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A tracer of organic matter of prebiotic interest in space, made from UV and thermal processing of ice mantles

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ABSTRACT

Aims. Our main goal was to identify an infrared spectral feature that can serve as a tracer of O and N-rich solid organic matter in space. Such material is expected to result from UV-irradiation and sublimation of icy grain mantles in certain environments, including hot cores and regions around YSOs. Our analysis of the 3.4 μm feature, present in the spectra of organic refractory samples made from UV-irradiation of interstellar/circumstellar ice analogs, indicates that the 3.4 μm band is a potential tracer of O and N-rich solid organic matter of prebiotic interest in space.
Methods. We carried out simulation experiments of UV-photoprocessing and sublimation of ice mantles in dense clouds and circumstellar regions leading to the formation of organic refractory residues under different conditions. The analysis of the deposited ice and the organic residue products was made in situ by infrared spectroscopy. Spectral comparison of these residues to molecular standards for compositional characterization was performed.
Results. For ice mixtures of different composition, UV-photon dose and frequency, the 3.4 μm feature of the organic residue product at room temperature shows a broad double-peaked profile with subfeatures at ∼2926 cm^{-1} (3.42 μm) and 2876 cm^{-1} (3.48 μm), mainly due to CH$_2$ groups adjacent to OH groups. This feature profile was not reproduced in similar UV-irradiation experiments using non-realistic analogs of interstellar ice mantles. In the astrophysical context, this infrared feature is thus expected to be characteristic of the products resulting from ice UV-irradiation and sublimation; it is fully distinct from the 3.4 μm feature observed in the diffuse interstellar medium, which is attributed to hydrogenated amorphous carbon.
Conclusions. A 3.4 μm band with a similar broad double-peaked profile tracing organic refractory matter of prebiotic interest could be searched for in regions where icy grain mantles were exposed to UV-irradiation prior to sublimation, like hot cores and regions around YSOs. This band may also be present in some cometary nuclei that preserve such grains, provided that the annealing temperatures experienced were not higher than ∼400 K.

Key words. ISM: molecules – methods: laboratory – ultraviolet: ISM – dust, extinction – infrared: ISM

1. Introduction

Icy grain mantles, composed mainly of H$_2$O and species like CH$_3$OH, CO, CO$_2$ and NH$_3$ (hydrated or as NH$_4^+$), are observed in dense interstellar clouds and circumstellar regions (Gerakines et al. 1999; Ehrenfreund et al. 1999; Dartois et al. 1999; Gibb et al. 2001; Schutte & Khanna 2003; Thi et al. 2002; Pontoppidan et al. 2005). They are submitted to UV irradiation in those environments. Shen et al. (2004) show that the energy input by the cosmic-ray induced ultraviolet field is almost one order of magnitude greater than the direct energy input by cosmic-ray particles. Ice mantles in hot cores and regions around YSOs are processed by the UV flux emitted by the central object and that impinging from the surrounding interstellar medium. In addition, the temperature increases close to the central object, leading to sublimation of the ice mantles, see Muñoz Caro & Schutte (2003) for a short summary.

Experimental simulations of ice photo- and thermal processing in the interstellar/circumstellar medium lead to the formation of an organic refractory residue that is observed after warm-up to room temperature. Abundant species detected in these residues are hexamethylenetetramine [(CH$_2$)$_6$N$_4$], ammonium salts of carboxylic acids [(R-COO$^-$)(NH$_4^+$)], amides [H$_2$NC(=O)-R], esters [R-C(=O)-O-R'], and species based on polyoxymethylene [(-CH$_2$O-)$_n$]. Other residue components of clear prebiotic interest are amino acids or their precursors and N-heterocyclic molecules, both present with an abundance of the order of ∼1% by number of molecules (Agarwal et al. 1985; Briggs et al. 1992; Bernstein et al. 1995, 2002; Muñoz Caro et al. 2002; Muñoz Caro & Schutte 2003; Meierhenrich et al. 2005; Nuevo et al. 2006).

Irradiation of ice mantles by UV photons should be considered a common phenomenon in circumstellar regions and dense clouds. There is, however, no current evidence for the presence of relatively large organic species, like those made by ice photoprocessing in the laboratory, embedded in the ice matrix (along with the common ice components mentioned above, the largest species detected in the infrared spectra of ice mantles are CH$_3$CHO, HCOOH, OCN$^-$, and OCS). This could be due to the broad features of abundant volatile ices which hinder the detection of minor organic components (Muñoz Caro & Schutte 2003).

Here we search for an infrared feature that could serve as a tracer of O and N-rich solid organic matter of prebiotic interest in space, made by UV-photoprocessing and sublimation of icy grain mantles, in environments such as hot cores and regions around YSOs; our search is based on experimental simulations of ice processing by UV photons, leading to the formation of

organic refractory residues. Firstly, such tracer of organic matter should preferably be a feature with a characteristic band profile, to ensure that the feature is not confused with other absorption bands in the same spectral region. Secondly, the feature should be present in the spectra of organic refractory residues, made in the laboratory under different but astrophysically relevant conditions; that way, we tried to select a feature that could be observed in a variety of regions where ice mantles are exposed to UV-irradiation followed by sublimation.

