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Journal:	<i>Monthly Notices of the Royal Astronomical Society</i>
Manuscript ID:	MN-11-2721-MJ.R2
Wiley - Manuscript type:	Main Journal
Date Submitted by the Author:	12-Apr-2012
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Keywords:	ISM: molecules < Interstellar Medium (ISM), Nebulae, molecular data < Physical Data and Processes, astrochemistry < Physical Data and Processes, methods: laboratory < Astronomical instrumentation, methods, and techniques

INFRARED SPECTROSCOPY OF HYDROGENATED FULLERENES (FULLERANES) AT EXTREME TEMPERATURES

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ABSTRACT

The infrared spectra, as well as the integrated molar absorptivity (Ψ) and the molar extinction coefficient (ϵ) of each infrared transition of the hydrogenated fullerenes (known as fulleranes) $C_{60}H_{36}$, $C_{60}H_{18}$, and $C_{70}H_{38}$, and a mixture of fulleranes generally referred as 77% of $C_{60}H_x$ and 22% $C_{70}H_y$ with $x \approx y > 30$, are presented and discussed. These data are useful for the search, identification, and quantitative determination of fulleranes in space after the recent discovery that their parent molecules, C_{60} and C_{70} , are more abundant in space than initially thought, being present in a variety of H-rich circumstellar environments such as planetary nebulae and only mild H-deficient R Coronae Borealis stars, and in the interstellar medium. It is shown that the C-H stretching band of the fulleranes $C_{60}H_{36}$, $C_{60}H_{18}$, and $C_{70}H_{38}$, and their mixture may be the most useful for the identification of these molecules because their Ψ and ϵ values are unique in terms of strength overcoming by far the typical Ψ and ϵ values of reference molecules such as adamantane and docosane, as well as typical ϵ literature data for aliphatic molecules. In contrast with the rather simple infrared spectra of $C_{60}H_{36}$ and $C_{60}H_{38}$, the infrared spectra of two $C_{60}H_{18}$ isomers are reported as characterized by a rich number of bands which may allow an easier identification than the higher homologues. The dependence of the infrared bands of fulleranes on temperature was studied over a wide range of temperatures (from -180°C to $+250^\circ\text{C}$) and extrapolated to 0 K.

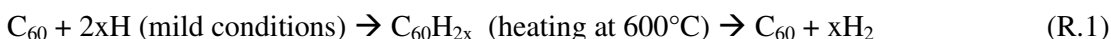
Key words: Fulleranes; $C_{60}H_{36}$, $C_{60}H_{18}$ and $C_{70}H_{38}$; adamantane; docosane; infrared spectroscopy; integrated molar absorptivity; molar extinction coefficient

1. Introduction

Immediately after the discovery of fullerenes (Kroto 1988), their possible existence around late-type carbon-rich stars was postulated (Kroto 1992; Hare & Kroto 1992). Particularly attractive was the thesis of the fullerene formation around the R Coronae Borealis (RCB) class of stars (Goeres & Sedlmayr 1993), characterized by a very low hydrogen content and high helium and carbon enrichment, conditions which are analogous to those employed in the laboratory synthesis of fullerenes (Kratschmer et al. 1991). The first hint of the possible existence of fullerenes in the interstellar medium (ISM) was suggested from the identification of C_{60}^+ transitions with certain diffuse interstellar bands (Foing & Ehrenfreund 1994). More firm evidence that fullerenes occur naturally in the ISM was obtained only recently when the infrared transitions of C_{60} and C_{70} were detected as neutral molecules around the young planetary nebula Tc1 (Cami et al. 2010). The detection of fullerenes was then reported also in a series of H-containing planetary nebulae (PNe), challenging our knowledge of the fullerene formation mechanism (García-Hernández et al. 2010); these latter detections showed that, contrary to many theoretical and experimental expectations,

fullerenes are found (and may be formed) in H-rich circumstellar envelopes. The C₆₀ infrared signature was also reported in two RCB stars having a certain degree of hydrogen depletion, but not enough to justify the presence of fullerenes unless it is admitted that in this case fullerenes are formed by the shock decomposition of hydrogenated amorphous carbon (HAC) grains (García-Hernández, Rao & Lambert 2011). The shock-induced decomposition of HACs as the preferred fullerene formation scenario in the circumstellar shell of evolved C-rich stars is also suggested by new detections of C₆₀ and C₇₀ fullerenes in several PNe of the Magellanic Clouds (García-Hernández et al. 2011). C₆₀ has also been detected in other H-rich astrophysical environments such as reflection nebulae (Sellgren et al. 2010) and the proto-PN IRAS 01005+7910 (Zhang & Kwok 2011).

The next anticipated discovery will be with regard to hydrogenated fullerenes, known as fulleranes, as first suggested by Webster (1992, 1993) and as proposed more recently by Cataldo and Iglesias-Groth (2009 and 2010a). The fact that their parent molecules (e.g., C₆₀, C₇₀) are found in several H-rich astrophysical environments implies that they are more abundant than initially believed, and that their hydrogenated derivatives, the hydrogenated fullerenes, may be widespread in the Universe. The reason for this statement is our knowledge that fullerenes, when exposed to atomic hydrogen, are easily hydrogenated in laboratory conditions, but are not reactive with molecular hydrogen (H₂). Indeed, in the laboratory it is easy to produce C₆₀H₃₆ or C₇₀H₃₈ in one shot and their perdeuterated analogues (Cataldo et al. 2009a; Cataldo et al. 2009b). In contrast, it is more difficult, and in some conditions impossible, to produce hydrogenated fullerenes with a lower degree of hydrogenation. The thermal annealing at about 350°C of C₆₀H₃₆ causes the elimination of part of the hydrogen content leading to the formation of C₆₀H₁₈. Further thermal processing of both C₆₀H₃₆ and C₇₀H₃₈ for instance at 600°C, again in vacuo or in an inert atmosphere, leads to the complete elimination of hydrogen and the restoration of the pristine C₆₀ and C₇₀ (Cataldo & Iglesias-Groth 2009a; Cataldo & Iglesias-Groth 2010b; Cataldo et al. 2010). Thus, we can summarize these results in a simple scheme:



A similar scheme can obviously be written for C₇₀. It is worth underlining that the easy reactivity of fullerenes occurs with atomic hydrogen and not with molecular hydrogen. Therefore, the scheme R.1 shows that the hydrogenation and dehydrogenation of fullerenes has the neat effect of transforming atomic hydrogen into molecular hydrogen in space, and fullerenes and their derivatives may play a key role in molecular hydrogen formation in space starting from atomic hydrogen (Cataldo & Iglesias-Groth 2010a). Furthermore, C₆₀ and C₇₀ fullerenes are remarkably stable to high energy radiation (Cataldo et al. 2009c) while fulleranes are photolyzed by UV radiation, losing hydrogen and also undergoing deuterium enrichment under these photolytic conditions (Cataldo and Iglesias-Groth 2009; Cataldo et al. 2009d; Cataldo et al. 2009e).

In order to permit the identification of C₆₀ and C₇₀ fullerenes, and the quantification of their column density, we have studied the dependence of the infrared band intensity and band position of these molecules with temperature from 93 K to 523 K, extrapolating the data to 0 K and to 1000 K (Iglesias-Groth, Cataldo & Manchado 2011). Furthermore, the molar extinction coefficient and the integrated molar absorptivity of each infrared band of fullerenes C₆₀ and C₇₀ were determined. These data have been extremely useful for an accurate and quantitative determination of the C₆₀ and C₇₀ abundances in several PNe (García-Hernández et al. 2011). Since it is expected that “fulleranes” the hydrogenated derivatives of C₆₀ and C₇₀ may also be present in space, we have synthesized a series of hydrogenated fullerenes (C₆₀H₃₆, C₇₀H₃₈, and C₆₀H₁₈; the latter obtained in two isomers) and recorded their infrared spectra, measuring the molar extinction coefficients and integrated

molar absorptivity on a laboratory scale. This information will undoubtedly permit the search for, and accurate abundance determination of, these molecules in astrophysical environments.

