# Spectral features of presolar diamonds in the laboratory and in carbon star atmospheres

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**Abstract.** Laboratory analyses on fine-grained diamond residues from primitive meteorites have shown that nano-diamonds represent the most abundant form of presolar dust preserved in meteoritic samples. The presolar diamonds carry isotopic anomalies which indicate a very complex formation history. Several groups of diamonds may exist with origin in different types of stars. In order to identify the sites of formation observationally, we have extracted presolar diamonds from the Allende meteorite and measured the monochromatic absorption coefficient in a form which is useful for stellar atmosphere calculations. The monochromatic absorption coefficient was measured in the wavelength ranges 400–4000 cm$^{-1}$ (2.5–25 $\mu$m) and 12200–52600 cm$^{-1}$ (190–820 nm). We have made identical laboratory measurements on CVD diamonds as on the meteoritic diamonds, in order to get a more solid basis for the interpretation of the diamond spectrum. The monochromatic absorption coefficient for the presolar diamonds was incorporated in self-consistent carbon star photospheric models. The main influence of the diamond dust in our photospheric models is a heating of the upper photospheric layers and a reduction of the $C_2H_2$ abundance. Due to the relatively small absorption coefficient of the diamonds compared to other stellar dust grains, their spectral appearance is weak. However, the weak interaction of the diamonds with the radiation field may give them an important role in the dust nucleation process. The gas pressure will stay high and the gas will be much closer to hydrostatic equilibrium during possible diamond nucleation than is normally the case in dust forming stellar regions, and therefore allow ample time for the nucleation process.

**Key words:** stars: atmospheres – stars: carbon – stars: abundances – infrared: stars

## 1. Introduction

Until 1987, dust particles around stars had only been recognised by their appearance in stellar spectra, but the possibility of studying unprocessed stellar condensates directly in the laboratory has given important information not only about the Solar System formation, but has also provided precise data for testing astrophysical stellar models.

Presolar diamonds were the first grains to be isolated from meteorites of the carbonaceous chondrite type, which could be shown to have originated from outside the Solar System (Lewis et al. 1987). The identification of their presolar origin has been possible on the basis of isotopic anomalies that appear inconsistent with any known solar system process (Anders & Zinner 1993). Primitive meteorites show the presence of two different components. One component consist of chondrules and other inclusions which have experienced various melting processes during the formation of the solar system. The other component, called the matrix, is fine grained and has experienced little or no heating. It is in the matrix that the presolar grains are found. The presolar diamond content is very similar for all chondrite classes, around 500–1000 ppm of the matrix (Alexander et al. 1990; Huss 1990). Their median grain size is about 2 nm (Fraundorf et al. 1989), which means that each diamond contain only about one thousand carbon atoms. A large fraction of the atoms are therefore on the surface of the crystal, and the meteoritic diamonds therefore consist of a mixture of diamond and hydrogenate amorphous carbon (a-C:H). The amorphous part has been estimated to account for 0.46 the volume fraction of the presolar diamonds (Bernatowicz et al. 1990).

The size distribution of the presolar diamonds is log-normal rather than power-law, reflecting growth rather than fragmentation and suggesting a short interstellar residence time (Lewis et al. 1989). This size distribution is surprising, as interstellar dust normally shows a power-law distribution, which is the steady state form for fragmentation. A log-normal distribution reflects either size-sorting or growth followed by partial conversion of

small grains to large ones (Lewis et al. 1989). The good fit for the size distribution obtained by Lewis et al. (1989) down to small sizes suggests minimal contributions from processes that affect small grains preferentially, such as fragmentation, sputtering and erosion. This suggests that the distribution is young and unevolved.

Various mechanisms have been proposed to account for the production of diamond grains in space, but the most likely scenario appears to be that the nano-diamonds have condensed directly from stellar outflows (Lewis et al. 1987; Jørgensen 1988; Clayton 1989; Clayton et al. 1995). The conditions in cool stellar outflows are remarkably similar to those employed in industry to produce diamonds by Chemical Vapour Deposition (CVD) (Angus & Hayman 1988). The CVD mechanism makes use of the fact the the free energy difference between diamond and graphite is only around 1 kcal/mol. Almost any chemical reaction yielding graphite as the thermodynamically stable product can, in principle, yield diamond as a metastable product. The trick is to steer the kinetics so as to favour diamond over graphite. It has been suggested by Krüger et al. (1996), that in circumstellar envelopes the surface growth processes on carbonaceous seed particles will take place at $sp^3$ bonded carbon atoms rather than at $sp^2$ bonded carbon atoms, which suggest that the grain material formed in circumstellar envelopes will be amorphous diamond-like carbon.

