H$_2$ formation via the UV photo-processing of a-C:H nano-particles

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ABSTRACT

Context. The photolysis of hydrogenated amorphous carbon, a-C(H):dust by UV photon-irradiation in the laboratory leads to the release of H$_2$ as well as other molecules and radicals. This same process is also likely to be important in the interstellar medium.

Aims. To investigate molecule formation arising from the photo-dissociatively-driven, regenerative processing of a-C(H) dust.

Methods. We explore the mechanism of a-C(H) grain photolysis leading to the formation of H$_2$ and other molecules/ radicals.

Results. The rate constant for the photon-driven formation of H$_2$ from a-C(H) grains is estimated to be $2 \times 10^{-11}$ cm$^3$ s$^{-1}$. In intense radiation fields photon-driven grain decomposition will lead to fragmentation into daughter species rather than H$_2$ formation.

Conclusions. The cyclic re-structuring of aromatic a-C(H) nano-particles appears to be a viable route to formation of H$_2$ for low to moderate radiation field intensities ($1 \leq G_0 \leq 10$), even when the dust is warm ($T \sim 50 – 100$ K).

Key words. Interstellar Medium: dust, emission, extinction – Interstellar Medium: molecules – Interstellar Medium: general

1. Introduction

The evolution of hydrocarbon solids was considered in detail in our preceding works [Jones 1990, 2009, 2012a, b, c, Jones et al. 2013, Jones 2014, Jones et al. 2014]. Here we extend that work and explore the formation of molecules arising from the vacuum ultraviolet (VUV, $\lambda \approx 120$ nm) and extreme ultraviolet (EUV, $\lambda \sim 10 – 13.6$ eV) photon-driven processing and decomposition of hydrogenated amorphous carbon particles, a-C:H, in the interstellar medium (ISM). The designation a-C:H is used to indicate the entire range of hydrogen-poor (a-C) to hydrogen-rich (a-C:H) carbonaceous solids. The UV photolysis or ion irradiation of a-C:H materials leads to their aromatisation, H atom loss and the in situ formation of molecular hydrogen (e.g., Smith 1984; Adel et al. 1989; Maree et al. 1996; Godard et al. 2011; Alata et al. 2014). The most recent of these experiments by Alata et al. (2014) show that the VUV ($E \sim 6.8 – 10.5$ eV, $\lambda \sim 120 – 180$ nm) photolysis of hydrogenated amorphous carbons is indeed a viable mechanism for the formation of H$_2$, and also CH$_4$, within an astrophysical framework. The photo-processing of a-C:H particles by VUV/EUV photons (hereafter referred to as UV photons) from the ambient ISRF leads to re-structuring/decomposition, H$_2$ formation and the liberation of H$_2$ and hydrocarbon daughter products (e.g., Smith 1984; Alata et al. 2014; Duley et al. 2015). This process could also liberate (the precursors to) species such as CCH, C$_2$H$_2$, C$_3$H$_2$, C$_4$H$^+$, C$_2$H, which have been observed in ISM regions with moderate UV radiation fields (e.g., Pety et al. 2003, 2012; Guzmán et al. 2015).

In the classical picture of H$_2$ formation in the ISM an H atom physisorbed on a grain surface reacts with a second from the gas phase (Eley-Rideal mechanism) or with another on the grain surface (Langmuir-Hinshelwood mechanism) before reacting to form an H$_2$ molecule which is then ejected into the gas phase. In their recent study [Bron et al. 2014] showed that the Langmuir-Hinshelwood mechanism on small grains with fluctuating temperatures can still be an efficient route to H$_2$ formation in unshielded photon dominated regions (PDRs). The detailed analysis of Bron et al. (2014) shows that surface reactions on small, stochastically-heated particles are therefore no barrier to H$_2$ formation in PDRs and can provide means to form H$_2$ where the classical mechanisms do not appear to work. Here we describe a new mechanism for H$_2$ formation via the photolysis of stochastically-heated a-C nano-particles, which is complementary to that proposed by Bron et al. (2014). In this new scenario the H atoms involved in H$_2$ molecule formation are chemically-bonded within the grains, as in the experiments of Alata et al. (2014). The mechanism appears to be viable route to molecule formation in PDRs with moderate-strength radiation fields where the grains are warm.

