

Diffuse interstellar medium organic polymers Photoproduction of the 3.4, 6.85 and 7.25 μm features^{*}

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Abstract. We discuss the production of a hydrogenated amorphous carbon polymer (a-C:H) via the photolysis of methane at low temperature, resulting in a network made of CH_2 and CH_3 groups with some contribution of unsaturated bonds ($\text{C}=\text{C}$, $\text{C}\equiv\text{C}$). This solid provides an excellent fit to the Diffuse Interstellar Medium (DISM) 3.4, 6.85 and 7.25 μm features, as observed either in our Galaxy or towards external galaxies lines of sight. The photoproduction and thus photoresistance of this a-C:H made under conditions that resemble those of the DISM (low temperature, UV field) are relevant for astrophysical applications. The profiles of the absorption bands of this material are closer to the astrophysical ones than any previously reported carbonaceous analogs of the DISM organics.

Key words. ISM: dust, extinction, lines and bands

1. Introduction

The so-called “3.4 μm ” absorption feature (in the 3150–2750 cm^{-1} range) is observed toward diffuse cloud Galactic lines of sight (e.g. Rawlings et al. 2003; Pendleton & Allamandola 2002; Pendleton et al. 1994; Sandford et al. 1991) as well as in a few external galactic nuclei (Imanishi 2000; Dartois et al. 2004). Toward the few lines of sight where fluxes allow satellite observations to probe the mid infrared spectra counterpart of the 3.4 μm feature, additional related solid state bands at 6.85 and 7.25 μm are observed (Chiar et al. 2000; Dartois et al. 2004). The material observed via these C–H stretching (3.4 μm) and bending (6.85–7.25 μm) vibrations plays an important role, not only because it represents about 5 to 30% of the carbon cosmic abundance (Duley et al. 1998; Sandford et al. 1991), but also as a unique tracer of the Interstellar medium solid phase chemistry. It resides in an environment where, in the gas phase, only short length molecules or radicals are observed (e.g. Lucas & Liszt 2000, and references therein), questioning the origin/formation of this carbonaceous material. At a later stage in the galactic cycle, when entering dense clouds, its characteristic infrared CH signatures disappear, another observational fact which remains to be explained. Together with the 9.8 and 18 μm silicates features, the 3.4 μm and associated 6.85 and 7.25 μm bands, ubiquitously observed in the DISM, represent a highly significant dust component of galaxies. To date, more than ten candidate materials have been proposed to account for the 3.4 μm absorption feature (e.g., Greenberg et al. 1995; Schnaiter et al. 1998; Pendleton & Allamandola 2002). In this letter we present experiments that lead to the production of

amorphous hydrogenated carbon (a-C:H) via photolysis of methane (Sect. 2) and characterise its chemical composition by means of infrared spectra (Sect. 3). We compare the a-C:H with Galactic and extragalactic observations, discuss its formation and survival in the diffuse ISM (Sect. 4).

2. (a-C:H) Synthesis and spectral analysis

We perform three experiments based on the photolysis of the simplest hydrocarbon, CH_4 , summarized in Fig. 1. In the first (Exp. 1) one, CH_4 is condensed on a KRS5 (Thallium Bromide/Iodide) infrared window placed in an evacuated (10^{-7} mbar) cryostat cooled down to 10 K. The methane film deposition takes place at a rate of less than 0.1 μm thickness per hour whilst it is subjected to the UV irradiation of an H_2 discharge lamp. This lamp is interfaced to one of the cryostat ports by a MgF_2 window allowing up to 10 eV energetic photons to impinge on the film, at a rate of about 10^{14} photons/s/cm². This irradiation/codeposition lasts one day in order to continuously produce the a-C:H film. The sample is then smoothly warmed-up to a temperature of 40 K in order to let the methane trapped in the film diffuse and evaporate. The cryogenic cool down is then stopped to let the sample return to room temperature (RT, 300 K), the only remaining film being the produced a-C:H. In the second experiment (Exp. 2) we proceed by cycles of irradiation/evaporation. A CH_4 very thin film is deposited, then irradiated for an hour and a half, then the sample is annealed at 40 K to evaporate the residual CH_4 , and then cooled down again at 10 K. This cycle is repeated five times. The sample is also brought up to RT. In the third experiment (Exp. 3), a thick (relative to UV cross section) CH_4 film was deposited and irradiated during a full day. Consequently, the photons only affected the upper part of the deposited sample. The sample is

^{*} Based on Experiments performed at IAS-CNRS and observations from ESO-VLT and Spitzer Space Telescope.