2. Experimental

2.1 Materials and equipment

The fullerenes C_{60} and C_{70} were high purity grades (99.95% and 99.0+% respectively) from MTR Ltd, (USA). They were converted into $C_{60}H_{36}$ and $C_{70}H_{38}$ respectively according to the hydrogenation procedure already detailed elsewhere (Cataldo and Iglesias-Groth, 2010a; Cataldo et al. 2009a; Cataldo et al. 2009b; Cataldo and Iglesias-Groth 2009). Mixture of fullerenes produced by dry hydrogenation under pressure of both C_{60} and C_{70} were obtained from ABCR GmbH (Germany) and were fully characterized, as reported previously (Cataldo and Iglesias-Groth 2010b). The fullerane mixture consisted of 77% of $C_{60}H_x$ and 22% $C_{70}H_y$ with $x \approx y > 30$. Fullerane $C_{60}H_{18}$ was synthesized by the action of hydrogen iodide on C_{60} following by thermal annealing (Cataldo and Iglesias-Groth 2010c).

As reference materials for the measurement of the ϵ and Ψ values of the C-H stretching bands, use was made of a straight chain paraffin *n*-docosane $C_{22}H_{46}$ (obtained from Merck, Germany) and of a cage compound adamantane $C_{10}H_{16}$ obtained from Sigma-Aldrich (USA).

Potassium bromide (infrared spectroscopy grade) was obtained from Sigma-Aldrich (USA). The infrared spectra were recorded on a Thermo-Fischer FT-IR spectrometer model Nicolet IR-300 at a resolution of 1 cm^{-1} . The variable temperature cell from Specac model P/N 21525 equipped with KBr windows was used to record the spectra under vacuum at room temperature. The cell was evacuated with a Buchi vacuum pump (model V-710) equipped with four diaphragm heads and a three-stage vacuum creation process that delivers $3.1 \text{ m}^3/\text{h}$ and an absolute vacuum of 2 mbar. Low temperature spectra down to -180°C were acquired with the above mentioned apparatus (Specac model P/N 21525) using liquid nitrogen, while higher temperatures up to $+250^\circ\text{C}$ were reached with a dedicated heating system of the cell Specac model P/N 21525.

2.2 – Sample preparation and FT-IR spectrum registration

$C_{60}H_{36}$ and $C_{70}H_{38}$ were used in KBr pellet preparation as soon as synthesized and isolated after solvent evaporation under vacuum. Instead, $C_{60}H_{18}$ was used immediately after the thermal decomposition of its precursor as reported by Cataldo and Iglesias-Groth (2010c). As a general procedure, 2-4 mg of sample under study were accurately weighed and then quickly mixed with 300 mg of KBr (accurately weighed) in an agate mortar. The ground mixture was transferred in a KBr pellet die designed for a 13 mm diameter pellet. The KBr pellets were produced in a Silfradent press equipped with a pressure meter; the KBr pellets were compressed at a pressure of between 4.0 and 5.0 ton/cm^2 . The thickness of the KBr pellets immediately after the extraction from the die was measured with a Somet digital micrometer having a sensitivity of 0.01 mm. Typically, thicknesses of around 1.0 mm were achieved. A background was collected with the FT-IR spectrometer on the empty and evacuated Specac cell. Afterwards, the cell was opened and the KBr pellet mounted on the sample holder inside the cell, which was then evacuated for the recording of the sample spectra normally at a temperature between 30°C and 55°C .

For the spectra taken at -180°C , the cell was filled with liquid nitrogen and the temperature of the sample holder monitored with a thermocouple until a stable temperature was achieved. A temperature of $+250^\circ\text{C}$ was reached using the Joule effect provided by an external thermal control unit.

3. Results

3.1 – General aspects on the FT-IR spectra of fullerenes.

The infrared spectra of fullerenes mixture (77% of $C_{60}H_x$ and 22% $C_{70}H_y$ with $x \approx y > 30$) are dominated by very strong absorption bands due to the C-H stretching between 3.44 and 3.54 μm as shown in Fig. 1. In comparison to the intensity of the C-H stretching transitions all the other transitions in the infrared spectrum of fullerenes appear rather weak. It can therefore be anticipated that the bands at about 3.44 and 3.54 μm , being the strongest bands of fullerenes, will be the right bands for searching these molecules in the circumstellar and interstellar environments. The detail of the C-H stretching band of fullerenes is shown in Fig. 2. In this spectral region it is possible to distinguish quite easily the fullerene C-H stretching at 3.44, 3.51 and 3.54 μm from the aromatic C-H stretching of PAHs occurring at shorter wavelengths at about 3.30 μm (Colthup et al. 1990; Nakanishi 1972).

The infrared spectra of the hydrogenated fullerenes and their perdeuterated derivatives have been discussed previously (Cataldo et al. 2009a; Cataldo et al. 2009b; Cataldo & Iglesias-Groth 2010a; Cataldo & Iglesias-Groth 2010b) and will not be pursued further here. It is worth remembering that deuterated fullerenes are slightly more stable to photolysis and thermal decomposition than the hydrogenated isomer (Cataldo & Iglesias-Groth 2010a; Cataldo & Iglesias-Groth 2009; Cataldo et al. 2009d; Cataldo et al. 2009e), and that this may give rise to the deuterium enrichment of the surface of hydrogenated/deuterated fullerenes in space due to this isotope effect.

The focus of present paper is on the temperature dependence of fullerene infrared absorption bands and on the molar extinction coefficient (ϵ) and the integrated molar absorptivity (Ψ) of these molecules, which will be discussed in the following sections.

3.2 - Low temperature FT-IR spectra of mixture of fullerenes $C_{60}H_x$ (77%) and $C_{70}H_y$ (22%)

When a mixture of C_{60} and C_{70} fullerenes is subjected to dry hydrogenation at high pressure and temperature, a mixture of products generally referred as fullerene hydrides or fullerenes $C_{60}H_x$ (77%) and $C_{70}H_y$ (22%) are obtained (Cataldo & Iglesias-Groth 2010a). The mixture of fullerenes $C_{60}H_x$ (77%) and $C_{70}H_y$ (22%) shows remarkable stability in humid air and this has permitted us to record their spectra in the range of temperatures between +250°C and -180°C. The infrared spectra taken at room temperature and at the two extreme temperatures are shown in Fig. 1 and 2. The spectra are dominated by the strong C-H stretching band.

The position of the C-H stretching bands appears almost independent of the temperature and can be followed in Table 1. The bands in the fingerprint region of the spectrum of the $C_{60}H_x$ and $C_{70}H_y$ mixture show a dependence on temperature as shown in Table 1. The shift towards shorter wavelengths at lower temperatures appears evident for certain bands. There are just three absorption bands that deviate from this trend, showing an opposite wavelength dependence on temperature, but this could also be due to phase transitions and the formation of new phases.

Table 1 shows also the extrapolation to 0 K of the infrared absorption bands of the fullerenes $C_{60}H_x$ (77%) and $C_{70}H_y$ (22%), an extrapolation that should be taken with the usual limitation derived from the fact that we are measured the spectra in a KBr solid matrix and not in the gas phase. Thus, the real values at 0 K in the gas phase are expected with a further correction of 5-10 cm^{-1} toward higher frequencies. The extrapolation of the infrared absorption bands to high temperature has not been made since the fullerenes $C_{60}H_x$ (77%) and $C_{70}H_y$ (22%) start to decompose in an inert atmosphere at 478°C returning the fullerenes C_{60} and C_{70} .