For studies of radiative processes in stellar environments, knowledge of opacities of the relevant atoms, molecules and grains are essential. In order for the grains to be taken into account in stellar atmosphere computations, knowledge of the spectral properties of the relevant grains are needed. Transmission spectroscopic measurements of presolar diamonds from the Allende meteorite in the ultra-violet, the optical and the infrared region are presented in this paper. The measurements were designed such that it has been possible to determine the monochromatic absorption coefficient. This coefficient is necessary in order to include the nano-diamonds in model atmosphere calculations and in synthetic spectrum calculations. By use of the derived absorption coefficient, synthetic spectra of carbon stars with the nano-diamonds included have been calculated, under the assumption that the diamonds we have extracted have the same optical properties as they had when they formed in a stellar atmosphere. Finally, we have performed similar laboratory measurements on CVD diamonds, in order to get a more solid basis for understanding the spectral features of the presolar diamonds.

## 2. Experiments

The presolar diamonds were extracted using the method described by Tang & Anders (1988). A 10.8 g piece of the Allende meteorite was dissolved by alternating treatment with 10 N HF–1 N HCl and 6 N HCl (10 ml/g meteorite) to remove the silicates. The sulfur was removed with a $CS_2$ treatment and the reactive kerogen was destroyed by oxidation with $HNO_3$ and $HClO_4$. To separate the diamonds the sample was dispersed by ultrasoni-
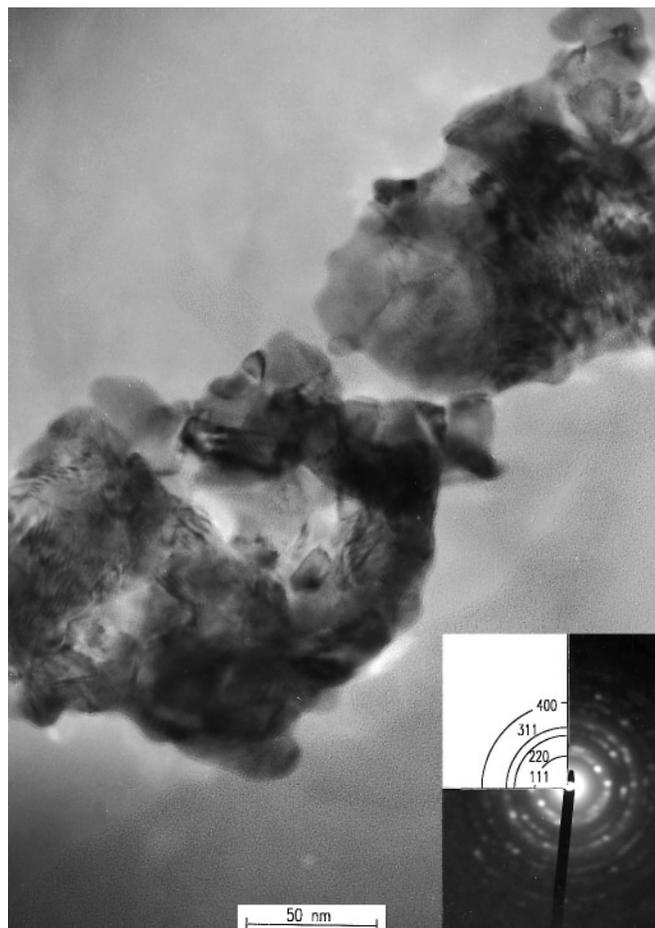


**Fig. 1.** A transmission electron microscope bright-field micrograph showing a cluster of presolar nm-sized diamond crystallite. Each cluster consists of about 1000 diamonds. The corresponding diffraction pattern is shown indicating the (111), (220), (311) and (400) spacings for diamond crystallite (d = 2.065 (2.06), 1.281 (1.26), 1.035 (1.0754) and 0.8892 (0.8916) Å, respectively, with the table values in parenthesis).

fication in 0.1 M $NH_4OH$, producing a diamond colloid, which was extracted after centrifugation.