In this paper we propose a molecule/radical formation pathway via the UV photon-driven C–H and C–C bond dissociation within, and the associated decomposition of, a-C(H) nanoparticles, which is consistent with carbonaceous dust evolution in the ISM. The paper is organised as follows: Section 2 presents a new mechanism for molecular hydrogen and daughter molecule formation. Section 3 quantifies H$_2$ formation in a-C(H) solids and Section 4 presents the conclusions of this work.

2. A mechanism for molecule formation

Experimental evidence shows that methyl groups, CH$_3$, within a-C:H materials probably play an important role in H$_2$ and CH$_4$ formation during UV photolysis (e.g., Alata et al. 2014). In the diffuse ISM and PDRs it will be the small, stochastically-heated grains that dominate H$_2$ formation because of the large sur-

1 The physical depth into a-C:H materials at which the optical depth is unity for VUV and EUV photons ($E \sim 7 – 13.6$ eV) varies little with wavelength and material composition (e.g., Jones 2012b) and we can therefore consider the collective effects of VUV and EUV photons.

2 The physisorption interaction energy is $\sim 0.01 – 0.1$ eV.

3 The aliphatic C–H bond energy is $\sim 4.2 – 4.6$ eV, while that for olefinic and aromatic C–H bonds is $\sim 4.8 – 4.9$ eV.
The key structural component in molecule formation from and within a-C nano-particles (\(a \leq 5\) nm Jones 2012c) would appear to be the presence of the aliphatic and olefinic bridging groups, which link the aromatic structures in these aromaticic structures (e.g. Jones 2012c, Micelotta et al. 2012). Fig. 1 shows a schematic view of part of an a-C(H) nano-particle where the aliphatic –CH2 –CH2 – and olefinic –CH=CH – bridges between aromatic clusters are indicated by the ellipsoidal areas A and B, respectively. A longer –C3H6 – mixed aliphatic-olefinic bridge is indicated by the dashed ellipse on the right of Fig. 1. The dehydrogenation and dissociation of such structures could be at the heart of molecule formation within a-C(H) grains.

H2 molecule formation in a-C(H) is somewhat analogous to that arising from the aromatic-aliphatic transformation on the periphery of PAH molecules proposed by Rauls & Horneck 2008 and the catalytic formation of H2 by coronene as studied experimentally by Mennella et al. 2012. However, it is here hypothesised that H2 formation occurs at the aliphatic/olefinic bridging structures that link the aromatic clusters in a-C(H) in nano-particles (e.g. the A and B sites in Fig. 1). As Ferrari & Robertson 2004, Hu et al. 2007b and Hu et al. 2007a point out, sp2 chain and cage-like clusters may be rather common structures in a-C:H materials. Our own work indicates aromatic sp2 clusters containing 3 – 8 rings in a-C nano-particles with radii \(\approx 0.2 – 0.4\) nm Jones 2012c, Micelotta et al. 2012. As Fig. 1 shows the aromatic domains and the aliphatic/olefinic bridges in these aromaticic-type structures are not co-planar but rather cage-like. Hence, under the effects of CH bond UV photodissociation the aliphatic/olefinic (A/B) bridging structures are unable to transform into aromatic structures, or increase the aromatic domain size, without compromising the cage-like structure, i.e., without breaking CC bonds. An aliphatic bridge (A) can, however, transform into an olefinic bridge (B), which is likely to be sterically-strained because of the distortions introduced by the random network structure. The olefinic bridge could then flip between olefinic (B) and radical aliphatic states (C) with dangling bonds, i.e., undergo \(B \rightarrow C\) isomerisational flipping. Such a mechanism is also consistent with the formation of daughter hydrocarbon radicals and molecules.