It was observed that bands due to functional groups in the spectra of organic refractory residues differ, depending on experimental parameters like the starting ice composition (Muñoz Caro & Schutte 2003). We found that, among the bands present in the spectra of organic refractory residues, the best candidate as a tracer of organic matter made by ice UV-processing in space was the 3.4 μm feature, in the region $3000-2750$ cm^{-1}. This feature fulfills the first condition given above, as it displays a characteristic profile composed of two main bands, attributed to CH$_2$ stretching modes (Allamandola et al. 1988). Although the 3.4 μm feature of organic refractory residues can overlap with the red wing of the broad absorption band due to the O-H stretching in H$_2$O ice, or the C-H stretching modes in simple ice species like CH$_3$OH and CH$_4$, the band profiles are notably different, and after ice sublimation only the 3.4 μm feature of the organic refractory residue remains. The second requirement, i.e. whether or not the double-peaked 3.4 μm feature is present in the spectra of organic refractory residues made in the laboratory under different astrophysically relevant conditions, is studied here in detail, by varying the composition of the starting ice mixture, UV-irradiation dose, and UV frequency. In addition, the organic components responsible for the infrared 3.4 μm feature observed in the organic refractory residue spectra are characterized in this paper.

2. Experimental

The experimental setup consists of a high vacuum chamber where a gas mixture is deposited onto a cold finger and UV-irradiated. The pressure of the system at room temperature is $P \approx 1 \times 10^{-7}$ torr. At the cold finger the temperature is $T \approx 12$ K. The cold finger consists of a sample holder, in which an IR-transparent CsI window is mounted.

The gas mixture is prepared by filling a bulb with different gases while the partial vapor pressures are monitored. The vacuum pressure of the gas line is $P \approx 10^{-5}$ torr. The typical rate of deposition was 2×10^{15} molecules cm^{-2} s^{-1}, and the deposition time was 13 h. During the deposition, the ice layer is simultaneously UV-irradiated with a microwave stimulated hydrogen flow discharge lamp (output $\approx 1.5 \times 10^{15}$ photons s^{-1}, Weber & Greenberg 1985; $E_{\text{photon}} = 7.3-10.5$ eV), separated from the vacuum chamber by a MgF$_2$ window. The main peak emission is at Lyman-α (121 nm or 10.2 eV) for a hydrogen pressure $P_{\text{H}} = 0.5$ torr. The UV photon flux at the position of the sample is $F_{\text{UV}} \approx 5 \times 10^{14}$ photon cm^{-2} s^{-1}, resulting in an average dose of $\sim$0.25 UV photon molec^{-1}. The long simultaneous deposition and irradiation time of 13 h, and the high photon dose of $\sim$0.25 UV photon molec^{-1}, served to obtain a sufficient amount of organic refractory residue to allow infrared spectroscopy (Muñoz Caro & Schutte 2003; this paper), and characterization by chromatographic techniques (e.g. Muñoz Caro et al. 2004). For one of the experiments a quartz window was placed in the interface between the UV lamp and the high vacuum chamber, replacing the usual MgF$_2$ window; the quartz transmission has a cutoff at about 140 nm (8.9 eV)

giving an output $\approx 4 \times 10^{14}$ photons s^{-1} (henceforth *soft* UV spectrum). After irradiation, the system is warmed up gradually by means of a temperature controller. For details on the experimental protocol see Muñoz Caro & Schutte (2003).

The evolution of the sample during irradiation and warm-up was monitored by Fourier transform infrared, FT-IR, transmission spectroscopy at a resolution of 2 cm^{-1}. For all the experiments, the final spectrum of the organic refractory residue that remains after ice sublimation was taken under high vacuum after 10 hours at room temperature.

3. Experimental results

3.1. The carriers of the 3.4 μm feature of organic refractory residues

Figure 1 shows the aliphatic C-H stretching bands (3.4 μm feature) of organic refractory residues made starting from different ice mixtures, UV dose and frequency, see Table 1 adapted from Muñoz Caro & Schutte (2003). This band falls between 3000 and 2750 cm^{-1} and generally presents a characteristic broad double-peaked profile in the organic refractory residue spectra. The common peaks at 2926 cm^{-1} and 2876 cm^{-1} correspond mainly to the aliphatic CH$_2$ asymmetric and symmetric stretching modes, although we will later show that there is some contribution from CH$_3$ stretchings to these subfeatures. A subfeature peaking around 2790 cm^{-1}, attributed to CH$_3$ groups attached to N, is observed in some of the organic refractory residue spectra of Fig. 1. Hexamethylenetetramine (HMT, [(CH$_2$)$_6$N$_4$]) is a contributor to this band; it has peaks at 2874 (ν_{18} sym. CH$_2$ stretch), 2924 (2 ν_{19} CH$_2$ deformation), and 2949 (ν_{17} asym. CH$_2$ stretch) cm^{-1} (Bernstein et al. 1994, 1995). The specific HMT fingerprints, however, are two sharp peaks at 1234 and 1007 cm^{-1} that correspond to the ν_{21} and ν_{22} CN stretch. Other HMT features are seen at 1461 cm^{-1}, 1368 cm^{-1}, 815 cm^{-1} and 671 cm^{-1} (Bernstein et al. 1995). Indeed, the HMT band at 2949 cm^{-1} is best observed in the 3.4 μm spectrum of OR16, the residue with the highest concentration of HMT (see Fig. 1 and Table 1). Nevertheless, the CH stretching modes of HMT at $3000-2825$ cm^{-1} account only for $\sim$15% of the 3.4 μm (2941 cm^{-1}) feature in residue OR1, our standard residue; that value is inferred from integration of the 3.4 μm (2941 cm^{-1}) and 1007 cm^{-1} features in the spectrum of OR1, and using the absorption ratio between the 3.4 μm and the 1007 cm^{-1} bands in pure HMT from Bernstein et al. (1994). Thus, typically about 85% of the 3.4 μm feature is due to aliphatic carriers different from HMT, which we try to characterize below. To facilitate this, we tried to reproduce the 3.4 μm feature of organic refractory residues using ice mixtures with the simplest composition.