The CVD diamonds were prepared as a hetero-epitaxial diamond film on a silicon (100) substrate which had been polished with 0.25 $\mu$g of diamond powder before depositing the CVD diamonds. The CVD diamonds were deposited in a hot filament reactor with 8% $CH_4$ in the $H_2$ source gas. The filament temperature was between $2200°$ C and $2400°$ C, the substrate temperatures were between $700°$ C and $900°$ C and the pressure was 5 mbar. This gives a growth rate of about 1 $\mu$g/hour. The CVD diamonds were scraped off from the silicon substrate with a diamond needle.

Transmission electron microscopy (TEM) was carried out on both the presolar diamonds and the CVD diamonds, using a Philips EM 430 transmission electron microscope operated at 300 keV (Fig. 1). With this instrument we performed conventional imaging, electron diffraction and energy-dispersive X-ray spectroscopy (EDS) with a sensitivity down to Boron. We esti-

mated that the sizes of the CVD diamonds are between 1.4 nm and 14 nm, from visual inspection of the TEM images. The CVD diamonds are hence, approximately three times bigger than the meteoritic diamonds.

The spectral measurements were carried out in the infrared (400–4000 cm$^{-1}$; 2.5–25 $\mu$m) and in the UV/VIS (12200–52600 cm$^{-1}$; 190–820 nm) region.
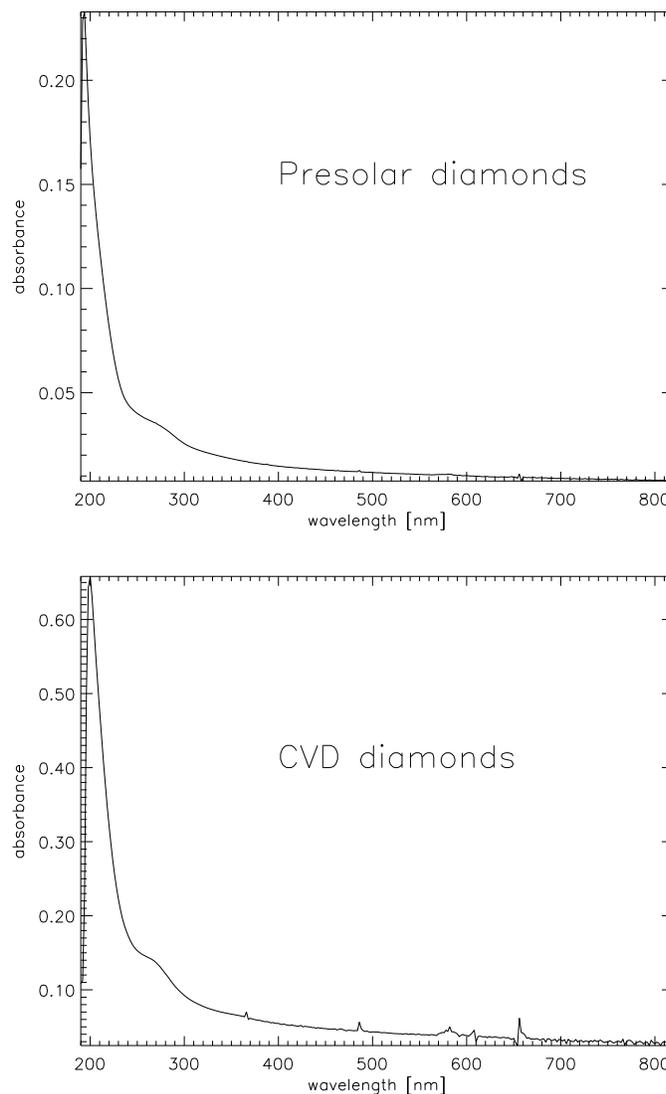
The UV/VIS spectra of the presolar and CVD diamonds were taken on a very dilute solution of 350 $\mu$g diamonds in distilled water. The spectra were obtained with a HP 8452A Diode-Array Spectrophotometer, which is a single-beam microprocessor-controlled spectrophotometer with a deuterium lamp as the light source giving 190 nm – 820 nm wavelength range. The wavelength accuracy was $\pm$ 2 nm. The sample cell was a small quartz container with dimensions 40 mm × 10 mm × 1 mm. During the measurements, a reference spectrum of distilled water was used. The difference of the signals obtained for the quartz container filled with distilled water and the one filled with diamonds in distilled water was attributed to the absorption of the diamonds.