For a single, two-carbon atom aliphatic bridge, A, the underlying H2 formation process depends on an equilibrium between UV photolysis and H atom addition (e.g., Muñoz Caro et al. 2001, Mennella et al. 2001, Alata et al. 2014), see also Section 3. The mechanism for H2 formation proposed here relies on the aliphatic bridges being dehydrogenated, i.e.,

\[
-\text{CH} - \text{CH}_2 - \rightarrow -\text{CH} = \text{CH} - + \text{H}_2
\]

and H atom addition being aided by the potential for sterically-hindered, de-hydrogenated aliphatic bridges to isomerise, i.e.

\[
-\text{CH} = \text{CH} - \leftrightarrow -\text{C}^\text{H} - \text{C}^\text{H} -
\]

where A, B, C, etc. also refer to Fig. 1 and the * symbol is used to indicate a radical species with dangling bonds on a carbon atom that can chemisorb H atoms. As detailed above this isomerisation scheme involves an aliphatic-to-olefinic transition that cannot proceed to aromatisation in aromatic structures because of steric limitations (e.g. Jones 2012c, Micelotta et al. 2012).

As implied above, and adopted in the following analysis, a UV photon is assumed to dissociate a single C–H bond releasing an H atom that can then react with a bonded H atom to form H2. In the above, and for simplicity in what follows, we show adjacent H atoms forming an H2 molecule. However, the reacting H atoms need not necessarily be adjacent because the C–H bond dissociation-release H atom can migrate through the structure and react with a more distant H atom.4

The full sequence for H2 formation and aliphatic bridging structure re-cycling can be summarised by the following schematic of the UV-catalysed, H2 formation cycle:

\[
-\text{CH}_2 - \text{CH}_2 - \rightarrow [\text{aliphatic bridge}] \rightarrow
\]

\[
\text{A}
\]

\[
(hv^\ast : \text{H}_2) \rightarrow -\text{C}^\text{H} - \text{C}^\text{H} - \leftrightarrow -\text{CH} = \text{CH} - \rightarrow \text{B} \rightarrow \text{C}
\]

\[
(\text{H} : ) \rightarrow -\text{CH}_2 - \text{C}^\text{H} - \rightarrow \text{A/C}
\]

\[
(\text{H} : ) \rightarrow -\text{CH}_2 - \rightarrow \text{C} \rightarrow [\text{generated aliphatic bridge}] \rightarrow \text{A}
\]

where we adopt the descriptor (reactant : product); with hv* and H being dehydrogenating UV photons and adsorbing H atoms, respectively, and H2 the UV-photolysis product. The label A/C is used to indicate a mixed A and B bridge. For this H2 formation cycle to operate efficiently it relies on the re-generating H atom addition time-scale being, at least, of same order of magnitude as that for the UV-photolysis step, which appears to be the case (see section 3.2). However, as the radiation field intensity increases the cycle will be increasingly interrupted by the competing dehydrogenation processes

\[
-\text{CH}_2 - \text{C}^\text{H} - \rightarrow (hv^\ast : \text{H}_2) \rightarrow -\text{CH} = \text{C}^\text{H} -
\]

\[
^4\text{Reaction with an H atom in an aliphatic C–H bond will be favoured because of the lower bond energy, compared to olefinic and aromatic C–H bonds (see footnote 2).}
\]
The formation of H$_2$, associated with the aliphatic to aromatic transformation of a-C(H) dust, should also occur in the ISM where UV photons progressively de-hydrogenate and aromatise a-C(H) materials. This coupled dehydrogenation/ aromatisation process will clearly be accompanied by a de-volatilisation due to the associated loss of small molecules (e.g., Smith 1984; Jones 2012b; Alata et al. 2014; Duley et al. 2015). Thus, the chemistry in PDRs would appear to be an ideal laboratory to search for tracers of this H$_2$ and small molecule formation mechanism, which will depend upon the radiation field intensity rather than, simply, the gas density.