From the common molecular components of icy grain mantles in interstellar and circumstellar environments, i.e. H$_2$O, CH$_3$OH, CO, CO$_2$, and NH$_3$, the only molecule deposited as pure ice that leads to a significant amount of residue after UV-irradiation and warm-up was found to be CH$_3$OH (Fig. 2, top panel). This spectrum shows features at 3404 (H-bonded OH str.), 1712 (C=O str. in saturated aliph. ketones), and 1107 cm^{-1} (C-O-C asym. str. in aliph. ethers). Bands due to aliphatic -CH$_2$- and -CH$_3$ groups are observed at 2971 (-CH$_3$ asym. str.), 2935 (-CH$_2$- asym. str.), 2875 (-CH$_3$ sym. str.), 1455 (-CH$_2$- bend), and 1376 (aliph. -CH$_3$ sym. bend).

Only when CH$_3$OH is co-deposited with H$_2$O does the residue obtained from ice irradiation and warm-up show the 3.4 μm feature with the broad double-peaked profile of organic

Table 1. Experimental parameters.

Exp. OR#[1]	Comment	Ice mixture $H_2O:NH_3:CH_3OH:CO:CO_2$	Dose $\frac{photon}{molec}$	$\frac{N_C(HMT)}{N_C(ice)}$ (%)	$\frac{N_C(c.a.salt)}{N_C(ice)}$ (%)	$\frac{N_C(amide)}{N_C(ice)}$ (%)	$\frac{N_C(ester)}{N_C(ice)}$ (%)	$\frac{N_C(total)}{N_C(ice)}$ (%)
1	standard exp.	2:1:1:1:1	0.25	6.4 ± 0.3	1.8	0.33	0.16	8.7
4		2:1:1:1:1	3.33	5.6 ± 0.1	1.5	1.2	0.9	9.2
5		2:1:1:1:1	0.031	2.4 ± 0.1	0.3	0.04	0.10	2.8
7	*soft* UV spectrum	2:1:1:1:1	0.66	7.0 ± 0.3	0.4	0.15	0.13	7.7
9		0:1:1:0:0	0.32	0.6 ± 0.1	0.09	0.27	0.05	1.0[2](1.5)
13		2:1:1:0:0	0.25	0.4 ± 0.2	0.08	≤0.01	≤0.01	0.5[2](0.8)
16		20:1:1:1:1	0.22	15.0 ± 0.7	0.3	0.28	0.11	15.7

[1] Experiments are named "OR" followed by a number. OR stands for organic refractory residue.
[2] In addition to the listed species, the spectrum shows a large abundance of POM-like species. The values in brackets include the POM abundances assuming the band strength of pure POM (9.7×10^{-18} cm (C atom)$^{-1}$ from Schutte et al. 1993).
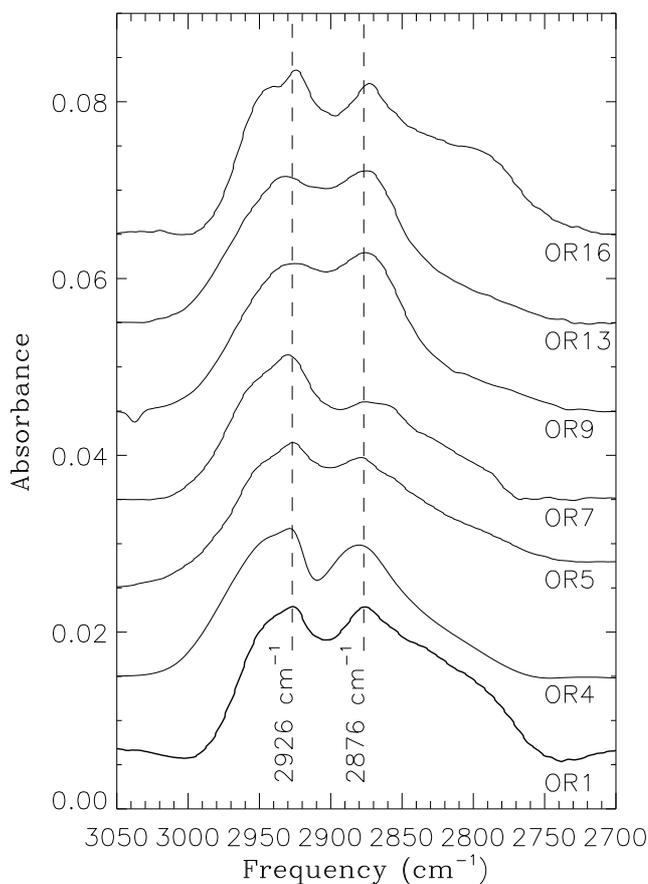

Fig. 1. Organic refractory residue spectra from photoprocessing of different ice mixtures. See Table 1 for experimental parameters of the samples.