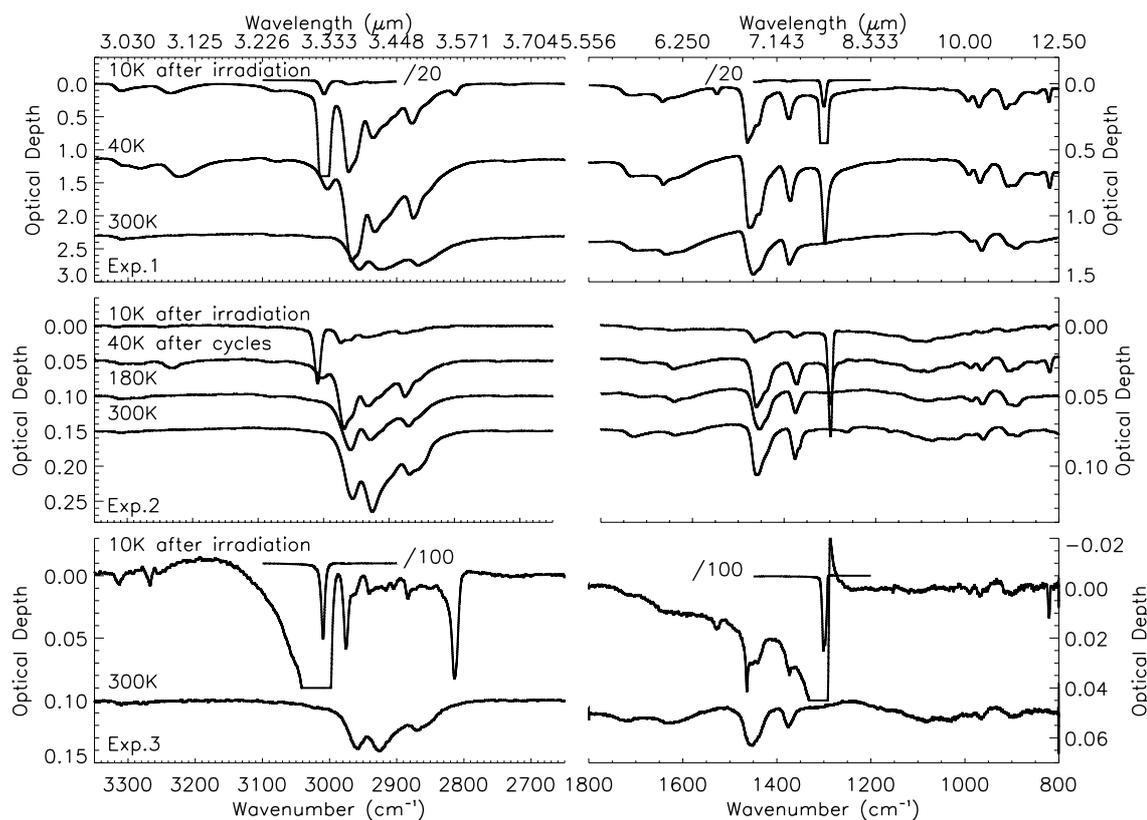


Fig. 1. Experiments of a-C:H production via solid CH₄ photolysis at 10 K, described in Sect. 2. The 2650–1800 cm⁻¹ region is not shown, for clarity, because no strong absorptions are present, only trace CO₂ and CO resulting from residual contamination of H₂O photolysis in the presence of CH₄, that evaporates during warm-up. This residual H₂O is also responsible for the formation of the carbonyl absorption seen at 1715 cm⁻¹.

also returned to RT. The experiments are presented from Exp. 1 to 3 in increasing amount of energy deposited per molecule. In each of these experiments the a-C:H was returned to RT to demonstrate that it is an extremely stable polymer.