The infrared spectra of the presolar and CVD diamonds were obtained with a FT-IR Perkin Elmer 1760 Infrared Spectrometer. The spectrometer operates in the region 400–5000 cm$^{-1}$. The instrument operation is driven by a computer station which allowed us to record the spectra in digital form. All measurements were performed with 64 scans and a resolution of 1–2 cm$^{-1}$. For sample preparation the KBr technique was used, where small quantities of the sample are mixed throughly with powdered KBr (300 mg). Because of the softness of KBr and its bulk transparency between 40 and 0.2 $\mu$m, the KBr and particle mixture can be pressed into a clear pellet (diameter = 13 mm) (Colthup et al. 1990). Around 300 $\mu$g of presolar diamonds was added to the KBr as a suspension in ethanol. The diamonds were suspended in order to separate them, so that they would not be stuck in big clumps, because the diamonds are likely to have formed individually, not in agglomeration in stellar atmospheres. By suspending them we therefore expect to obtain a spectrum which compare best with the possible stellar spectrum. Around 200 $\mu$g of CVD diamonds was added to the KBr in the same way and the KBr for the reference pellets were also suspended in ethanol. The ethanol was removed by pumping on the sample before pressing the tablet. Despite this, we still had traces of ethanol in our spectra, so it was necessary to compensate for this by the use of the reference spectra.

## 3. Interpretation of the experimental spectra

### 3.1. The UV/VIS spectra of the diamonds

The UV/VIS spectra of our presolar and CVD diamond samples are very similar to one another, showing strong absorption in the UV, with a distinct band at 217 nm (46 000 cm$^{-1}$), a flat maximum around 270 nm (37 000 cm$^{-1}$) and declining absorption towards the visual end of the spectrum (Fig. 2). These absorption characteristics are also typical for terrestrial diamond containing pairs of nitrogen atoms (Davies 1984). These bulk



**Fig. 2.** The UV/VIS absorbance spectrum of the presolar and the CVD diamonds, respectively.

UV/VIS features deviate significantly from the results by Lewis et al. (1989), but correspond well with the measurements obtained by Mutschke et al. (1995) on presolar diamonds from the Murchison meteorite, except that the strength of the flat maximum around 270 nm seem to be much stronger for the Murchison presolar diamonds.

The position of the band around 217 nm coincides with that of the interstellar extinction bump at 217.5 nm, as it has also been found by Mutschke et al. (1995) for the Murchison meteorite.

### 3.2. The IR spectrum of the presolar diamonds

The infrared absorbance spectrum of the presolar diamonds shows several peaks (Table 1 and Fig. 3). The strong peaks are mainly due to impurities, meaning the presence of atoms other than C. These impurities are most likely situated at the grain surface, some of which may be due to the chemical process-

**Table 1.** Wavenumber of our measured IR bands, in cm$^{-1}$, detected in the spectra of the presolar diamonds from the Allende meteorite and from CVD diamonds, respectively. Also listed are our suggestions for assignments of the bands.

| Presolar | CVD | Assignment |
|---|---|---|
| 3420$^{sp}$ | 3418 | O–H stretch (in H$_2$O) |
| 3236$^{sh}$ | | N–H stretch |
| 2954$^{sh}$ | 2972 | C–H stretching from CH$_3$/CH$_2$ |
| 2924 | 2927 | groups |
| 2854 | 2856 | |
| | 1719 | C=O stretch (strained ring) |
| 1632$^{sp}$ | 1640 | O–H bend (in H$_2$O) |
| 1462 | | C–H deformation (CH$_3$/CH$_2$) |
| 1456 | 1456 | |
| 1402$^{sh}$ | 1401$^{sh}$ | C–H deformation (CH$_3$)/inter- |
| 1385$^{sp}$ | 1385$^{sp}$ | stitial N |
| 1122 | 1122 | C–O/C–N/C–C stretch |
| 1109 | 1112 | |
| 1090 | 1089 | |
| 1054 | 1051 | |
| 721$^{w}$ | | C–H out-of-plane bend in alkene residues |
| 633$^{sh}$ | | C–Cl stretch |
| 607 | 579$^{br}$ | O–H bend/torsion in bonded |
| 471 | | water |