Fig. 2. *Top*: residue spectrum from UV-irradiation of methanol ice. *Bottom*: residue spectrum from UV-irradiation of $H_2O:CH_3OH$ = 1:1 ice. The band between $2400-2300$ cm^{-1} is CO_2 gas absorbing along the beam of the infrared spectrometer.

refractory residues. This is illustrated in Fig. 2, bottom panel, showing the organic refractory residue spectrum obtained from overnight UV-irradiation of $H_2O:^{13}CH_3OH$ = 1:1 ice. The -CH_2- and -CH_3 bendings are seen at 1448 and 1367 cm^{-1}. Other features are the prominent band between $3600-2600$ cm^{-1} (H-bonded OH str. in polymers, probably due to alcohols and carboxylic acids), 1677 cm^{-1} (C=O str. of carboxylic acid dimers), 1568 cm^{-1} (unknown), 1207 cm^{-1} (possibly the C-O-C str. in ethers) and 1029 cm^{-1} (possibly the CH_2OH in primary alcohols).

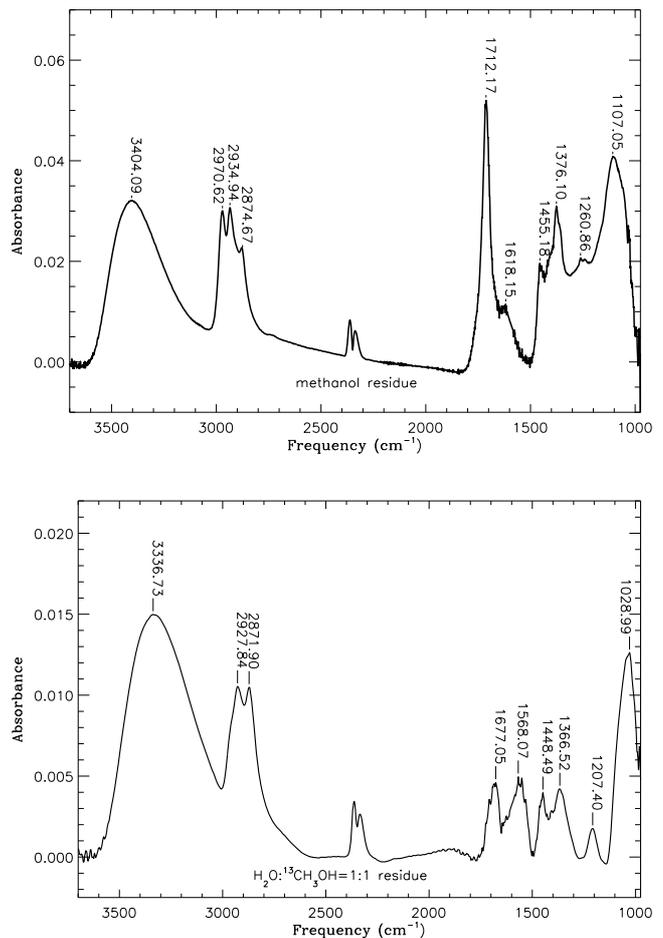The results from the above experiment show that the broad double-peaked 3.4 μm feature of organic refractory residues is also obtained by irradiation of ices that do not contain N. That means that HMT, a N-bearing molecule, cannot be present in those organic refractory residues, and yet the spectra of these residues show the characteristic broad double-peaked 3.4 μm feature. If CH_3OH is not a component of the starting ice mixture, the absorbance values of the 3.4 μm feature are reduced (Jenniskens et al. 1993), suggesting that CH_3OH, that converts efficiently into formaldehyde (H_2CO) upon irradiation initiating chemical reactions is the main precursor of the 3.4 μm

feature carriers. Although CH$_3$ groups are present, as shown by the band at 1367 cm^{-1} attributed to the CH$_3$ symmetric deformation mode, the carrier species of the 3.4 μm feature must have high -CH$_2$-/-CH$_3$ ratios because the -CH$_3$ asym. str. mode around 2960 cm^{-1} is relatively weak or not observed compared to the asym. and sym. -CH$_2$- str. modes observed at ~2926 and 2876 cm^{-1}, indicating different options: i) the aliphatic chains are long and poorly branched; ii) cyclic or cage molecules with CH$_2$ and no CH$_3$ groups; iii) chains of the type R-(CH$_2$)$_n$-R′ where n does not need to be a large number because there are no -CH$_3$ bonds in the molecular structure. These three options are discussed below:

i) This possibility is unlikely because the O in O-bearing ice species enters the composition of the irradiation products, e.g. the commonly dominant H$_2$O abundance in interstellar ice mantles leads to OH$^\bullet$ radical formation upon irradiation and those radicals are incorporated into the structure of organic refractory residue species.

ii) Evidence of this is the mentioned above presence of HMT in organic refractory residues, a cage structure molecule, especially when CH$_3$OH is one of the starting ice components.

iii) The 3.4 μm subfeatures in organic refractory residue spectra are shifted to higher frequencies compared to the -CH$_2$- str. modes of polyethylene (-CH$_2$-)$_n$ at 2917 and 2855 cm^{-1}. That shift in frequency and the width of the subfeatures suggests that functional groups, like hydroxy (OH), carbonyl (C=O) and other electrophylic groups observed in the organic refractory residue spectra, interact with the adjacent CH$_2$ bonds that constitute organic refractory residues, supporting this option. As mentioned by Jenniskens et al. (1993), according to Wexler (1967) the intensity of the C-H stretch is significantly reduced if functional groups like C=O and OH are adjacent, resulting in the relatively weak 3.4 μm feature of most organic refractory residue spectra. In addition, many molecules detected by gas chromatography coupled to mass spectrometry or inferred from infrared spectra of organic refractory residues are of the R-(CH$_2$)$_n$-R′ type, such as alcohols, carboxylic acids and their ammonium salts, amides, amines, and polyoxymethylene-like species (Agarwal et al. 1985; Briggs et al. 1992; Bernstein et al. 1995; Muñoz Caro & Schutte 2003).