At low temperature, the photolysis of CH₄ produces mainly radicals (CH₂, CH₃), higher alkanes or alkenes (C₂H₆) as well as olefinic radicals (i.e. C=C bonds) and molecules, and little aromatic like material. The reader is referred to Table 2 in Gerakines et al. (1996) for the identification of the peaks appearing at low temperature in photolysed CH₄. Under photolysis (and also annealing for radicals) they start to form a three dimensional network, which progressively becomes stable to evaporation, but also to hard UV irradiation. An alkane precursor seems more suited to the production of the DISM carbonaceous solid rather than the photolysis of typical interstellar mixtures, which produces O-rich residues. Indeed, the oxygen content of the produced polymer must be rather low, to agree with the absence of the strong carbonyl stretching mode, observationally constrained. The result of these experiments compares very well with the plasma produced a-C:H, but without requiring energetic phenomena and pressures that would not be relevant in the astrophysical context. Excellent review for plasma produced polymers from the infrared spectroscopic point of view are given by Ristein et al. (1998) and Dischler (1987). The a-C:H produced by UV irradiation here is similar to the plasma produced one without applying any bias voltage, as described in their review. However, it must

be considered different, as the full widths at half maximum (*FWHM*) of the plasma analogs individual stretching modes are 20% to 50% higher. This makes the fit of the DISM 3.4 μm with our residue much better than the plasma residue, even if the produced organic network is similar. Following the precited work for plasma a-C:H, we decompose the 3.4 μm profile using Gaussian fits of the individual stretching modes present in the film. Such a decomposition is shown in Fig. 2 for the three a-C:H films produced. The width of the more spectroscopically isolated mode, i.e. the CH₃ asymmetric stretching mode, is higher than pure alkanes one, even when studying large chains. In this analysis one recognises the methyl (CH₃) and methylene (CH₂) symmetric and asymmetric modes. However, for the fit we need to include an additional band around 2900 cm⁻¹ which is in fact due to a wing of the CH₂ asymmetric absorption. The resultant fits parameters are given in Table 1.

3. DISM polymers: Observations and perspectives

We display in Fig. 3 the comparison of the optical depth spectra in the C–H stretching and bending modes of the laboratory produced a-C:H with the line of sight to the center of our Galaxy, probing the interstellar diffuse medium matter. The adopted continuum for the astronomical data was done in the same way as the one shown in Dartois et al. (2004). The obtained fits are excellent both in width and position, revealing we are dealing with the same kind of material. The same kind

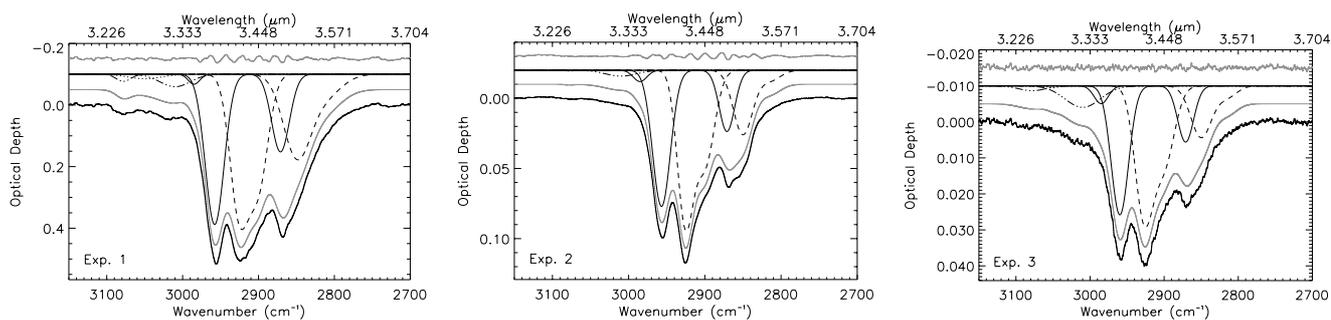


Fig. 2. Line profiles fits to the C–H stretching mode region of the photo-produced a-C:H in the three experiments. The decomposition into Gaussians follows the extensive study of plasma produced a-C:H of Ristein et al. (1998). In each panel, *from bottom to top*: experimental spectrum at 300 K; resulting fit; fit components by groups (CH₂: dashed line, CH₃: full line, olefinic: dot-dashed line, aromatic: dotted line); difference between experiments and fit. The fits and difference were off shifted for clarity. The corresponding fits values are given in Table 1.

Table 1. 3.4 μm profile fitting results (normalised to the aliphatic CH₃ asymmetric mode).