TABLE 1 - Summary of C₆₀H_x + C₇₀H_y infrared absorption bands in μm

0 K KBr matrix extrap. to 0 K	98 K KBr matrix	523 K KBr matrix	Shift from 523 K to 98 K
3.44	3.44	3.44	0.00
3.51	3.51	3.51	0.00
3.52	3.52	3.52	0.00
3.54	3.54	3.54	0.00
6.54	6.56	6.63	0.08
6.76	6.77	6.79	0.02
6.81	6.83	6.90	0.07
6.91	6.92	6.96	0.04
7.30	7.30	7.34	0.04
7.53	7.52	7.47	-0.05
7.71	7.69	7.62	-0.07
7.90	7.90	7.90	0.00
8.14	8.15	8.17	0.02
8.46	8.47	8.49	0.03
8.69	8.69	8.70	0.01
9.91	9.90	9.85	-0.05
10.67	10.68	10.71	0.03
	11.53	11.54	0.01
12.24	12.24	12.27	0.03
22.22	22.28	22.54	0.27

3.3 - Low temperature FT-IR spectra of C₆₀H₁₈ fullerane

Among the numerous hydrogenated fullerenes synthesized till now, the most stable and accessible is C₆₀H₁₈. Fullerenes with a higher degree of hydrogenation tend to decompose thermally to C₆₀H₁₈ or undergo oxidation and hydrolysis (Cataldo and Iglesias-Groth 2010a). C₆₀H₁₈ is easily accessible through the high pressure hydrogenation reaction or through the reaction between hydrogen iodide and C₆₀ followed by a moderate thermal annealing of the product in an inert atmosphere (Cataldo & Iglesias-Groth 2010c). Once produced, C₆₀H₁₈ shows remarkable hydrolytic stability and oxidation resistance in air. This has permitted us to study its infrared absorption spectrum from +250°C (523 K) to -175°C (98 K). The infrared spectra of C₆₀H₁₈ recorded at room temperature are shown in Fig. 3-5. Two spectra are shown: they are very similar, but between 18 and 19 μm there are important differences suggesting that we are dealing with two different C₆₀H₁₈ isomers. In fact the spectrum at the top of Fig. 3 and Fig. 5 shows two bands at 18.35 and 18.94 μm while the spectrum at the bottom of the two figures shows the two bands at 18.40 and 18.65 μm. These small spectral differences can be interpreted in terms of two different C₆₀H₁₈ isomers that reflect the two different synthetic approaches to producing these molecules - i.e., using hydrogen iodide or direct hydrogenation with metal hydrides. The isomerism of hydrogenated fullerenes has already been discussed by other authors (Bini et al. 1998; Meletov et al. 2001; Clare and Kepert 2003), who have also made a series of remarkable theoretical calculations showing the symmetry of the potentially most stable isomers.

TABLE 2 - Summary of C₆₀H₁₈ infrared absorption bands in μm

0 K KBr matrix extrap. to 0 K	98 K KBr matrix	523 K KBr matrix	Shift from 523 K to 98 K
3.42	3.42	3.42	0.00
3.46	3.46	3.46	0.00
3.51	3.51	3.51	0.00
	6.10		
6.21	6.21	6.24	0.03
		6.63	
6.66	6.67	6.72	0.04
6.79	6.80	6.83	0.04
		6.87	
7.05	7.06	7.07	0.02
		7.48	
7.52	7.52	7.54	0.02
7.60	7.60	7.62	0.02
7.71	7.71	7.74	0.03
7.87	7.88	7.90	0.02
8.05	8.05	8.06	0.01
8.20	8.21	8.23	0.02
8.35	8.35	8.36	0.01
8.49	8.50	8.51	0.01
8.64	8.65	8.67	0.02
8.98	8.99	9.06	0.07
9.16	9.17	9.19	0.03
9.60	9.61	9.67	0.06
12.65	12.68	12.78	0.10
13.07	13.07	13.07	0.00
13.72	13.73	13.76	0.03
14.25	14.26	14.29	0.03
14.51	14.52	14.55	0.03
15.14	15.15	15.19	0.03
15.54	15.56	15.64	0.08
16.67	16.68	16.72	0.04
17.46	17.46	17.46	0.00
18.43	18.44	18.49	0,05
	18.71		
19.97	19.96	19.90	-0.06
21.02	21.03	21.10	0.07
21.65	21.68	21.83	0.15
		22.46	
		23.64	

The infrared spectra of C₆₀H₁₈ were also recorded at extreme temperatures from -175°C to +250°C and the main absorption bands are reported in Table 2. The most common trend of the infrared absorption bands in passing from high to low temperature is the shift towards slightly shorter wavelengths of the absorption bands although in some cases there are bands that appears almost insensitive to the temperature change. In Table 2, it can be seen that the C-H stretching modes of C₆₀H₁₈ are practically insensitive to temperature.

In the previous section we have also described our approach to extrapolate the infrared absorption bands measured at +250°C and -175°C to 0 K. The results of such an extrapolation are shown in Table 2. The limitations of such an approach have already been described: the matrix effect plays an important role. In fact in earlier studies (Cataldo et al. 2010) it was shown that the extrapolation to 0 K from gas phase spectral data leads systematically to band position shift at higher frequencies than those extrapolated from spectra of fullerenes embedded in a KBr matrix. The shift towards higher frequency is from 5 to 10 cm⁻¹ by passing from KBr to gas phase data extrapolated to 0 K.

3.4 – About the molar extinction coefficient of fullerenes

In another study, Iglesias-Groth et al. (2011) have reported in full detail the definitions and the meaning of the molar extinction coefficient of the infrared absorption bands of organic molecules. Here we simply recall the relationship linking the molar extinction coefficient ϵ_λ with the absorbance A_λ read at a given wavenumber:

$$\epsilon_\lambda = A_\lambda(bc)^{-1} \quad (\text{eq.1})$$

The value of $(bc)^{-1}$ is the geometric factor taking into account the sample dimensions and the KBr density of 2.753 g/cm³, where b is the optical path length measured in cm and c is the concentration of the fullerane sample in a KBr matrix measured in mol/cm³ (Iglesias-Groth et al. 2011).

From the infrared spectra of the hydrogenated fullerenes, the absorbance values A_λ have been determined using the EZ Omnic (version 6A) software of the infrared spectrometer. Tables 3 and 4 summarize the results of such measurements and give the molar extinction coefficient values ϵ_λ calculated according to eq. 1.

From the data in Table 3 and 4 it is immediately evident that the ϵ_λ of the ν_{C-H} of all the four fullerane samples (namely, C₆₀H₃₆, C₇₀H₃₈, C₆₀H_x+C₇₀H_y, and C₆₀H₁₈) considered in this study are extremely high, exceeding by far the ϵ_λ of the ν_{C-H} of the reference straight chain paraffin docosane and the cage compound adamantane.

In more detail, $\epsilon_{3.44}$ is 182.2 L•cm⁻¹•mol⁻¹ for C₆₀H₃₆ and 148.8 L•cm⁻¹•mol⁻¹ for C₇₀H₃₈ and 167.2 L•cm⁻¹•mol⁻¹ for the fullerane mixture C₆₀H_x+C₇₀H_y; this is in contrast with the value of $\epsilon_{3.44}$ =35.0 L•cm⁻¹•mol⁻¹ for the small cage compound adamantane, which contains hydrogenated tertiary carbon atoms such as fullerenes and the paraffin docosane, which is instead characterized by hydrogenated primary and secondary carbon atoms and whose $\epsilon_{3.38}$ = 23.0 L•cm⁻¹•mol⁻¹ and $\epsilon_{3.43}$ = 84.4 L•cm⁻¹•mol⁻¹. The last two ϵ_λ values are completely in line with literature data since Nakanishi (1972) quotes $\epsilon_{3.38} \approx 70$ L•cm⁻¹•mol⁻¹ for methyl groups and $\epsilon_{3.43} \approx 75$ L•cm⁻¹•mol⁻¹ for methylene groups.