sp = sharp; sh = shoulder; br = broad; w = weak

ing in the laboratory, other, of which may refer to the astrophysical environment the grains have experienced. The strong peaks at 3420 cm$^{-1}$ and 1632 cm$^{-1}$ are most likely due to H$_2$O (Chrenko et al. 1967). These peaks are strong and sharp, which makes tightly bound water a likely possibility (Nyquist & Kagel 1971). This interpretation of the spectrum is further supported by the peaks at 607 cm$^{-1}$ and 471 cm$^{-1}$.

The shoulder peak at 3236 cm$^{-1}$ can be assigned to N–H stretching.

The peak frequencies and shapes of the triplet at 2954 cm$^{-1}$, 2924 cm$^{-1}$ and 2854 cm$^{-1}$, can be attributed to long aliphatic hydrocarbon chains C$_n$ with n$\geq$8 and indicating the presence of both –CH$_3$ and –CH$_2$ symmetric and antisymmetric deformation modes. This is further supported by part of the broad peak between 1462 cm$^{-1}$ and 1385 cm$^{-1}$ and the weak absorption at 721 cm$^{-1}$ (Trombetta et al. 1991). The broad peak between 1462 cm$^{-1}$ and 1385 cm$^{-1}$ can also partly be assigned to interstitial N in diamond (Lewis et al. 1987).

The broad peak at 1122–1054 cm$^{-1}$ can be attributed to C–O stretching in aliphatic ethers and/or C–N stretching.

The shoulder at 633 cm$^{-1}$ could be due to a C–Cl stretch, see later in the text.

### 3.2.1. The O–H bands

The indication of tightly bound water which may be intrinsic, is not found in the other spectra obtained on presolar diamonds from the Allende meteorite that has been published (Lewis et al. 1989; Koike et al. 1995). See Table 2. Normally a diamond cannot be wetted with water, but under certain conditions the
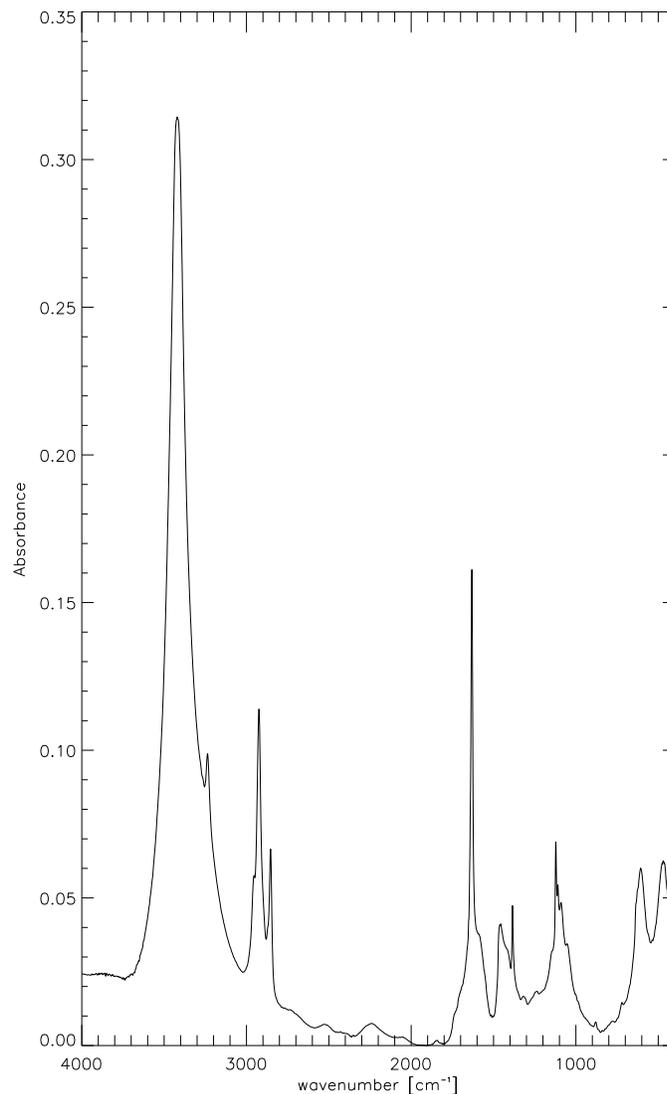