Vibrational mode	Exp. 1			Exp. 2			Exp. 3		
	Position (cm ⁻¹)	FWHM (cm ⁻¹)	Ampl.	Position (cm ⁻¹)	FWHM (cm ⁻¹)	Ampl.	Position (cm ⁻¹)	FWHM (cm ⁻¹)	Ampl.
Olef.CH ₂ asym.	3078	22.6	0.05	3078	13.3	0.005	3078	42.4	0.04
Arom.CH	3050	53.1	0.03	3050	49.4	0.001	3050	15.8	0.02
Olef.CH	3010	47.1	0.08	3010	48.1	0.043	3010	56.3	0.17
Olef.CH ₂ sym.	2985	17.7	0.07	2985	20.7	0.08	2985	22.2	0.14
Aliph.CH ₃ asym.	2957.8	29.3	1	2956.8	27.6	1	2959.8	27.6	1
Aliph.CH ₂ asym.	2925.6	28.9	0.91	2925.9	24.6	1.09	2927.3	28.9	0.99
Aliph.CH ₂ asym.(wing)	2900	30.2	0.72	2900	29.6	0.69	2900	32.7	0.56
Aliph.CH ₃ sym.	2871	27.8	0.52	2871	23.9	0.45	2871	25.2	0.44
Aliph.CH ₂ sym.	2850	41.8	0.52	2850	29.8	0.47	2850	33.1	0.4
Aliph.CH ₂ sym.(wing)	2815	53.6	0.15	2815	32.5	0.08	2815	31.0	0.09

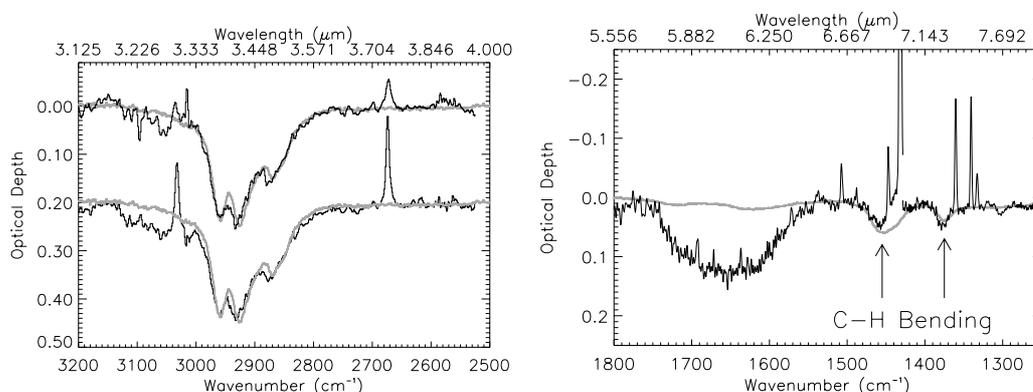


Fig. 3. Comparison between optical depth spectra of the Galactic Center IRS7 line of sight with photoproduced a-C:H. *Left* (C–H stretch region): the laboratory spectrum (grey) is superimposed on two independent VLT-ISAAC spectra (black) taken at different position angle in the sky. *Right* (C–H bend region): corresponding bending mode region recorded by the ISO-SWS instrument. Note that strong emission lines of H₂ S(5) at 6.910 μm and ArII at 6.985 μm (Lutz et al. 1996) fill part of the a-C:H CH₂ bending mode absorptions. See text for details.

of comparison is done for the bending modes for extragalactic sources lines of sight, thought to be Seyfert 2 galaxies. Due to the faintness of these later sources in the *L* band of the spectrum we unfortunately do not have their 3.4 μm C–H stretching absorption counterpart. However, as described for other similar Seyfert 2 extragalactic lines of sights by Dartois et al. (2004), the 3.4 μm line profiles should be the same. Using these data we can predict that observed with the same aperture, the 3.4 μm optical depth in these lines of sight should be of the order of 1.2

and 3 for IRAS F00183–7111 and NGC 4418, respectively. We have produced via photolysis of a simple alkane a material that matches perfectly the stretching and bending mode spectra of the DISM solids observed in absorption. This production was obtained at 10 K, far from the energetic plasma synthesis generally used to produce thin a-C:H films. These experiments are relevant with respect to the DISM, as the only produced species are short radical and molecules at low temperature. The diffuse clouds CH, C₂H, C₃H₂, C₃, HC₄H species can contribute to