The other fullerane infrared bands due to C-H stretching occur at 3.54 μm (see Table 3) and again are characterized by a considerably high $\epsilon_{3.54}$ value of 134-138 L•cm⁻¹•mol⁻¹ for both C₆₀H₃₆ and C₇₀H₃₈ and 154.4 L•cm⁻¹•mol⁻¹ for the fullerane mixture. These high $\epsilon_{3.54}$ values of fullerenes are again in contrast with the “normal” $\epsilon_{3.52}$ = 16.2 and 67.7 L•cm⁻¹•mol⁻¹ respectively for adamantane and docosane. Nakanishi (1972) indeed quotes $\epsilon_{3.51} \approx 30-45$ L•cm⁻¹•mol⁻¹, while for aromatic hydrocarbons the $\epsilon_{3.30} \leq 60$ L•cm⁻¹•mol⁻¹ (Nakanishi 1972; Colthup et al. 1990).

Table 3 - MOLAR EXTINCTION COEFFICIENTS OF FULLERANES, ADAMANTANE, DOCOSANE
(ϵ values in $L\ cm^{-1}\ mol^{-1}$)

μm	ϵ_{λ}	ϵ_{λ}	ϵ_{λ}	ϵ_{λ}	ϵ_{λ}	(*) ϵ_{λ}/nCH	(*) ϵ_{λ}/nCH	(*) ϵ_{λ}/nCH	(*) ϵ_{λ}/nCH	(*) ϵ_{λ}/nCH
wavelength	$C_{60}H_{36}$	$C_{70}H_{38}$	$C_{60}H_x+$ $C_{70}H_y$	Adaman- tane $C_{10}H_{16}$	Docosa- ne $C_{22}H_{46}$	$C_{60}H_{36}$	$C_{70}H_{38}$	$C_{60}H_x+$ $C_{70}H_y$	Adaman- tane $C_{10}H_{16}$	Docosa- ne $C_{22}H_{46}$
3,38					23.0					0.5
3,43					84.4					1.8
3,44	182.2	148.4	167.2	35.0		5.1	3.9	4.6	2.2	
3,52				16.2	67.7				1.0	1.5
3,54	134.1	138.0	154.4			3.7	3.6	4.3		
5,92			23.7					0.7		
6,12	25.7					0.7				
6,79					78.1					1.7
6,86	11.5					0.3				
6,92		23.9	26.7	20.2			0.6	0.7	1.3	
7,30					8.2					0.2
7,41				18.0					1.1	
8,10	31.6					0.9				
8,20			22.2					0.6		
8,89					5.1					0.1
9,11		25.8		10.9			0.7		0.7	
9,29	9.1					0.3				
9,36					3.4					0.1
9,85			16.1					0.4		
9,75	11.6					0.3				
10,34				5.5					0.3	
10,53				1.4					0.1	
11,24					7.3					0.2
12,58				9.8					0.6	
13,95					57.7					1.3
22,73				1.8					0.1	

(*) ϵ_{λ} values normalized for the number of CH groups in the molecule = $\epsilon_{\lambda} / n (C-H)$

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Table 4 - MOLAR EXTINCTION COEFFICIENTS ϵ_λ AND INTEGRATED MOLAR ABSORPTIVITY OF FULLERANE $C_{60}H_{18}$

μm	$\epsilon_\lambda (\text{L}\cdot\text{cm}^{-1}\cdot\text{mol}^{-1})$	$\epsilon_\lambda / n (\text{CH}) (*)$	$\Psi (\text{km mol}^{-1})$
wavelength	$C_{60}H_{18}$	$C_{60}H_{18}$	$C_{60}H_{18}$
3.43	77.4	4.3	
3.45	84.5	4.7	178.1 (**)
3.52	110.4	6.1	
5.89	30.5	1.7	8.2
6.22	62.3	3.5	17.5
6.32			
6.52	4.2	0.2	
6.67	14.6	0.8	2.6
6.81	34.7	1.9	4.9
7.05	29.3	1.6	4.3
7.50	15.5	0.9	
7.60	17.6	1.0	
7.70	18.4	1.0	
7.87	61.5	3.4	8.3
8.05	26.8	1.5	0.7
8.20	39.3	2.2	2.2
8.34	33.5	1.9	
8.47	48.9	2.7	6.5
8.64	13.0	0.7	
9.00	5.0	0.3	
9.16	5.0	0.3	
9.64	5.0	0.3	
12.71			
13.06	7.1	0.4	
13.72	15.1	0.8	1.90
14.25	7.5	0.4	0.36
14.48	9.2	0.5	0.52
15.16	7.1	0.4	0.46
15.62	7.5	0.4	0.60
16.64	22.2	1.2	1.97
17.40	39.7	2.2	2.62
18.45	56.0	3.1	1.5
18.99	99.9	5.6	5.04
19.94	38.5	2.1	1.59
20.66	29.7	1.7	
21.00	31.4	1.7	2.26
21.61	17.1	1.0	0.48

(*) ϵ_λ values normalized for the number of CH groups in the molecule = $\epsilon_\lambda / n (\text{C-H})$

(**) Integrated over the entire C-H stretching band

The position of the $\nu_{\text{C-H}}$ stretching bands of $\text{C}_{60}\text{H}_{18}$ are slightly different in wavenumbers from those of the other fullerenes (see Table 4). Indeed, the most intense C-H stretching band occurs at $3.52 \mu\text{m}$ with $\epsilon_{3.52} = 110.4 \text{ L}\cdot\text{cm}^{-1}\cdot\text{mol}^{-1}$, the same order of magnitude shown by other fullerenes, while the other C-H stretching bands of $\text{C}_{60}\text{H}_{18}$ occur at 3.43 and $3.45 \mu\text{m}$ with $\epsilon_{3.43} = 77.4 \text{ L}\cdot\text{cm}^{-1}\cdot\text{mol}^{-1}$ and $\epsilon_{3.45} = 84.5 \text{ L}\cdot\text{cm}^{-1}\cdot\text{mol}^{-1}$ respectively.

As shown in Table 3, the higher molar extinction coefficient of the C-H stretching bands of fullerenes is also confirmed after normalization of the ϵ value with the number of the C-H groups present in the molecule considered. For example, the band at $3.44 \mu\text{m}$ of $\text{C}_{60}\text{H}_{36}$ once normalized for the number of C-H bonds becomes $(\epsilon_{3.44}/n\text{CH}) = 5.1$, while for $\text{C}_{70}\text{H}_{38}$ 3.9 and 4.6 for the mixture $\text{C}_{60}\text{H}_x + \text{C}_{70}\text{H}_y$, in all cases much higher than the $(\epsilon_{3.44}/n\text{CH}) = 2.2$ measured on adamantane. Similarly, for $\text{C}_{60}\text{H}_{18}$ the molar extinction coefficient the C-H stretching bands after normalization becomes $(\epsilon_{3.45}/n\text{CH}) = 4.7$ and $(\epsilon_{3.52}/n\text{CH}) = 6.1$; hence, once again much higher than the corresponding values of the normalized molar extinction coefficients of adamantane which are 2.2 and 1.0 respectively and of docosane with 1.8 and 1.5 values respectively (Table 3).

From these data derives the peculiarity of the fullerene bands at 3.44 and $3.52 \mu\text{m}$ not only for their position and their insensitivity to a broad range of temperatures but also for their unique intensity. A closer compound to fullerenes is dodecahedrane ($\text{C}_{20}\text{H}_{20}$) a hydrogenated hydrocarbon cage compound which exhibits three C-H stretching bands at 3.45 , 3.44 and $3.39 \mu\text{m}$ whose molar extinction coefficient is still unknown (Hudson et al. 2005). Guillois et al. (1999) have reported that the surface of nanodiamond exhibits C-H stretching bands at 3.43 and $3.53 \mu\text{m}$ and have indicated a circumstellar envelope where such spectral features are present (HD 97048). However, knowing the complete infrared spectra of fullerenes (Fig. 1-5), it will be possible to distinguish the fullerenes from nanodiamonds quite easily. In particular, the infrared spectrum of $\text{C}_{60}\text{H}_{18}$ (Fig. 3-5) is particularly characteristic and rich in bands in the medium infrared region and could be easily and firmly identified.