**Fig. 3.** Infrared absorbance spectrum of the presolar diamonds from the Allende meteorite.

water-repelling nature of the surface disappears (Davies 1984.) It has been shown for terrestrial diamonds that if the diamond is heated to a few hundred degrees centigrade in O$_2$, the water-repelling nature of the surface disappears; while heating the diamond in vacuum or in an atmosphere of H restores its water-repelling nature (Sappok & Boehm 1968). This means that, if these water features are intrinsic (as oppose to being an effect of not fully reduced water spectral features from humidity in the KBr pellet), they cannot originate from when the diamonds were formed in a carbon/hydrogen rich atmosphere, but rather is an artifact which most likely originates from the very rough chemical treatment that was used in order to extract the diamonds.

The peak around 3400 cm$^{-1}$ obtained by Lewis et al. (1989), for diamonds from the Allende meteorite, was interpreted by them as coming from –COOH. We consider this peak to be too high in wavenumber and too narrow to be assigned OH in

**Table 2.** Spectral bands, in cm$^{-1}$ unless otherwise stated, detected in the obtained spectra of the presolar diamonds from the Allende, Murchison and Orgueil meteorites. The different interpretations by the various authors are indicated by corresponding numbers.

| ALLENDE | | | MURCHISON | | ORGUEIL | Assignment by different authors |
|---|---|---|---|---|---|---|
| [1]This paper | [2]Lewis et al. 1989 | [3]Koike[ab] et al. 1995 | [4]Colangeli et al. 1994 | [5]Mutschke et al. 1995 | [6]Hill et al. 1996 | |
| 217 nm 270 nm | | | | 217 nm 270 nm | | [5]π − π* transition of aromatically bonded C, [1]paired N in diamond |
| 3420 | 3402 | 3401 | 3450 | 3400 | | [2]O–H in –COOH, [1,3,4,5,6]O–H stretch (in H$_2$O) |
| 3236 | 3210 | 3115 | 3164 | | | [1,2,3,4,5,6]N–H stretch |
| 2954 2924 2854 | 2919 2849 | 2976 2924 2849 | | 3000 2800 | 2985 2935 2875 | [1,2,3,4,5,6]C–H stretching from CH$_3$/CH$_2$ groups |
| | 1774 | | 1771 | 1746 | 1728 | [2,4]C=O in –COOH, [1]C=O (strained ring) [5]C=O bonds in ester, [6]C=O or C=C |
| 1632 | 1640 | 1634 1590 | 1616 | | | [2,4]aromatic C=C/C=O stretch, [3]C=O/N-H stretching, [1]O–H bend (in H$_2$O) |
| 1462 1456 | | | | | | [1]C–H deformation (CH$_3$/CH$_2$) |
| 1402 1385 | 1403 1361 | 1401 1399 | 1399 | | | [1,2,4]C–H deformation (CH$_3$)/interstitial N |
| 1122 1109 1090 1054 | 1234 1173 1108 1090 1028 | 1178 1122 1108 1080 | 1084 | 1175 1090 | 1289 1125 1072 | [3,4,5,6]C–O/C–N stretch [1]C–O/C–N/C–C stretch/interstitial N [2]C–O stretch/interstitial N |
| 721 | | | 744 | 725 | 745 | [1]C–H out-of-plane bend in alkene residues |
| 633 | 637 | 636 630 626 | | 630 | | [1]C–Cl stretch |
| 607 471 | | | | | | [1]O–H bend/torsion in water |
| | | | | 396 367 310 | | [5]C=O=C or C=N=C |
| | | | | 130 120 | | ?? not yet identified |

[a] = the spectra were obtained on diamond-like residues.
[b] = transformed to cm$^{-1}$ from their tabulated values given in $\mu$m.

–COOH, while we find a good fit with known spectral bands of water. Also the band at 1774 cm$^{-1}$ is somewhat high in wavenumber for a –COOH interpretation. The –COOH interpretation has also been questioned by Mutschke et al. (1995) and Hill et al. (1996). Variations in the intensity and in the presence of a peak around 1740 cm$^{-1}$ have also been observed in the spectra of CVD diamonds, where the peak varied considerably for spectra obtained at different times and with different IR spectrometers (Janssen 1991).

