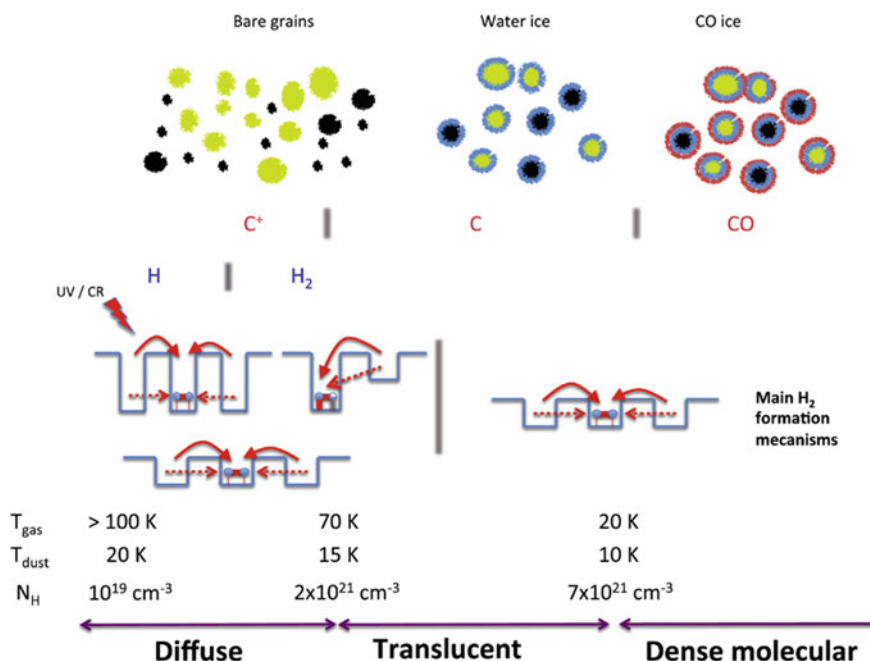
**Fig. 2** Sketch of the main H$_2$ formation processes from the diffuse to the dense interstellar medium. From Wakelam et al. (2017) (Color figure online)

2007; Pilleri et al. 2012; Arab et al. 2012; Köhler et al. 2014; Pilleri et al. 2015). The fraction of carbon locked in dust grains is tied up in the carriers of the aromatic infrared bands (AIBs). The most intense AIBs are observed at 3.3, 6.2, 7.7, 8.6, 11.3, and 12.7 $\mu$m and are generally attributed to stochastically heated PAHs. The ratio of the 3.4 and 3.3 $\mu$m band intensity (I 3.4/I 3.3) decreases in the PDR from the more UV-shielded layers to the more exposed layers. Such decrease indicates the destruction of very small grains and formation of PAHs due to photons (Pilleri et al. 2015). Deeper inside the PDRs, the UV field decreases. In this case, small grains must coagulate onto the surface of big grains (Köhler et al. 2011; Arab et al. 2012). Therefore, the H$_2$ formation rate in PDRs predicted by models strongly depends on the grain model which is used. In different PDRs, the H$_2$ formation rate has been measured and is reported as a function of dust temperature in Fig. 3 as red symbols (Habart et al. 2005). The point at lower temperature illustrates a diffuse cloud (Gry et al. 2002) and shows a high H$_2$ formation rate which can be explained by the involvement of physisorbed H atoms. For higher dust temperatures, the H$_2$ formation rate declines. For models considering grain size distributions (Weingartner and Draine 2001), H$_2$ can form on PAHs (Fig. 3, red line), on amorphous carbon grains (Fig. 3, blue line) or on silicates (Fig. 3, green line). The decrease in H$_2$ formation with increasing dust temperature is due to the fact that H$_2$ formation involves chemisorbed H atoms at high temperatures and that this reaction is associated with a barrier. While PAHs could explain the H$_2$