3.5 – The integrated band intensities of fullerenes at ambient temperature

The integrated band intensity corresponds to the measurement of the total intensity of the band intended as the measurement of the area below a given absorption band. The EZ Omnic software (version 6A) of our FTIR spectrometer is able to measure either the height of a given absorption band or the total area below the same band, in both cases subtracting the baseline automatically. Thus, the integrated intensity has been determined in the infrared spectra of fullerenes at ambient temperature.

The integrated intensity expressed as the integrated absorptivity Ψ , as already detailed in a previous study (Iglesias-Groth et al. 2011), was determined according to:

$$\Psi = (bc)^{-1} \int A_{\lambda} d\lambda \quad (\text{eq.2})$$

If the optical path length b is measured in cm and the concentration is measured in mol/cm^3 and the spectrum is plotted using the wavenumber scale in cm^{-1} versus the absorbance A_{λ} , then the integrated absorbance Ψ is expressed in $\text{cm}\cdot\text{mol}^{-1}$ or $10^{-5} \text{ km}\cdot\text{mol}^{-1}$ (Colthup et al. 1990).

With these premises, the integrated molar absorptivity of all the infrared absorption bands of fullerenes was determined at ambient temperature and are shown in Table 4 for $\text{C}_{60}\text{H}_{18}$ and Table 5 for all the other fullerenes. The uncertainty of the data reported in Tables 4 and 5 pertaining the Ψ values are in the range of $\pm 10\%$.

In the measurement of the integrated molar absorptivity of the C-H stretching band of fullerenes we proceeded in two different ways. In the first approach, the two stretching bands respectively at 3.44 and 3.54 μm were integrated separately while in the second case the entire group of bands in the C-H stretching region was integrated together. Therefore, in Table 5 the columns with the symbol Ψ refer to the first case: separate integration of the stretching bands while the symbol $\int_{\nu_{\text{C-H}}}$ refers instead to the integration over the entire set of bands in the C-H stretching region. The $\Psi_{3.44} = 55.4 \text{ km}\cdot\text{mol}^{-1}$ for $\text{C}_{60}\text{H}_{36}$, $45.8 \text{ km}\cdot\text{mol}^{-1}$ for $\text{C}_{70}\text{H}_{38}$ and $42.7 \text{ km}\cdot\text{mol}^{-1}$ for the mixture of fullerenes. As expected, $\Psi_{3.44} = 19.0 \text{ km}\cdot\text{mol}^{-1}$ for adamantane, thus considerably lower than the analogous band of fullerenes. Similarly, also the $\Psi_{3.38} = 4.2 \text{ km}\cdot\text{mol}^{-1}$ and $\Psi_{3.43} = 23.7 \text{ km}\cdot\text{mol}^{-1}$ for docosane. Also the infrared band at higher wavelengths i.e. at 3.55 μm is intense for fullerenes $\Psi_{3.54} = 109.0 \text{ km}\cdot\text{mol}^{-1}$ for $\text{C}_{60}\text{H}_{36}$, $81.5 \text{ km}\cdot\text{mol}^{-1}$ for $\text{C}_{70}\text{H}_{38}$ and $93.9 \text{ km}\cdot\text{mol}^{-1}$ for the fullerene mixture. The analogous band of adamantane shows $\Psi_{3.52} = 3.2 \text{ km}\cdot\text{mol}^{-1}$, extremely low, and for docosane we have measured $\Psi_{3.52} = 13.2 \text{ km}\cdot\text{mol}^{-1}$. Thus, as expected, the high intensity of the C-H stretching bands of fullerenes is reflected also in the integrated molar absorptivity values. Bauschlicher et al. (2007) have reported the C-H stretching bands for a series of diamondoids at 3.467 and 3.396 μm with an average molar absorptivity of 51.3 and 48.0 $\text{km}\cdot\text{mol}^{-1}$ respectively, thus much lower than the values found in the fullerene sample reported above.

As shown in Table 5, the integration of the entire C-H stretching region yields for $\text{C}_{60}\text{H}_{36}$ a $\int_{\nu_{\text{C-H}}} = 309.4 \text{ km}\cdot\text{mol}^{-1}$ and lower values but with the same order of magnitude were found for $\text{C}_{70}\text{H}_{38}$ ($257.4 \text{ km}\cdot\text{mol}^{-1}$) and for the fullerene mixture ($232.2 \text{ km}\cdot\text{mol}^{-1}$). Table 4 (last column in the right) reports the Ψ values of all the infrared absorption bands of $\text{C}_{60}\text{H}_{18}$. Only the C-H stretching region of $\text{C}_{60}\text{H}_{18}$ spectrum has been integrated and the value reported is $\int_{\nu_{\text{C-H}}} = 178.1 \text{ km}\cdot\text{mol}^{-1}$. It is a lower value in comparison to the $\int_{\nu_{\text{C-H}}}$ values observed by $\text{C}_{60}\text{H}_{36}$ and $\text{C}_{70}\text{H}_{38}$ justified by a lower hydrogen content in the $\text{C}_{60}\text{H}_{18}$ molecule. However, the integration of the C-H stretching region in the adamantane spectrum yields $\int_{\nu_{\text{C-H}}} = 41.4 \text{ km}\cdot\text{mol}^{-1}$, an order of magnitude lower. The value $\int_{\nu_{\text{C-H}}} = 178.1 \text{ km}\cdot\text{mol}^{-1}$ of $\text{C}_{60}\text{H}_{18}$ it is higher than the $\int_{\nu_{\text{C-H}}}$ of adamantane but it is closer to $\int_{\nu_{\text{C-H}}} = 143.1 \text{ km}\cdot\text{mol}^{-1}$ measured for docosane. In its turn, the value $\int_{\nu_{\text{C-H}}} = 143.1 \text{ km}\cdot\text{mol}^{-1}$ measured for docosane is still less than half the value measured for $\text{C}_{60}\text{H}_{36}$.

The normalization by the number C-H bonds contained in each molecule of the molar absorptivity measured after the integration of the entire C-H stretching region yields the following values in ($\int_{\nu_{\text{C-H}}} / n \text{ C-H}$): 9.89 for $\text{C}_{60}\text{H}_{18}$, 8.59 for $\text{C}_{60}\text{H}_{36}$, 6.77 for $\text{C}_{70}\text{H}_{38}$, 6.45 for the fullerenes mixture $\text{C}_{60}\text{H}_x + \text{C}_{70}\text{H}_y$, and only 2.59 for adamantane and 3.11 for docosane, confirming once again the uniqueness of the higher intensity of the C-H bands of fullerenes measured either as a molar extinction coefficient or as the integrated molar absorptivity.

4. Discussion and conclusions

Fullerenes have been found in different H-rich environments in space and it is probable that further research will show how ubiquitous these molecules are in space. In fact, fullerenes are very stable molecules which can survive for a very long time in the harsh circumstellar and interstellar environment resisting the action of high energy photons irradiation and also cosmic rays (Cataldo et al. 2009c). Since fullerenes are easily reactive with hydrogen and are transformed into the hydrogenated derivatives known as fulleranes (Cataldo & Iglesias-Groth 2010a), it is reasonable to anticipate that fulleranes will be the next fullerene derivatives to be found in space. The hydrogenated fullerenes and their possible contribution to certain unidentified astronomical features such as the diffuse interstellar bands were first explored by Webster (1992; 1993). In addition, more recently we discovered that the UV spectra of fulleranes match the peak and the shape of the “bump” at 220 nm observed in the interstellar light extinction curve (Cataldo & Iglesias-Groth

2009). This implies that fullerenes, which are indeed a form of hydrogenated carbon, may be key contributors of the interstellar light extinction feature at 220 nm. Electric dipole emission by fullerenes may also contribute to the anomalous microwave emission detected in several molecular clouds and star-forming regions (Iglesias-Groth 2005, 2006).