### 3.2.2. The C-H bands

The triplet around 2900 cm$^{-1}$ and the peaks around 1400 cm$^{-1}$ can all be ascribed to the presence of saturated hydrocarbons (aliphatic compounds), but the peaks around 1400 cm$^{-1}$ are also in the right range for N in diamond (Lewis et al. 1989).

### 3.2.3. The nitrogen bands

The N–H stretch at 3236 cm$^{-1}$ and the broad band around 1100 cm$^{-1}$ present in most of the published spectra of meteoritic diamonds can be ascribed to various forms of nitrogen in and on the diamonds. Presolar diamonds have been shown by Russel et al. (1991) to be nitrogen rich.

Part of the 1100 cm$^{-1}$ peak can also be attributed to C–O stretching in aliphatic ethers but the feature around 1084 cm$^{-1}$ could just as well be due to C–N stretching and is in the right range for single N in terrestrial diamonds (Clark et al. 1979).

### 3.2.4. The C–Cl bands

We attribute the weak shoulder at 633 cm$^{-1}$ to C–Cl stretch based on a comparison with the spectra obtained by Koike et al. (1995), of diamond-like residues from the Allende meteorite

and on the fact that terrestrial diamonds do not show absorption in this wavelength region (Davies 1977). In the spectra obtained by Koike et al. (1995) they have a very sharp peak at $630\,\mathrm{cm}^{-1}$ which fits the pattern of a CCl stretch and the small splitting of the feature in their spectra could be due to isotopic effects ($^{35}$Cl, $^{37}$Cl). Since they have used part of the same treatment as we did, it seems very likely that both spectra could contain an impurity which originates from HCl.

### 3.3. The IR spectrum of the CVD diamonds

The infrared absorbance spectrum of the CVD diamonds also show several peaks, many of which correspond to the peaks found for the presolar diamonds. The primary differences between the spectral properties of the presolar diamonds and the CVD diamonds, are that the CVD diamonds have spectral characteristics closer related to soot than have the presolar diamonds.

The nitrogen which is present in the CVD diamonds is due to nitrogen impurities in the $\mathrm{CH_4/H_2}$ gas mixture that was used during the deposition (Locher et al. 1994).

The peaks we attribute to O–H at $3418\,\mathrm{cm}^{-1}$, $1640\,\mathrm{cm}^{-1}$ and $579\,\mathrm{cm}^{-1}$ are broader for the CVD diamonds than for the presolar diamonds, indicating that the water present here is not tightly bound.

### 3.4. Discussion

The IR spectra of pure diamond have very few absorption features. For terrestrial diamonds the intrinsic absorption present in all types of diamonds are at wavenumber greater than $1400\,\mathrm{cm}^{-1}$ ($\lambda < 7.1\,\mu\mathrm{m}$), with a peak around $2000\,\mathrm{cm}^{-1}$ ($5\,\mu\mathrm{m}$) for pure diamond, while that below $1400\,\mathrm{cm}^{-1}$ ($\lambda > 7.1\,\mu\mathrm{m}$) is specimen dependent both in strength and shape (Davies 1977) and is caused by impurities, typically nitrogen.

The features that are present in the spectra of presolar diamonds are results of O–H, N–H, C–H, C=O, C=C, C–O, C–N and C–C interactions. It is not possible by IR-spectroscopy to distinguish whether the impurities in or on the diamonds are due to the chemical processing in the laboratory, in the interstellar space, during the Solar System formation or whether the "impurities" are original features which refer to the astrophysical environment the grains have experienced. It has been shown by Russel et al. (1991) that the presolar diamonds carry isotopic anomalous nitrogen with $^{14}\mathrm{N}/^{15}\mathrm{N} = 406$ (terrestrial = 272) and by Virag et al. (1989) that the presolar diamonds also carry anomalous hydrogen with $^1\mathrm{H}/^2\mathrm{D} = 5193$ (terrestrial = 6667) implying that at least some of the H and N must be presolar. From a spectroscopic point of view it does not really matter whether the hydrogen bonds on the surface of the grains are "original" from the stellar environment or have been replaced at a later stage, as long as the presence of hydrogen is to be expected on the grain surface in the stellar environment. Of course, then a replacement by a different element will make a difference.