The H$_2$ formation rate in the ISM, $dn[H_2]/dt$, is classically described by the balance between its UV photo-destruction in the gas phase and its formation by H atom recombination on the surfaces of dust particles, i.e.,

$$\frac{dn[H_2]}{dt} = -\beta_0 n_{H_2} + R_{H_2} n_p n_{H_1}$$

where $\beta_0$ is the H$_2$ photo-dissociation rate coefficient ($5 \times 10^{-11}$ s$^{-1}$) in an unshielded interstellar radiation field (ISRF), $R_{H_2}$ is the H$_2$ formation rate coefficient for formation via H atom sticking and recombination on dust, $n_p$ is the total proton density, and $n_{H_1}$ and $n_{H_2}$ are the atomic and molecular hydrogen number densities, respectively. The observationally-determined H$_2$ formation rate coefficient in the diffuse ISM, $R_{H_2} = 3.4 \times 10^{-17}$ cm$^{-3}$ s$^{-1}$ (e.g., Gry et al. 2002), appears to be rather invariant, indicating a degree of uniformity in the H$_2$ formation process.

Alata et al. (2014) recently showed that the UV photo-processing ($\simeq 8.6$ eV per photon) of a-C(H) leads to bond photo-dissociation, decomposition and the formation of H$_2$ within the a-C(H) bulk material. The H$_2$ formation rate, $R_{H_2}$, is then a first order reaction with rate constant $k_f[CH]$ and Eq. (1) becomes

$$\frac{dn[H_2]}{dt} = -\beta_0 n_{H_2} + k_f[CH] n_p$$

and as per Alata et al. (2014), in their Section 4.1, both terms on the right hand side of Eq. (4), i.e., the H$_2$ destruction and formation rates, are directly proportional to the UV photon flux. As given by Eq. (39) in Jones (2012b), $k_f[CH]$ can be expressed as

$$k_f[CH] = \frac{A_{UV,pd}(a) N_{CH}(a,d_1) X(a)}{[ s^{-1}]}$$

where $A_{UV,pd}(a)$ is the UV photon-darkening (d) rate (Eq. 31 Jones 2012b), $X(a)$ is the grain relative abundance, $N_{CH}(a,d_1)$ is the number of CH bonds in a grain of radius $a$ photolysable to a depth $d_1$ ($\simeq 20$ nm) and therefore capable of forming H$_2$. Eq. (5) implicitly assumes that every absorbed UV photon leads to the photo-dissociation of a single CH bond and the formation of an H$_2$ molecule. This is almost certainly not the case because there will be competition from other channels, such as photon absorption leading to grain heating or photo-electron erosion. Recent experimental measurements indicate low photo-dissociation efficiencies, i.e., 0.014 (Mace 2014) and 0.025 (Alata et al. 2014) for the CH bonds in bulk a-C(H) materials. Here we assume a value in the dark, graphite-like or aromatic content in response to UV photon irradiation. Hence, the term photon-darkening is often used for the aromatisation of a-C(H) materials.

This is the path length corresponding to an optical depth of unity for UV photons in an homogeneous, bulk a-C(H) material. For $E > 10$ eV the optical depth is only weakly-dependent on the a-C(H) material band gap and the photon energy (see paper II). It could also perhaps be regarded as the depth into the grains at which UV photolysis is in equilibrium incident H atom re-hydrogenation.
size-dependent photo-dissociation efficiency $\epsilon = 2/a$ [nm] for $a \geq 2$ nm and $\epsilon = 1$ for $a < 1$ nm (see Jones et al. 2012c, 2014, for further details). Following Jones et al. (2012b,c) the UV photo-darkening rate, and hence the H$_2$ formation rate, is given by

$$\dot{N}_{\text{UV, pd}}(a) = F_{\text{UV}} \sigma_{\text{CH-diss}} \cdot Q_{\text{abs}}(a, E) \epsilon \left[ \text{s}^{-1} \right],$$