For these reasons, we have already synthesized a series of different hydrogenated and perdeuterated fullerenes and have studied their infrared transitions (Cataldo & Iglesias-Groth 2009; Cataldo et al. 2009a; Cataldo et al. 2009b; Cataldo & Iglesias-Groth 2010a; Cataldo & Iglesias-Groth 2010b; Cataldo & Iglesias-Groth 2010c). In this article, we have studied the infrared band shift of a series of fullerenes as a function of temperature over a wide range of temperatures between -180°C and $+250^{\circ}\text{C}$ and extrapolated the resulting experimental data to 0 K.

We have also shown that the infrared spectrum of all fullerenes, namely $\text{C}_{60}\text{H}_{36}$, $\text{C}_{70}\text{H}_{38}$, a mixture of fullerenes generally referred as 77% of C_{60}H_x and 22% C_{70}H_y with $x \approx y > 30$ and $\text{C}_{60}\text{H}_{18}$ display very strong transition bands in the C-H stretching region of the spectrum. First of all, these transitions are located at 3.44 and 3.55 μm ; they are thus far away from the aromatic C-H stretching expected at about 3.30 μm and can be easily distinguished. The laboratory infrared spectra of hydrogenated fullerenes reported here will permit the search for these molecules in astrophysical environments.

Furthermore, the intensity of the C-H transitions of fullerenes was found to be unique in terms of both the molar extinction coefficient ϵ_{λ} and the molar absorptivity Ψ in comparison to those of reference molecules such as adamantane and docosane and also literature data. Even the normalization of the molar extinction coefficient and the integrated molar absorptivity for the number of C-H bonds contained in each molecule examined in the present study show that fullerenes are unique in terms of intensity of the C-H stretching bands. To the best of our knowledge, there are no other molecules with such high values of ϵ_{λ} and Ψ values as those measured in fullerenes in the present study. Knowledge of these parameters will enable us to determine the abundance of fullerenes in space.

Acknowledgements

The present research work has been supported by grant AYA2007-64748 Expte. NG-014-10 of the Spanish Ministry of Science and Innovation (MICINN). D.A.G.H. also acknowledges support for this work provided by the MICINN under a 2008 JdC grant.

Table 5 - MOLAR ABSORPTIVITY OF FULLERANES, ADAMANTANE AND DOCOSANE
 (Ψ values in km mol^{-1})

μm	Ψ	$\int_{\text{V}_{\text{C-H}}}$	Ψ	$\int_{\text{V}_{\text{C-H}}}$	Ψ	$\int_{\text{V}_{\text{C-H}}}$	Ψ	$\int_{\text{V}_{\text{C-H}}}$	Ψ	$\int_{\text{V}_{\text{C-H}}}$
λ	$\text{C}_{60}\text{H}_{36}$	←	$\text{C}_{70}\text{H}_{38}$	←	$\text{C}_{60}\text{H}_x+\text{C}_{70}\text{H}_y$	←	Adamantane	←	Docosane	←
3.38									4.2	
3.43									23.7	
3.44	55.4	309.4	45.8	257.4	42.7	232.2	19.0	41,4		143.1
3.52							3.2		13.2	
3.54	109.0		81.5		93.9					
5.92					26.2					
6.12	25.5									
6.72	5.3									
6.79									18.7	
6.86	2.6									
6.92			14.5		18.2		4.1			
7.30									1.6	
7.41	4.9						1.9			
7.87					0.8					
8.10	26.6									
8.20					2.0					
8.49					1.2					
8.89									0.5	
9.11			39.3				1.6			
9.29	1.2									
9.36									0.3	
9.85					9.3					
9.75	2.1									
10.3							0.8			
10.5							1.4			
11.2	3.7								0.9	
12.6							1.0			
13.8	16.0									
13.9									7.9	
14.5	6.4									
21.4	3.3									
22.7							n.d.			

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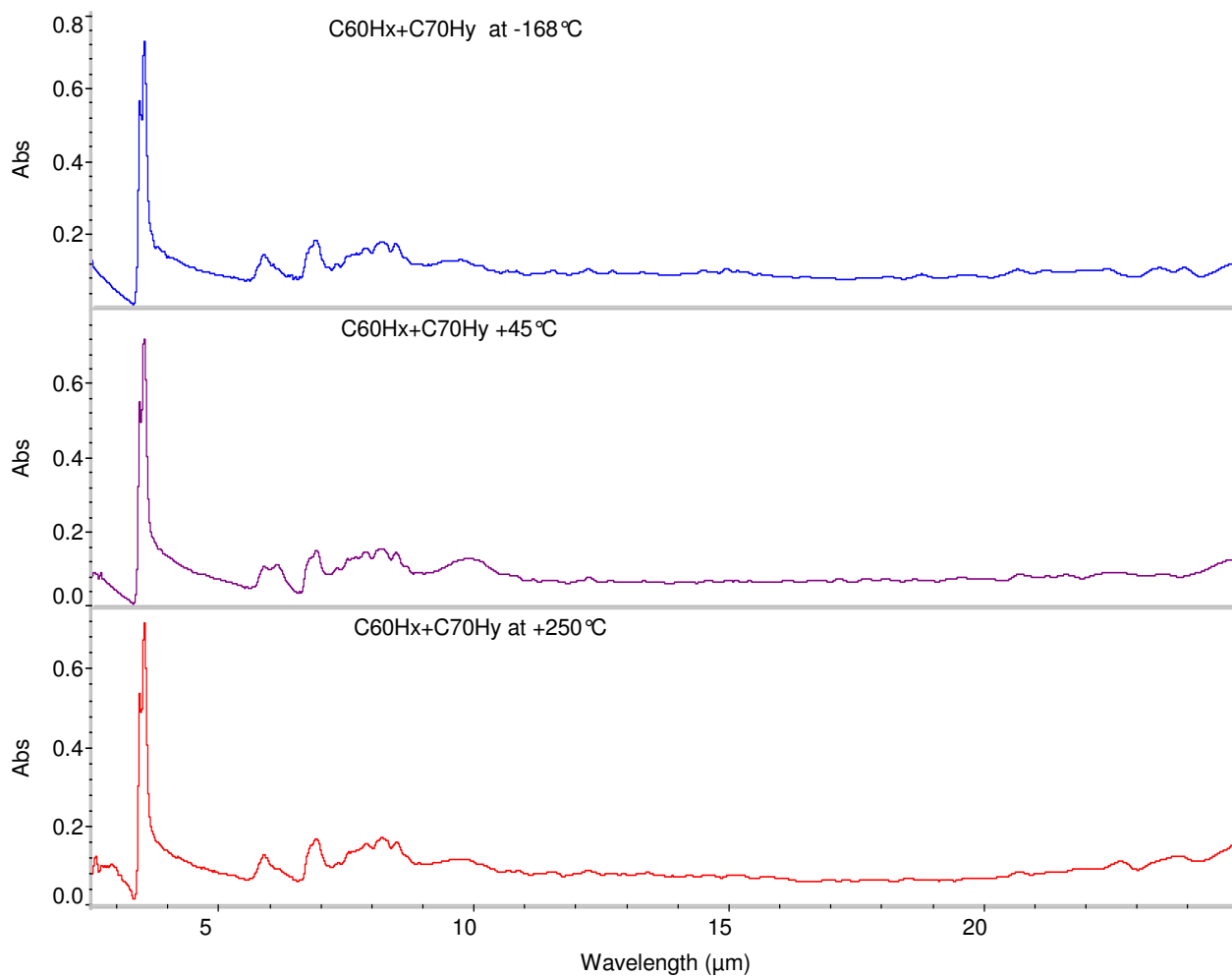


Fig. 1 – FT-IR spectrum in KBr of fullerenes mixture 77% of C₆₀H_x and 22% C₇₀H_y with $x \approx y \geq 30$. The spectrum at the top of the figure was taken at -168°C, that in the middle at +45°C and the one at the bottom at +250°C. Note the strong C-H stretching band.