**Fig. 3** H$_2$ formation rate in different PDRs as function of dust temperature. Red symbols show the observations for the different PDRs processes. The lines show the contribution from PAHs (red line), amorphous carbon (blue line) and silicates (green line). The red cross shows that this route is not feasible because of the fragility of PAHHs to radiation. While the green arrows show the increase of H$_2$ formation on silicates due to new findings in laboratory (He et al. 2011; Mennella et al. 2019). Adapted from Cazaux et al. (2005) (Color figure online)
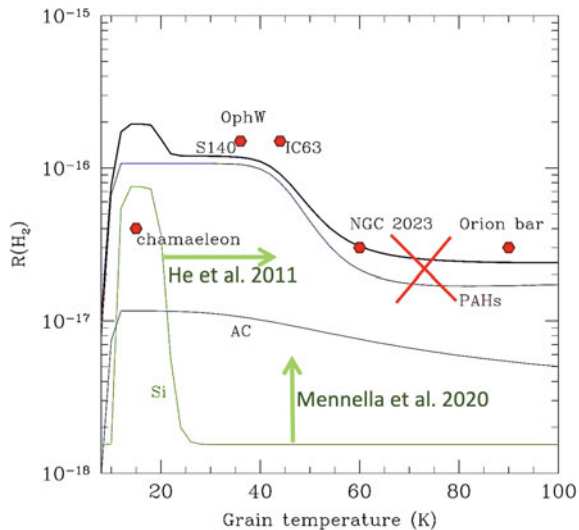


formation rate observed in these PDRs, it has been shown that hydrogenated PAHs are not stable in such environment and therefore that the channel involving such PAHHs cannot proceed (shown in Fig. 3, red cross; Boschman et al. 2015; Andrews et al. 2016). Several mechanisms have been proposed. At low temperatures, H$_2$ can form on dust grains involving chemisorbed H through the ER mechanism (Cazaux and Tielens 2004; Le Bourlot et al. 2012). Alternatively, H$_2$ can form on PAHs via the photodesorption of H$_2$ from PAHs for moderately/highly excited PDRs (Boschman et al. 2015). In this case a PAH absorbs a photon and ejects a H atom or a H$_2$ molecule and the competition between these two de-excitation mechanisms depends on the size of the PAHs (Castellanos et al. 2018). A third possible formation route is via LR on small grains with fluctuating temperatures for low/intermediate excitation (Bron et al. 2014). In PDRs the abstraction involving hydroxyl groups of silicate grains has been proposed as a barrier-less reaction to form H$_2$ (Mennella et al. 2019) and the binding energy of H atoms on silicates has been shown to be larger than previously derived (He et al. 2011). These two findings do increase the formation of H$_2$ on silicates substantially (illustrated by the green arrows showing that an high H$_2$ formation rate will extend to larger temperatures, and that the rate for large temperatures will be higher than previously assumed).

For models considering the coagulation of small grains on large grains, which are specifically developed to reproduce the optical and thermal properties of a-C:H grains in the ISM (Jones and Habart 2015), photon-processing of grain which involves chemisorbed H atoms could be a main contributor to the H$_2$ formation. As shown experimentally (Alata et al. 2014), UV photon-irradiation of a-C:H leads to very efficient production of H$_2$ molecules. Such UV-induced formation pathway has been investigated theoretically (Jones and Habart 2015) adopting the dust composition and size distribution from the dust model presented in Jones et al. (2013). In this work

it is shown that such a process would be sustainable as long as the radiation field is intense enough to photo-dissociate C-H bonds but not intense enough to break the C–C bonds.

## 5 Conclusions

H$_2$ forms on dust grains or involves PAHs in a wide variety of astrophysical environments. This suggests that H$_2$ formation involves both physisorbed H atoms at low temperatures and chemisorbed H atoms at high temperatures, so that the efficiency remains high. Such processes depend on the results of laboratory studies and how individual processes are understood and quantified (sticking, diffusion, desorption, energy partition, etc.). Evaluating the contribution of the different dust populations has been done to a certain extent for silicate surfaces, but more work is needed to better constrain both silicates and carbonaceous materials. New routes to H$_2$ formation, via UV irradiation of hydrogenated carbons, or via other energetic routes, have to be investigated in greater detail.