Among the different options given above, that is i) the aliphatic chains are long and poorly branched; ii) cyclic or cage molecules with CH$_2$ and no CH$_3$ groups; and iii) chains of the type R-(CH$_2$)$_n$-R′ where n does not need to be a large number because there are no -CH$_3$ bonds in the molecular structure, the main contribution to the 3.4 μm feature of organic refractory residues is thus given by species of the iii) type. Most CH$_n$ bonds in the organic refractory residue molecules reported in Table I of Briggs et al. (1992), resulting from GC-MS analysis of an organic refractory residue made from H$_2$O:NH$_3$:CO = 5:5:1 ice, are CH$_2$ bonds and there are no CH$_3$ bonds, in accordance with the predominance of CH$_2$ stretchings in the 3.4 μm feature profile of organic refractory residues (Fig. 1). In addition, there are in total 3.4 times more OH than COOH groups, the two most abundant functional groups in Table I of Briggs et al. (1992); furthermore, the intrinsic intensity of CH$_3$, and presumably also CH$_2$ groups, adjacent to OH groups is reduced by about 3 times, compared to a 7−9 times reduction when adjacent to carbonyl C=O groups (Wexler 1967) like the carboxy carbonyl group in the -COOH termination of carboxylic acids. That means that for the organic refractory residue molecules reported by Briggs et al. (1992), CH$_2$ bonds adjacent to OH groups
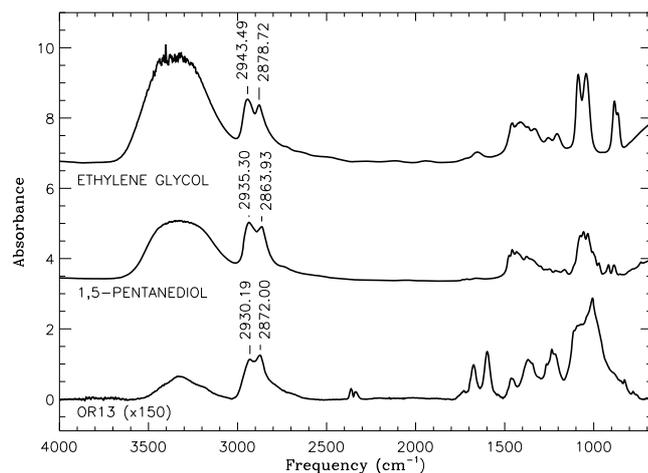

Fig. 3. Comparison between OR13 spectrum (bottom trace) and two alcohols, 1,5-pentanediol (middle trace) and ethylene glycol (top trace). The spectra were obtained at room temperature.

contribute roughly 9 times more to the intensity of the 3.4 μm feature than CH$_2$ bonds adjacent to C=O groups. Therefore, for the organic refractory residue molecules of Briggs et al. (1992), the 3.4 μm feature intensity and profile result mainly from the stretching modes of CH$_2$ groups adjacent to hydroxy OH groups.

The above conclusion was double checked by comparison of the 3.4 μm feature of organic refractory residues to that of alcohols with no CH$_3$ groups. Figure 3 compares the spectra of 1,5-pentanediol (HO-(CH$_2$)$_5$-OH, middle trace) and ethylene glycol (HO-(CH$_2$)$_2$-OH, top trace) to the spectrum of OR13 (bottom trace). It shows that the 3.4 μm feature profile of organic refractory residues resembles that of molecules of the above iii) type, of the form R-(CH$_2$)$_n$-R′ where R=R′=OH, and the other alcohol absorptions in the mid-infrared can be accomodated in the organic refractory residue spectrum shown. If R=R′=COOH the fit to the 3.4 μm feature profile of organic refractory residues is not as good and, furthermore, the intrinsically strong C=O str. intensity of carboxylic acids is weak or absent in many organic refractory residue spectra, indicating a smaller contribution of C=O relative to OH groups. Even the carboxylic acids in the organic refractory residues reported in Table I of Briggs et al. (1992), with glycolic acid (HOCH$_2$COOH) the most abundant, contain one or two OH adjacent to CH$_2$ groups, except the low-abundance oxamic acid (NH$_2$COCOOH). These carboxylic acids are mainly in the form of ammonium salts of carboxylic acids in the organic refractory residue samples containing N, i.e. made from ice mixtures with a NH$_3$ component, prior to the solution of organic refractory residues required for gas chromatographic analysis. The CH$_2$-OH groups in such salts contribute considerably to the 3.4 μm feature of organic refractory residues (Muñoz Caro & Schutte 2003, see Fig. 4 of that paper).