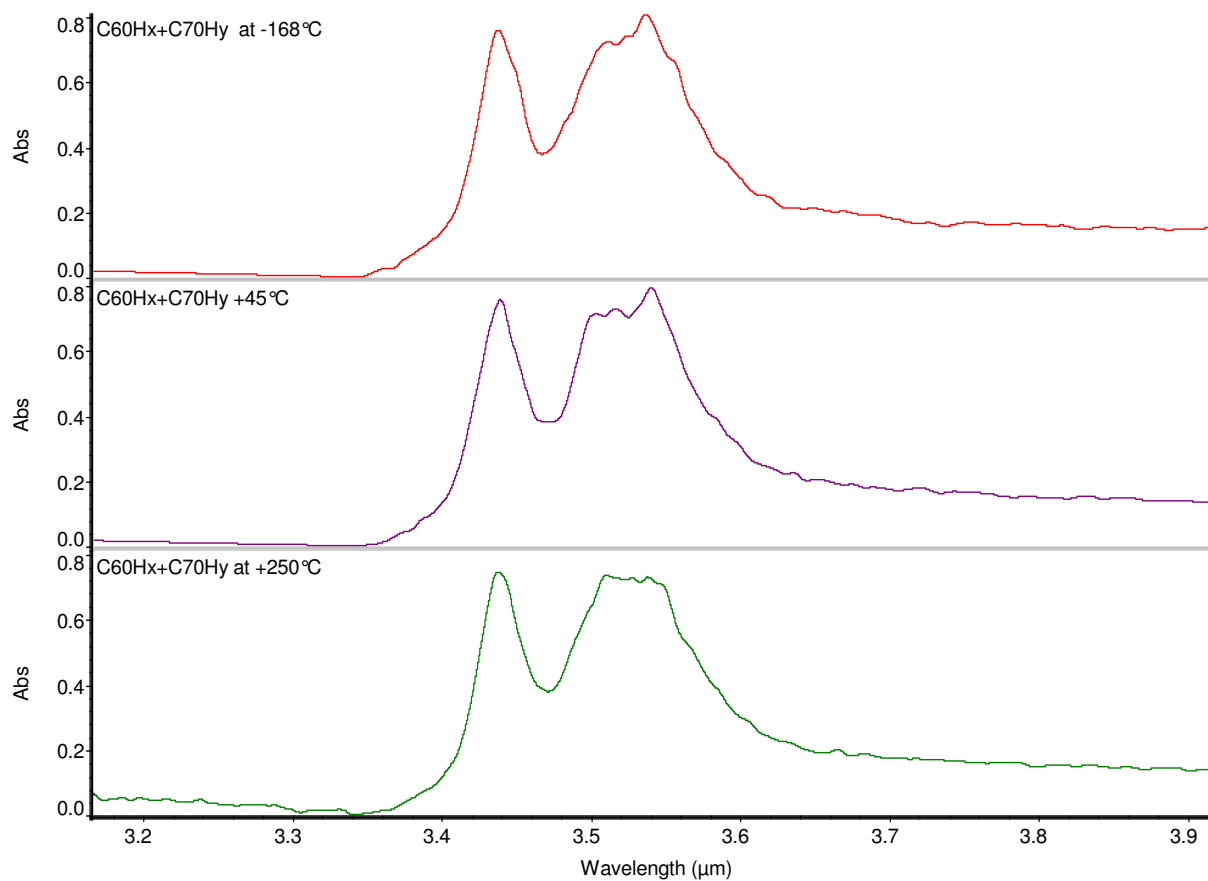


Fig. 2 – Detail of the C-H stretching region in the FT-IR spectra in KBr of fullerane mixtures 77% of C₆₀H_x and 22% C₇₀H_y with $x \approx y \geq 30$ recorded at three different temperatures. The spectrum at the top of the figure was taken at -168°C, that in the middle at +45°C and the one at the bottom at +250°C. Here is shown a detail of the strong C-H stretching bands at 3.44, 3.51 and 3.54 μm.

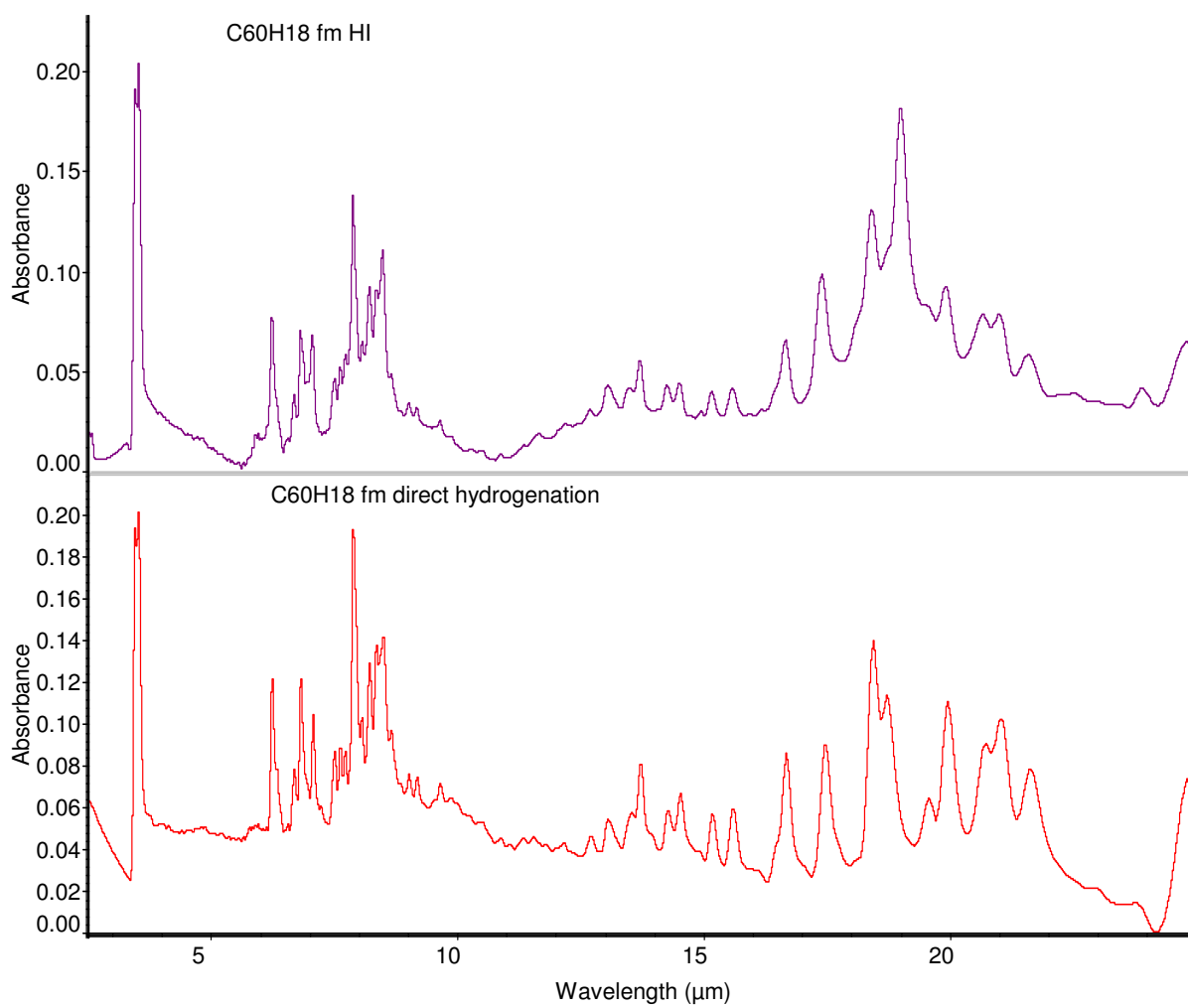


Fig. 3 - FT-IR spectra in KBr of fullerane $C_{60}H_{18}$ recorded at room temperature. The two spectra are very similar but the differences in the spectral region between 18 and 19 μm suggest that we are dealing with two different $C_{60}H_{18}$ isomers.