## References

Alata, I., Cruz-Diaz, G.A., Muñoz Caro, G.M. et al.: Vacuum ultraviolet photolysis of hydrogenated amorphous carbons - I. Interstellar H$_2$ and ch4 formation rates. A&A **569**, A119 (2014). https://doi.org/10.1051/0004-6361/201323118

Andrews, H., Candian, A., Tielens, A.G.G.M.: Hydrogenation and dehydrogenation of interstellar PAHs: Spectral characteristics and H$_2$ formation. A&A **595**, A23 (2016); https://doi.org/10.1051/0004-6361/201628819

Arab, H., Abergel, A., Habart, E., et al. : Evolution of dust in the Orion Bar with Herschel - I. Radiative transfer modelling. A&A **541**, A19 (2012). https://doi.org/10.1051/0004-6361/201118537

Berné, O., Joblin, C., Deville, Y., et al.: Analysis of the emission of very small dust particles from spitzer spectro-imagery data using blind signal separation method. A&A **469**(2), 575–586 (2007). https://doi.org/10.1051/0004-6361:20066282

Boschman, L., Cazaux, S., Spaans, M., et al.: H$_2$ formation on PAHs in photodissociation regions: a high-temperature pathway to molecular hydrogen. A&A **579**, A72 (2015); https://doi.org/10.1051/0004-6361/201323165

Bron, E., Le Bourlot, J., Le Petit, F.: Surface chemistry in the interstellar medium - II. H$_2$ formation on dust with random temperature fluctuations. A&A **569**, A100 (2014). https://doi.org/10.1051/0004-6361/201322101

Castellanos, P., Candian, A., Zhen, J., et al.: Photoinduced polycyclic aromatic hydrocarbon dehydrogenation the competition between H- and H$_2$-loss. A&A **616**, A166 (2018). https://doi.org/10.1051/0004-6361/201833220

Cazaux, S., Tielens, A.G.G.M.: H$_2$ formation on grain surfaces. ApJ **604**, 222–237 (2004)

Cazaux, S.M., Caselli, P., Walmsley, et al.: H$_2$ formation on grain surfaces. In: Lis, D.C., Blake, G.A., Herbst, E. (eds.), Astrochemistry: Recent Successes and Current Challenges, vol. 231, pp. 325–336 (2005)

Cazaux, S., Boschman, L., Rougeau, N., et al.: The sequence to hydrogenate coronene cations: a journey guided by magic numbers. In: Scientific Reports, vol. 6, p. 19835 (2016). https://doi.org/10.1038/srep19835

Cuppen, H.M., Herbst, E.: Monte Carlo simulations of $H_2$ formation on grains of varying surface roughness. MNRAS **361**(2), 565–576 (2005). https://doi.org/10.1111/j.1365-2966.2005.09189.x

Foley, N., Cazaux, S., Egorov, et al.: Molecular hydrogen formation on interstellar PAHs through Eley–Rideal abstraction reactions. MNRAS **479**(1), 649–656 (2018). https://doi.org/10.1093/mnras/sty1528

Gry, C., Boulanger, F., Nehmé, C., et al.: $H_2$ formation and excitation in the diffuse interstellar medium. A&A **391**(2), 675–680 (2002). https://doi.org/10.1051/0004-6361:20020691

Habart, E., Abergel, A., Walmsley, C.M., et al.: Density structure of the horsehead nebula photo-dissociation region. A&A **437**(1), 177–188 (2005). https://doi.org/10.1051/0004-6361:20041546

He, J., Frank, P., Vidali, G.: Interaction of hydrogen with surfaces of silicates: single crystal vs. amorphous. Phys. Chem. Chem. Phys. **13**, 15803–15809 (2011). http://dx.doi.org/10.1039/C1CP21601E

Hollenbach, D., Salpeter, E.E.: Surface Recombination of Hydrogen Molecules. ApJ **163**, 155 (1971)

Jensen, P.A., Leccese, M., Simonsen, F.D.S., et al.: Identification of stable configurations in the superhydrogenation sequence of polycyclic aromatic hydrocarbon molecules. MNRAS **486**(4), 5492–5498 (2019). https://doi.org/10.1093/mnras/stz1202

Jones, A.P., Fanciullo, L., Köhler, M., et al.: The evolution of amorphous hydrocarbons in the ISM: dust modelling from a new vantage point. A&A **558**, A62 (2013). https://doi.org/10.1051/0004-6361/201321686

Jones, A.P., Habart, E.: $H_2$ formation via the UV photo-processing of a-C:H nano-particles. A&A **581**, A92 (2015). https://doi.org/10.1051/0004-6361/201526487

Jura, M.: Formation and destruction rates of interstellar $H_2$. ApJ **191**, 375–379 (1974)