(4)

where $F_{\text{UV}} \approx 10^7$ photons cm$^{-2}$ s$^{-1}$ is the CH bond-dissociating UV photon flux in the local ISM (Henry 2002) for $G_0 = 1$, $\sigma_{\text{CH-diss}} = 10^{-19}$ cm$^2$ is the CH bond photo-dissociation cross-section for $E_{\text{UV}} \geq 10$ eV (Welch & Judge 1972; Gruzdkov et al. 1994; Mennella et al. 2001; Muñoz Caro et al. 2001; Alata et al. 2014) and $Q_{\text{abs}}(a, E)$ is the particle absorption efficiency factor in the cross-section, i.e., $\epsilon(a, E) = \pi a^2 Q_{\text{abs}}(a, E)$. The a-C(H) particle photo-processing time-scale, as a function of grain radius and the radiation field, can be expressed as

$$\tau_{\text{UV, pd}}(a, G_0) = \frac{1}{\dot{N}_{\text{UV, pd}}(a) G_0}. \tag{5}$$

From Eq. (4) the molecular hydrogen fraction, at equilibrium ($dn[H_2]/dt = 0$), is

$$n_{H_2} = \frac{k_J [\text{CH}]}{n_0},$$

$$= \frac{F_{\text{UV}} \sigma_{\text{CH-diss}}}{\beta_0} \left\{ Q_{\text{abs}}(a, E) \epsilon(a) N_{\text{CHH}}(a, d_i) X_i(a) \right\}. \tag{6}$$

Alata et al. (2014) derived a similar expression for this ratio (see in their Section 4.2) but did not include the size-dependent optical property terms for the dust.

Within the framework of the proposed model, the UV photon flux is therefore key in determining the H$_2$ formation and destruction rates, which scale with the local ISRF intensity and hardness. However, even if H$_2$ formation via a-C:H UV photolysis is viable, it will be hampered by the limited stock of H atoms within the dust, which is determined by the carbon depletion into dust, i.e., $[C/H] \approx 10^{-4}$. As shown by Jones (2012b), H$_2$ formation would be sustainable for only $\approx 10^4$ yr before all CH bonds were photo-dissociated and the grains completely de-hydrogenated during aromatisation. An a-C re-hydrogenation mechanism, such as that proposed by Mennella (2008, 2010), is therefore needed to replenish the stock of CH bonds. Thus, the complete dehydrogenation/aromatisation of a-C(H) grains must be hindered and suitably stable and numerous H atom chemisorption sites need to be preserved. These sites could be dangling bonds resulting from steric limitations on the $sp^2$ to $sp^3$ transformation (see Section 2) or due to the low-level doping of a-C:H with nitrogen atoms (e.g., Amir & Kalish 1991, 1993). In this case, H$_2$ formation would be sustainable as long as the radiation field is intense enough to photo-dissociate CH bonds but not intense enough to break the CC bonds in the aliphatic/olefinic bridging structure and hence to photo-fragmentation the a-C(H) grains. Thus, this H$_2$ formation mechanism will not work at high extinction because there are too few UV photons, nor will it work in intense radiation fields because of the rapid photo-fragmentation of the grains.

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8 With this definition of $\epsilon$ the experimentally-derived values of 0.014 and 0.025 (Mate 2014, Alata et al. 2014) are equivalent to $a \approx 140$ and 80 nm, respectively, which can be considered as bulk materials in terms of their optical properties (Jones et al. 2012b).

9 A dangling bond is an unsatisfied valence on an atom in a chemically-bonded network, which is an active chemisorption site.
The canonical interstellar H₂ formation rate constant (grey horizontal band, Gry et al. 2002) compared to that predicted for H₂ formation via CH bond UV photo-dissociation from a-C:H/a-C grains, \( k_f[CH]/n_{H} = 2.0 \times 10^{-17} \text{ cm}^3 \text{s}^{-1} \) shown at \( a = 0.5 \text{ nm} \) (squares with error bars). The green green square also includes H₂ formation in the a-C mantles on the large a-Sil grains into the ISM without destroying and/or fragmenting the structure. Small a-C:H/a-C (thick grey) and a-Sil/a-C (green) grain distributions and for gas temperatures of 50, 100 and 200 K (short-dashed, solid and long-dashed, respectively).