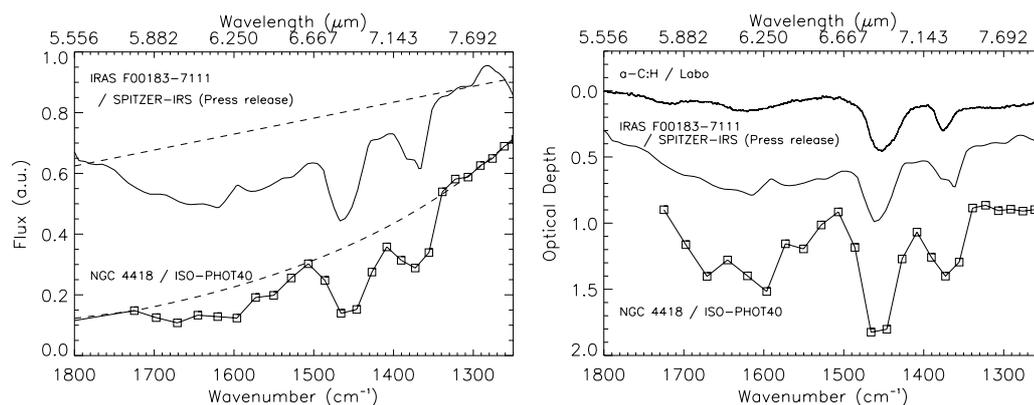


Fig. 4. Comparison between optical depth spectra of extragalactic nuclei absorptions with the photoproducted a-C:H in the C-H bending modes window. The laboratory spectrum is presented above the SPITZER-IRS press released spectrum of IRAS F00183-7111 (Credit: NASA/JPL-Caltech/L.Armus (SSC/Caltech), H.Kline (JPL), Digital Sky Survey) as well as an ISO-PHOT40 spectrum of NGC 4418. See text for details.

the formation of the observed polymers given their relatively high abundances (Lucas & Liszt 2000). However, given the low DISM density, unless the dominant C^+ ion is the precursor of the a-C:H, the collision timescale necessary for the formation of the observed abundance of this polymer is too large, and therefore favours a production in the ejecta of old stars losing mass. This might explain why the $3.4 \mu\text{m}$ feature is observed in some galaxies lines of sight but almost never toward starburst galaxies which possess young stars (Imanishi 2003), and also in the envelope of e.g. CRL618 (Chiar et al. 1998).

Amongst the possible a-C:H, the produced 3.4 , 6.85 and $7.25 \mu\text{m}$ absorptions profile that fits the ISM are typical of a polymer like carbon (PLC) possessing few olefinic bonds, and contains only few percents of aromatics, far from the view of kerogen like material. Based on our fits, and taking a ratio of integrated absorbance for the aromatic CH stretch and CH_3 asymmetric mode between 3 and 5 depending on the literature (Ristein et al. 1998; Joblin et al. 1994; Duley et al. 1998), the aromatics represent at the very most only 15% of the absorption. The notable absence of strong aromatic $\text{C}=\text{C}$ absorption at 1600 cm^{-1} in the DISM, with respect to the CH_3 bending, puts a stringent upper limit, because the relative integrated absorption of these mode is of the same order of magnitude, but moreover because it does not rely on the hydrogen coverage of these aromatics. The detection of the PAH $6.2 \mu\text{m}$ feature in absorption has been reported in the literature. However, the lack of correlation with the silicates features (Schutte et al. 1998) and its absence in otherwise highly extinct sources (Chiar & Tielens 2001) suggest a circumstellar and not DISM origin. In addition, the a-C:H presented here does not produce strong bands in the 6 to $12 \mu\text{m}$ wavelength range, which is the case of insoluble residues of carbonaceous meteorites or kerogen like material, generally used to fit the $3.4 \mu\text{m}$ band, in contradiction with actual astrophysical observations.

The produced material in our experiment is UV-resistant by definition, as is only allowed the organisation of an a-C:H network that can suffer a high dose of hard UV photons. The a-C:H produced was also irradiated during a full week without any significant spectral changes, although a proper UV destruction cross section was not measured. This resistance is an important criterium for its validity as a DISM solid given the

high UV field ($\sim 10^7 \text{ photons cm}^{-2} \text{ s}^{-1}$). Further detailed and dedicated studies of the photoproducted a-C:H are undertaken and an extensive analysis of this a-C:H polymer will follow.

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