We mentioned above that the 3.4 μm features of organic refractory residue spectra, shown in Fig. 1, resemble the same feature in the 1,5-pentanediol spectrum, shown in Fig. 3. In general, subtraction of both features after scaling shows a small excess in the blue wing of the 3.4 μm feature of the organic refractory residue spectra compared to the same feature in 1,5-pentanediol spectrum. This excess could be due to the asymmetric stretching mode of CH$_3$ bonds around 2960 cm^{-1}, since 1,5-pentanediol lacks CH$_3$ groups. Integration of the 3.4 μm feature of organic refractory residue spectra, and integration of the
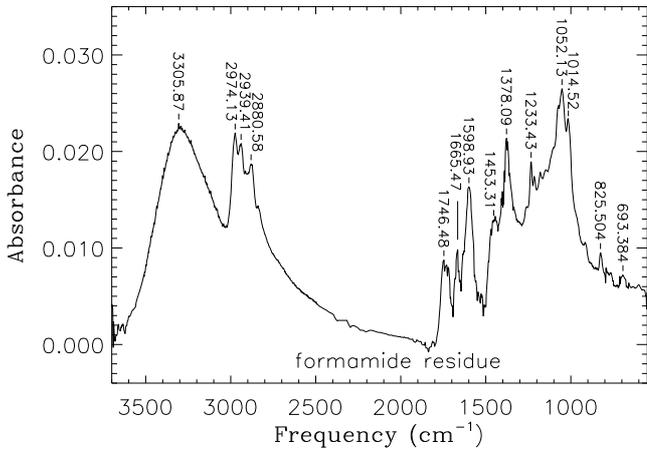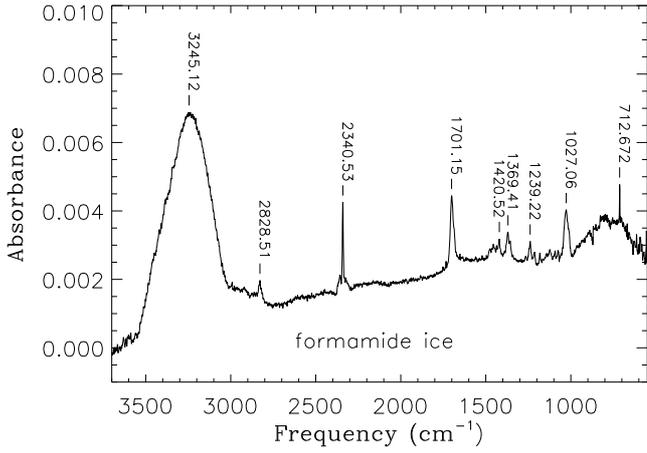
Fig. 4. *Top*: spectrum corresponding to deposition of formamide ice. *Bottom*: spectrum of residue made by simultaneous deposition and UV-irradiation of formamide, followed by warm-up to room temperature.

Fig. 5. *Top*: spectrum corresponding to deposition of 2,2-dimethoxypropane ice. *Bottom*: spectrum of residue made by simultaneous deposition and UV-irradiation of 2,2-dimethoxypropane, followed by warm-up to room temperature. The band between 2400−2300 cm^{-1} is CO$_2$ gas absorbing along the beam of the infrared spectrometer.

mentioned above excess on the blue wing, was performed, using the formula

$$N = \int_{\text{band}} \frac{\tau_\nu \mathrm{d}\nu}{A} \tag{1}$$

where N is the column density in cm^{-2}, τ is the optical depth of the band, dν is the wavenumber differential in cm^{-1}, and A is the band strength in cm molec^{-1}. We adopted the band strengths for hexane ice (Dartois et al. 2004a), $A(\text{CH}_3) = 1.25 \times 10^{-17}$ cm (C atom)$^{-1}$ and $A(\text{CH}_2) = 8.4 \times 10^{-18}$ cm (C atom)$^{-1}$, and obtained that $N(\text{CH}_3)/N(\text{CH}_2) \leq 0.1$. This value is an upper limit that should be regarded with caution, because the CH stretching modes are perturbed by the neighboring electrophilic groups, and the subfeatures due to the CH$_3$ stretchings are blended with those due to the CH$_2$ stretchings.

It is concluded that for organic refractory residues made from irradiation of realistic interstellar ice analogs, the main contribution to the 3.4 μm feature corresponds to the symmetric and asymmetric CH$_2$ stretching modes perturbated by adjacent hydroxyl OH groups.

3.2. Residues produced by "exotic" ice species compared to astrophysically relevant organic refractory residues

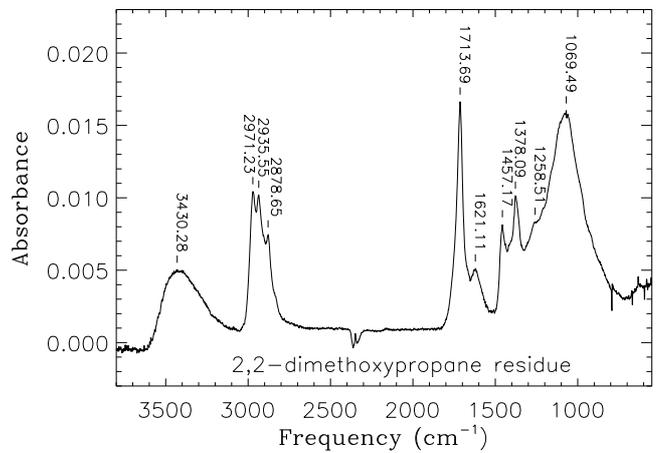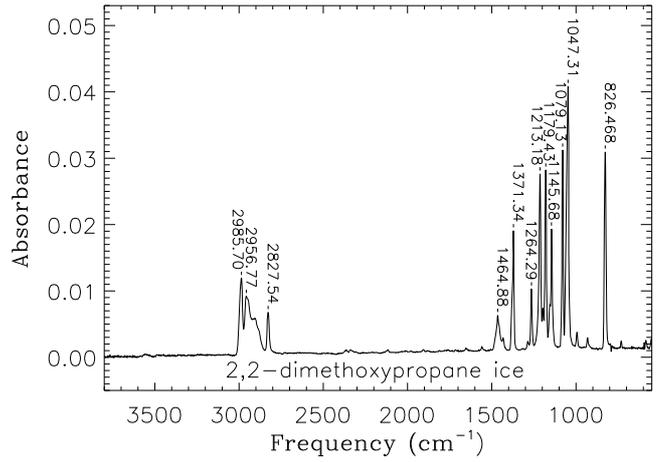Muñoz Caro & Schutte (2003) found that the relative abundances of the irradiation products present in organic refractory residues vary considerably as a function of the starting ice composition, UV dose, and frequency of the UV photons. Despite that, here we showed that those organic refractory residues share a similar 3.4 μm feature profile. An important question is thus whether the broad double-peaked 3.4 μm feature profile of organic refractory residues can be reproduced by UV-irradiation of "exotic" ice components, i.e. non-realistic analogs of interstellar and circumstellar ice mantles. That depends on whether there are strong *memory effects* on the synthesis of irradiation products as a function of the different composition of the starting ice, in other words if UV-irradiation can fragment the ice precursors sufficiently to fully *erase* the initial composition of the starting ice so that two different ices with the same elemental atomic composition would lead to the same residue after irradiation. For that purpose, pure formamide CHONH$_2$ and 2,2-dimethoxypropane (CH$_3$)$_2$C(OCH$_3$)$_2$ ices were UV-irradiated under the same conditions as interstellar ice analog mixtures. Their ice spectra are shown on top panels of Figs. 4 and 5. The residue spectrum of formamide in Fig. 4, bottom panel, is similar to that of pure methanol, and thus shows a 3.4 μm feature composed of subfeatures associated with CH$_3$ and CH$_2$ stretchings, different to the 3.4 μm feature of organic refractory residues. The same holds for the 3.4 μm feature of the 2,2-dimethoxypropane residue in