The H atom collision and sticking rate coefficient for a grain of radius \( a \) and relative abundance \( X_i(a) \) is given by

\[
R_{H} = \pi a^2 X_i(a) \left( \frac{8 k T_k}{\pi m_{H}} \right)^{\frac{1}{2}} n_{H},
\]

where \( T_k \) is the gas kinetic temperature and \( s_{H} \) is the H atom sticking efficiency. Fig. 2 shows this rate coefficient, \( R_{H}/n_{H} \), assuming \( s_{H} = 1 \), for gas temperatures of 50, 100 and 200 K.

The \( n_{H}\)-normalised, UV photon-induced, H₂ formation rate coefficients, \( k_f[CH]/n_{H} \), integrated over the small and large a-C:H grain size distributions are indicated in Fig. 2 by the large squares with error bars. These data give an good fit to the observationally-derived H₂ formation rate coefficient in the diffuse ISM, i.e., \( R_{H} = 3 - 4 \times 10^{-17} \text{ cm}^3 \text{s}^{-1} \) (Gry et al. 2002), which is indicated by the horizontal grey band.

The size-dependent a-C:H particle photo-darkening or CH bond photo-dissociation time-scale in the diffuse ISM was recently estimated by Jones et al. (2014). They found that the a-C:H photo-processing time-scale can be analytically expressed as a function of the grain radius, \( a \), in nm:

\[
\tau_{\text{UV, pd}}(a) = \frac{10^4}{G_0} \left( 2.7 + \frac{6.5}{(a \text{[nm]}^{1.3})} + 0.04(a \text{[nm]}^{1.1}) \right) \text{[yr]},
\]

which implies a minimum processing time-scale, of the order of \((4 \times 10^4/G_0) \text{yr}\), for particles with \( a \sim 3-10 \text{nm} \) and processing time-scales \( \geq \left( 10^5/G_0 \right) \text{yr} \) for the smallest and largest grains in the assumed a-C:H particle size distribution (Jones et al. 2014). Here we assume the particle size-dependent, photo-darkening efficiency factor, \( \epsilon(a) \) given above (see Section 3). For a-C:H grains such a size-dependent CH bond photodissociation efficiency appears to be a physically realistic because with increasing particle size other channels will compete with CH photo-dissociation, e.g., UV photon absorption leading to thermal excitation and/or fluorescence. However, the proposed H₂ formation mechanism is only viable if the H atom sticking rate is higher than the CH photo-dissociation rate and Fig. 2 shows that this is indeed the case. We find an H₂ formation rate constant of \( 2.0 \times 10^{-17} \text{ cm}^3 \text{s}^{-1} \) for a-C:H/a-C grains and \( 4.0 \times 10^{-17} \text{ cm}^3 \text{s}^{-1} \) if the a-C coated amorphous silicate grains, a-Sil/a-C, are also included. The error bar on the square data points in Fig. 2 conservatively reflects a factor of three uncertainty in the dust optical properties and a factor of ten in \( \epsilon \).

For the small a-C grains the bulk material band gap of 0.1 eV (\( X_{H} \sim 0.02 \)) required by the Jones et al. (2013) model implies that these particles cannot be completely aromatised to a graphite-like material with a band gap close to 0 eV. Small a-C grains are therefore able to preserve a residual hydrogenation fraction of a few percent that is seemingly hard to remove in the ISM without destroying and/or fragmenting the structure. They are therefore more resistant to UV photo-processing than
expected Jones (2012b), consistent with the H₂ formation mechanism proposed in Section 2. In addition to CH bond photo-dissociation by UV photons it is also possible that H₂ formation could be driven by thermal desorption during small grain, whole-particle stochastic heating events. However, as discussed by Jones (2012b, Section 5.1) the effects of a-C(H) dust thermal processing may only be lower limits. Given that the small a-C grain population is sensitive to photo-desorption during small grain, whole-particle stochastic heating events. However, as discussed by Jones (2012b), the more resistant large a-C(H) and a-SilC/a-C grains ought to provide a ‘background’ H₂ formation rate.