Köhler, M., Guillet, V., Jones, A.: Aggregate dust connections and emissivity enhancements. A&A **528**, A96 (2011). https://doi.org/10.1051/0004-6361/201016379

Köhler, M., Habart, E., Arab, H., et al.: Physical structure of the photodissociation regions in NGC 7023 - Observations of gas and dust emission with Herschel. A&A **569**, A109 (2014). https://doi.org/10.1051/0004-6361/201322711

Le Bourlot, J., Le Petit, F., Pinto, C., et al.: Surface chemistry in the interstellar medium - I. $H_2$ formation by langmuir-hinshelwood and eley-rideal mechanisms. A&A **541**, A76 (2012). https://doi.org/10.1051/0004-6361/201118126

LePage, V., Snow, T., Bierbaum, V.: Molecular hydrogen formation catalyzed by polycyclic aromatic hydrocarbons in the interstellar medium. ApJ **704**(1), 274–280 (2009); https://doi.org/10.1088/0004-637X/704/1/274

Mennella, V., Hornekaer, L., Thrower, J., et al.: The catalytic role of coronene for molecular hydrogen formation. Astrophys. J. Lett. **745**(1), L2 (2012); https://doi.org/10.1088/2041-8205/745/1/L2

Mennella, V., Suhasaria, T.: $H_2$ formation on Mg-rich amorphous silicates. Proc. Int. Astron. Union **15**(S350), 109–113 (2019). https://doi.org/10.1017/S1743921319008834

Montillaud, J., Joblin, C., Toublanc, D.: Evolution of polycyclic aromatic hydrocarbons in pho-todissociation regions. Hydrogenation and charge states. A&A **552**, A15 (2013). https://doi.org/10.1051/0004-6361/201220757

Pilleri, P., Joblin, C., Boulanger, F., et al.: Mixed aliphatic and aromatic composition of evaporating very small grains in NGC 7023 revealed by the 3.4/3.3 $\mu$m ratio. A&A 577, A16 (2015), https://doi.org/10.1051/0004-6361/201425590

Pilleri, P., Montillaud, J., Berné, O., et al.: Evaporating very small grains as tracers of the UV radiation field in photo-dissociation regions. A&A **542**, A69 (2012). https://doi.org/10.1051/0004-6361/201015915

Rapacioli, M., Joblin, C., Boissel, P.: Spectroscopy of polycyclic aromatic hydrocarbons and very small grains in photodissociation regions*. A&A **429**(1), 193–204 (2005). https://doi.org/10.1051/0004-6361:20041247

Rauls, E., Hornekaer, L.: Catalyzed routes to molecular hydrogen formation and hydrogen addition reactions on neutral polycyclic aromatic hydrocarbons under interstellar conditions. ApJ **679**(1), 531–536 (2008); https://doi.org/10.1086/587614

Skov, A.L., Thrower, J.D., Hornekaer, L.: Polycyclic aromatic hydrocarbons - catalysts for molecular hydrogen formation. Faraday Discuss. **168**, 223–234 (2014). http://dx.doi.org/10.1039/C3FD00151B

Snow, T.P., McCall, B.J.: Diffuse atomic and molecular clouds. ARA&A **44**(1), 367–414 (2006). https://doi.org/10.1146/annurev.astro.43.072103.150624

Thrower, J.D., Jørgensen, B., Friis, E.E., Baouche, S., et al.: Experimental evidence for the formation of highly superhydrogenated polycyclic aromatic hydrocarbons through H atom addition and their catalytic role in H$_2$ formation. ApJ **752**, 3 (2012)

Wakelam, V., Bron, E., Cazaux, S., et al.: H$_2$ formation on interstellar dust grains: the viewpoints of theory, experiments, models and observations. Mol. Astrophys. **9**, 1–36 (2017)

Weingartner, J.C., Draine, B.T.: Dust grain-size distributions and extinction in the milky way, large magellanic cloud, and small magellanic cloud. ApJ **548**, 296–309 (2001)

Wiersma, S.D., Candian, A., Bakker, J.M., et al.: Photolysis-induced scrambling of PAHs as a mechanism for deuterium storage. A&A **635**, A9 (2020). https://doi.org/10.1051/0004-6361/201936982