Fig. 5, bottom panel; the spectrum shows prominent bands due to functional groups at 3430 (OH str.), 1714 (C=O str. in saturated aliphatic ketones), and 1069 cm^{-1} (C-OH str. in alcohols). As a result, it was found that the 3.4 μm feature of organic refractory residues was not reproduced when formamide or 2,2-dimethoxypropane, two OH-free and non-realistic analogs of interstellar/circumstellar ices, were UV-irradiated.

4. Astrophysical implications

This work shows that the common characteristic broad double-peaked 3.4 μm feature profile of organic refractory residues, with subfeatures at $\sim$2926 cm^{-1} (3.42 μm) and 2876 cm^{-1} (3.48 μm), can be used as a tracer of refractory organic matter made from irradiation and subsequent sublimation of interstellar and circumstellar ice mantles, and this refractory organic matter might be observed on grains that were not further processed after sublimation of the ice. The 3.4 μm feature of organic refractory residues is a good tracer for several reasons: a) it has subfeatures that translate into a more specific band profile when compared to the bands attributed to functional groups in organic matter; b) bands due to functional groups in organic refractory residues can overlap with ice bands, or bands due to hydrated silicates or carbonates in grains, but the 3.4 μm feature of organic refractory residues could still be observed superposed on the red wing of water ice absorption; c) often the only observing infrared window available is the one corresponding to this band. In a recent publication, we searched for solid O- and N-rich organic matter of prebiotic interest in space that relied on the infrared and Raman spectroscopic comparison of organic refractory residues to diffuse interstellar medium carbon, and the carbon fraction in comets, meteorites and IDPs. It was found that comets are expected to be the main source of such organic matter for the early earth (Muñoz Caro & Dartois 2007). The results presented here validate previous publications where the 3.4 μm feature of organic refractory residues was compared to that found in different space environments, which main conclusions are summarized below.

Figure 6 shows a comparison of the 3.4 μm organic refractory residue feature to those of IDP L2036-R9, the carbon matrix of the Orgueil carbonaceous chondrite after hydrolysis, and the one observed toward GC IRS8 as a probe of the diffuse interstellar medium. Clearly, it shows that the 3.4 μm feature of organic refractory residues differs from that of hydrocarbon polymers that are poor in O and N, like the hydrogenated amorphous carbon, a-C:H (e.g. Sandford et al. 1991; Duley et al. 1998; Mennella et al. 1999; Dartois et al. 2004b, 2005), present in carbon grains of the diffuse interstellar medium (as reported by Pendleton & Allamandola 2002), carbonaceous chondrites like Orgueil, and IDPs (Muñoz Caro et al. 2006). The mid-infrared fingerprints of organic refractory residues are also different from those present in the spectra of IDPs, carbonaceous chondrites and diffuse medium carbon grains (Muñoz Caro et al. 2006; Dartois et al. 2005). This indicates that the chemical structure and composition of organic refractory residues is different to the a-C:H materials present in IDPs, carbonaceous chondrites, and diffuse medium carbon grains (Muñoz Caro et al. 2006; Muñoz Caro & Dartois 2007). Nevertheless, a fraction of the organic refractory residue matter, dating from the local dense cloud or the solar nebula, could still be preserved in cometary nuclei that did not experience heating at temperatures above 300 °C, and could be the precursor of the D and ^{15}N-enriched carbon component of IDPs and carbonaceous chondrites (Muñoz Caro et al. 2006; Muñoz Caro & Martínez-Frías 2007). The 3.4 μm
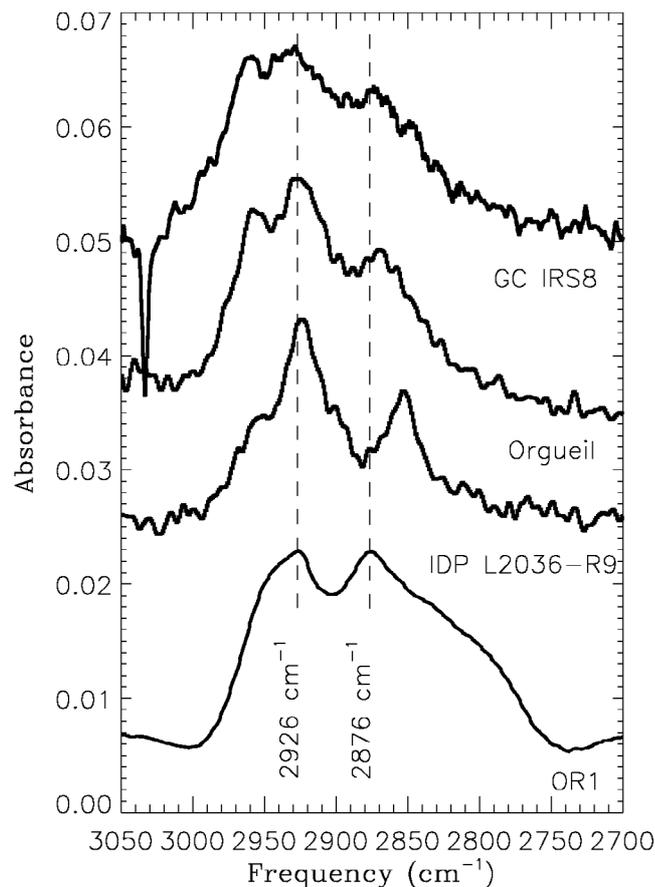