In their study Habart et al. (2004) found that in moderately excited PDRs (G₀ = 10⁷ – 10⁸) the H₂ formation rate is about five times the standard value but that in higher radiation field PDRs the standard value of 3 x 10⁻¹⁷ cm³ s⁻¹ is sufficient. Based on their observations they also inferred a link between H₂ formation and the aromatic emission band carriers. In a later study Habart et al. (2011) found that the observed column densities of rotationally excited H₂ in PDRs (G₀ = 5 – 10⁵) are higher than that predicted by PDR models. This discrepancy could be explained by an enhancement in the H₂ formation rate in PDRs (Habart et al. 2011). The observational evidence therefore seems to point towards PDRs as particularly efficient H₂-forming regions when the local radiation field is moderate, which appears to be in qualitative agreement with the model proposed here.

The Jones et al. (2013) dust model predicts an enhanced abundance of small a-C grains in PDRs due to the photo-fragmentation of larger a-C(H) grains, which is consistent with the findings of Compiègne et al. (2008) and Arab et al. (2012). This implies an enhanced H₂ formation rate in moderate PDRs where the radiation field is not intense enough to destroy a-C nano-particles. In very intense radiation fields (G₀ > 10⁵) the destruction of the emission band carriers is observed (e.g., Boulanger et al. 1994). Here we assume that the a-C(H) nano-particles responsible for the IR emission bands are also the source of H₂ formation, and that both processes are driven by UV photon absorption. Interestingly, the work of Pillieri et al. (2012) shows that the photo-fragmentation of very small carbonaceous grains, which are PAH-based in their model, occurs in regions where H₂ rotational line emission is observed. Nevertheless, extremely intense radiation fields that lead to the photo-fragmentation and destruction of a-C(H) nano-particles Jones et al. (2013) will close the door on H₂ formation and also the IR band emission in such regions. Hence, the absolute value of G₀ is a key parameter in the proposed H₂ formation mechanism, which is likely to be efficient over a wide range of the G₀/ν_lines parameter space, e.g., 0.01 < G₀/ν_lines < 1.0 unless the local ISRF is extremely intense, i.e., G₀ > 10⁵ Boulanger et al. (1994).

3.3. Daughter-molecule formation

The photolysis and associated aromatisation of a-C:H materials yields decomposition products other than molecular hydrogen (Section 3). However, the other released species contain at least one carbon atom and result in decomposition and a structural re-adjustment to a lower hydrogen and carbon content. Smith (1984) and Alata et al. (2014) showed that a-C(H) loses its hydrogen as H₂ but also as small hydrocarbon molecules. Thus, a-C(H) photolytic decomposition leads to significant mass loss from the material during thermal- photo-processing. It is likely that the release of daughter radical or molecular species will be more pronounced in smaller particles e.g., Duley et al. (2000). Scott et al. (1997) Duley et al. (2000). Jones (2009). Pety et al. (2005) proposed that the small hydrocarbon molecules that they observed in PDR regions i.e., CCH, C₂H₂, C₆H₁₄ derive from pre-existing PAHs, which are undergoing UV photon-induced destruction. A similar hypothesis was proposed by Scott & Duley (1996) and extended by Jones (2009), who postulated that the precursors for the ‘PAHs’ are themselves derived from the UV photolytic de-construction of small a-C(H) particles in the transition regions between molecular clouds and PDRs. Such a process is supported by the laboratory work of Smith (1984, Alata et al. 2014) and Duley et al. (2013), which indicates that small molecules are formed during the degradation of bulk a-C(H) materials. As shown by Duley et al. (2015) the primary a-C(H) photo-decomposition products are hydrocarbon species (molecules and radicals) with less than four carbon atoms, e.g., C₂H₂, C₄H₄ and C₆H₂–1 alkyl radicals. The experimental evidence therefore favours a top-down photo-processing route to small hydrocarbon formation in PDRs (see Sect. 2). However, Duley et al. (2015) also note the release of C₆H₆ (phenyl) and C₆H₆ (benzene) in their a-C(H) photo-decomposition experiments, indicating that the loss of single six-fold ring systems (the smallest possible aromatic domains) also needs to be included into the aliphatic/olefinic bridge-breaking and a-C(H) re-structuring mechanism proposed in Sect. 2.