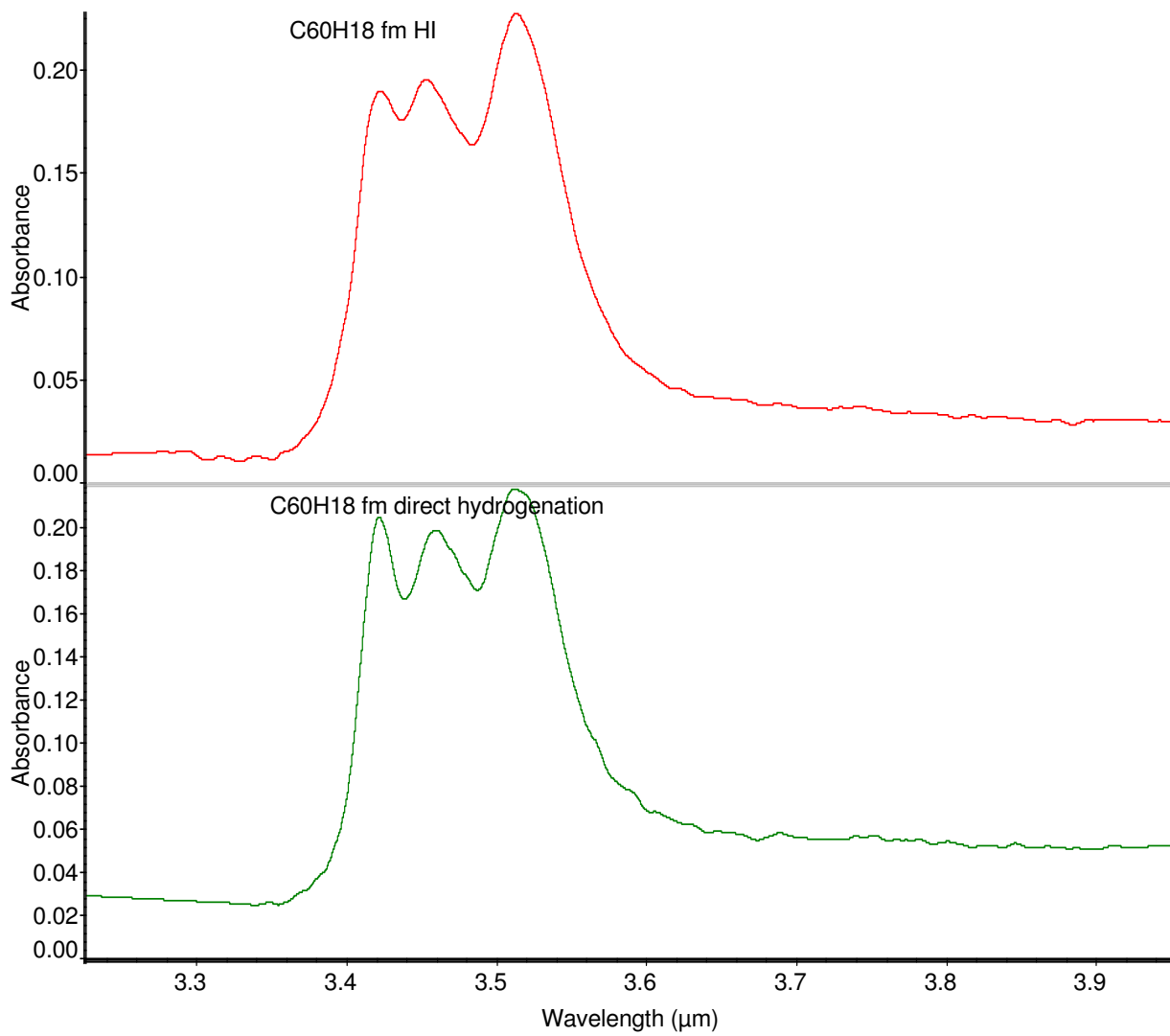


Fig. 4 – A detail of the C-H stretching region of the infrared spectra of the fullerane $\text{C}_{60}\text{H}_{18}$ isomers.

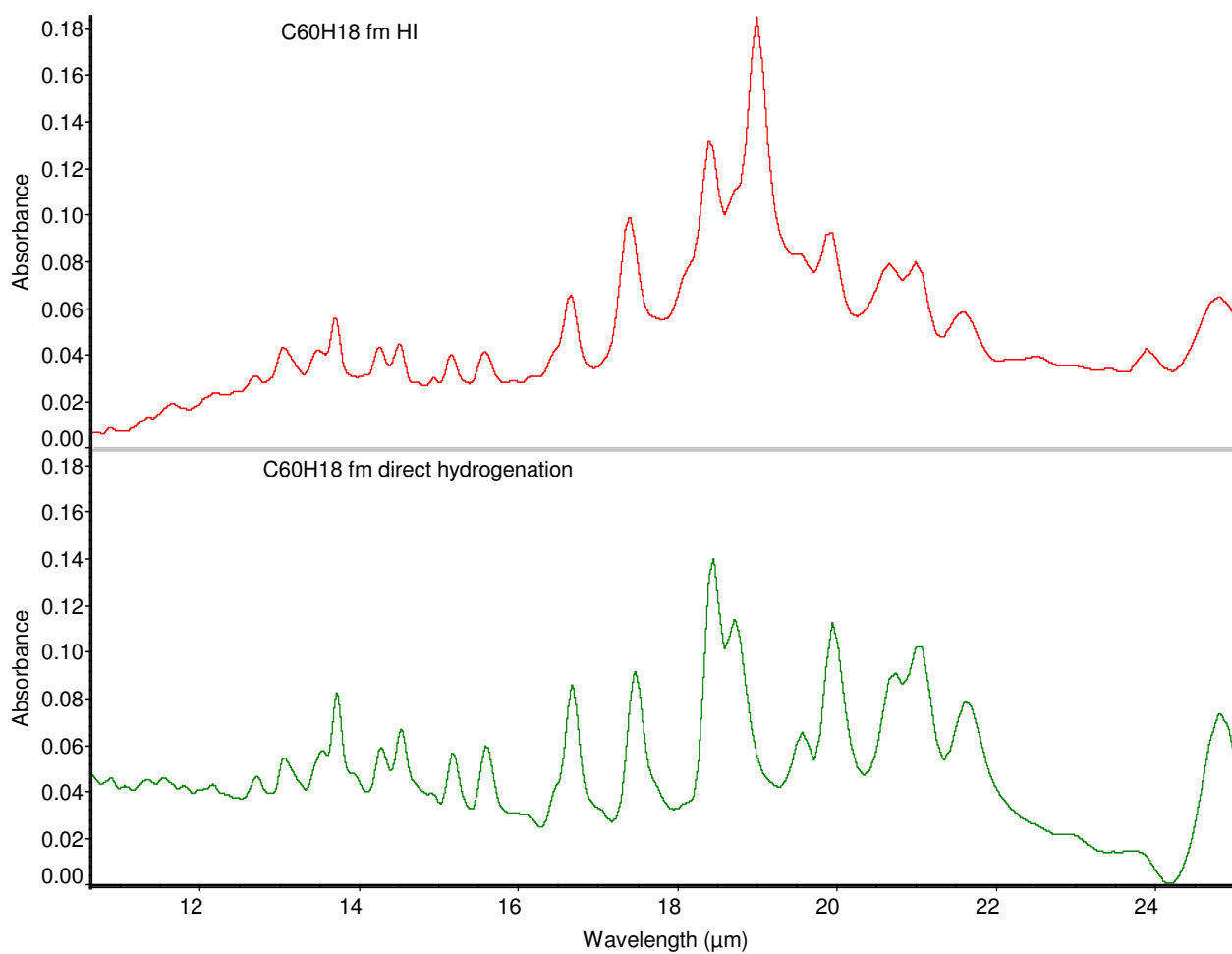


Fig. 5 – A detail of the infrared spectral region comprised between 13 and 25 μm of the spectra of the fullerane $C_{60}H_{18}$ isomers.