Fig. 6. Comparison of the infrared 3.4 μm features corresponding to an organic refractory residue (OR1, see Sect. 3.1), an IDP named L2036-R9, the Orgueil residue obtained from hydrolysis, and the Galactic Center source GC IRS8.

feature of organic refractory residues was also used recently for comparison to the carbon bulk in cometary grains collected by Stardust (Muñoz Caro et al. 2008), and found to be very different. IDPs collected prior to atmospheric entry heating and cometary grains that were not annealed at temperatures higher than 300 °C during capture might be richer in organic matter rich in O and N. The proportion of organic matter of prebiotic interest over the total carbon content in comets, meteorites and IDPs is a key parameter to constrain the contribution of extraterrestrial delivery to the origin of life on Earth.

This paper could serve to promote the search for solid organic matter made from ice photoprocessing followed by warm-up toward hot cores, regions around YSOs, and solar system bodies like comets. Infrared observations toward a few YSOs, like IRAS 04579+4703, show a 3.4 μm feature that is compatible with that of organic refractory residues (Ishii et al. 2002), but the resolution is still too poor for a proper comparison, and improved observations with higher resolution and signal-to-noise ratio are required. The same line of sight can intersect both circumstellar and diffuse interstellar carbon grains. Therefore, to assess the presence of organic refractory residue matter in circumstellar regions, the detected 3.4 μm feature profile should differ significantly from that detected toward diffuse medium lines of sight. By adding the 3.4 μm feature, attributed to diffuse interstellar carbon grains (top trace of Fig. 6), to the same feature of organic refractory residues (bottom trace of Fig. 6), we found that the 3.4 μm feature of organic refractory matter is clearly detected when its optical depth value is equal to or larger than the optical

depth value of the 3.4 μm feature of diffuse interstellar carbon grains.

5. Conclusions

The 3.4 μm feature of organic refractory residues has a characteristic band shape, consisting of two subfeatures around 2925 cm^{-1} (3.42 μm) and 2875 cm^{-1} (3.48 μm), that is not very sensitive to changes in the composition of the starting ice mixture. This feature, however, was not reproduced in irradiation experiments using non-realistic OH-free analogs of interstellar and circumstellar ice mantles; the reason for this is that the 3.4 μm feature of organic refractory residues is mainly attributed to the interaction of OH, and to a lesser extent other electrophylic groups, with the adjacent CH$_2$ bonds that constitute organic refractory residues.

This band was used for comparison of organic refractory residues to the carbon in diffuse interstellar grains (Pendleton & Allamandola 2002), or in solar system objects like comets and IDPs (Muñoz Caro et al. 2006, 2008), and here it was compared to the carbon fraction of the Orgueil carbonaceous chondrite; the 3.4 μm bands in the spectra of all these materials are different to the 3.4 μm band in the spectra of organic refractory residues. Indeed, many IDPs, carbonaceous chondrites like Orgueil and Murchison, and the infrared bands associated with diffuse medium carbon grains, contain different forms of hydrogenated amorphous carbon, a hydrocarbon polymer material poor in O and N, compared to the products of ice UV-irradiation that compose organic refractory residues (see Muñoz Caro & Dartois 2007, for a review). So far, no material from space has been found that produces a 3.4 μm feature with the same profile as the one present in the organic refractory residue spectra. Even so, IDPs collected prior to atmospheric entry heating, comets, and even some meteorites, might preserve organic matter rich in O and N made from ice photoprocessing. Organic globules, enriched in D and ^{15}N, were detected in the Tagish Lake meteorite; these globules probably originated as organic ice coatings on preexisting grains that were photochemically processed into organic refractory matter (Nakamura-Messenger et al. 2006). Using the 3.4 μm feature of organic refractory residues as a tracer, we propose new observations in the infrared, with improved resolution and signal-to-noise ratio, to probe the presence of organic matter made by ice UV-irradiation and warmup, toward hot cores, regions around YSOs, and icy bodies in the solar system.

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