To be viable an interstellar dust model must therefore be consistent with both the PDR observations Pety et al. (2005, 2012, Guzmán et al. (2015) and the laboratory-observed UV photolytic-formation of small aliphatic-rich species from carbonaceous materials e.g., Smith (1984, Scott & Duley (1996), Alata et al. 2014, Duley et al. 2015). In our recent work we used the optical and physical properties of a-C(H) materials within the framework of a new ISM core/mantle dust model, which is qualitatively-consistent with these data Jones et al. (2009, 2012, 2013). In this model a-C(H) nano-particles (with a number of C atoms N_C ≤ a few hundred) are of mixed aliphatic/aromatic (aromatic) composition and exhibit ‘cage-like’ cluster structures (see Fig. 1). Such structures have been proposed as fullerene precursors Micalotta et al. (2012) and are similar to the locally aromatic polycyclic hydrocarbons (LAPHs) proposed as IR emission band carriers by Petrie et al. (2003). The photon-driven fragmentation of such nano-particles in PDRs will disaggregate them into their their sub-component aliphatic/olefinic bridging structures with N_C ≤ 4) and small aromatics (with few rings, i.e., N_R = 3 – 8, Jones 2012). All of these daughter species will be more rapidly photo-dissociated in PDRs than the parent nano-particle. They are therefore transient species signalling the demise of a-C(H) nano-particles in intense radiation fields Jones et al. (2013) but at the same time they are the drivers of some interesting top-down interstellar chemistry.

In PDRs it is also possible that the a-C(H) grains are undergoing a sort of slow combustion by reaction with the abundant gas phase atomic oxygen, i.e.,

\[ \text{O}_2(g) + [a - \text{C}(\text{H})] \rightarrow [a - \text{CH}] + \text{CO}_2(g) \]

Such a process will lead to the formation of excited CO molecules in regions where the a-C(H) dust is being eroded.

To this list can now be added the ion C₆H⁺, which has also been observed in the Horsehead Nebula (Pety et al. 2012).
4. Conclusions

We have shown that the UV-UV photo-processing of the aliphatic/olefinic bridging structures in aromatic a-C(H) grains could provide a viable route to H$_2$ formation in the ISM, where the ISRF is sufficiently intense, i.e., $1 \leq G_0 \leq 10^2$.

A photon-driven mechanism for H$_2$ and daughter hydrocarbon radical and molecule formation is proposed, which operates through the chemisorption of H atoms at activated sites and CC bond destruction, respectively. It is also possible that this H$_2$ formation mechanism could be aided by the dangling bonds favoured by low N atom doping concentrations within a-C(H) nano-particles. The proposed process is not directly dependent on the grain temperature and therefore would provide a plausible route to H$_2$ formation in PDRs where the large grains are warm (i.e., $T_{dust} > 25$ K) and where experiments indicate that H$_2$ formation, involving H atom physisorption on grain surfaces, is not efficient. We note that even in the diffuse ISM ($G_0 = 1$) the nano-particles responsible for the bulk of the H$_2$ formation, from UV photon-induced CH bond dissociation, and also for the IR emission features have temperatures of the order of 50–70 K.

In more intense radiation fields these same nano-grains will have temperatures well in excess of 100 K. In PDRs where the large grains are much warmer ($T_{dust} \geq 50$ K), such as the Orion region, the proposed mechanism will no longer operate because the small a-C grains that dominate H$_2$ formation are destroyed.

In high extinction regions, the UV flux will be insufficient to drive H$_2$ formation and in extremely intense radiation fields H$_2$ formation will be severely limited because the active sites are destroyed as the grains undergo UV photon-induced fragmentation. It therefore appears that, for a given region of the ISM, there will be an optimum set of physical conditions that will favour H$_2$ formation by the proposed mechanism. The most favoured conditions would appear to be moderate densities and radiation fields but these will need to be quantified by detailed modelling. Seemingly, PDR regions are the ideal sites for H$_2$ formation from the photolytic processing of a-C(H) grains.

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