This makes the whole discussion about facts and artifacts in the spectra of presolar diamonds complicated, since if the presolar diamonds are exposed to a very rough chemical treat-
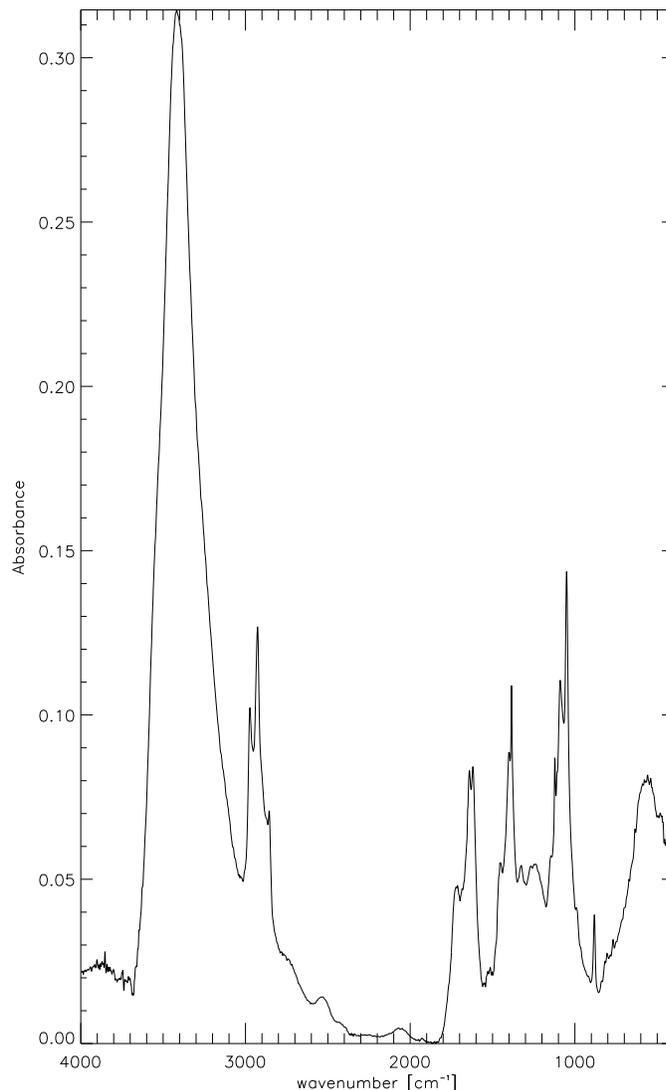


**Fig. 4.** Infrared absorbance spectrum of the CVD diamonds. Due to the compensation for the ethanol in which the diamonds were suspended (see Sect. 2), the spectrum is over compensated around $3640\,\mathrm{cm}^{-1}$ and $1640\,\mathrm{cm}^{-1}$.

ment to clean them as much as possible, it might be possible to get a clean surface of the diamonds, but the obtained spectra might not resemble what we can expect to observe if the nano-diamonds, at their place of origin, are not clean but characterised by C–N, N–H and C–H bonds on the surface.

## 4. Monochromatic absorption coefficient

The monochromatic absorption coefficient $\kappa$ can be derived from the Beer-Lambert law,

$$\frac{I}{I_0} = e^{-\rho \cdot l \cdot \kappa} \tag{1}$$

where $I_0$ and $I$ are the intensities of the incident and transmitted light, respectively, $\rho$ is the density of the absorbing substance,

$l$ is the path length of the absorbing substance and $\kappa$ is the monochromatic absorption coefficient.

For the UV/VIS measurements the absorption is measured as $\log_{10}(I_0/I)$, this give the following expression for the monochromatic absorption coefficient after Eq. (1):

$$\kappa = \frac{1}{\rho \cdot l} \cdot \ln\frac{I_0}{I} = \frac{2.30258}{\rho \cdot l} \cdot \log_{10}\frac{I_0}{I}. \tag{2}$$

The bulk density $\rho$ of the presolar diamonds have been found by Lewis et al. (1989) to be $2.22 - 2.33$ g/cm$^3$. The path length $l$ through the diamonds can be found as the volume of diamond sample divided by the area of the sample. The area of the diamond sample is identical to the area of the sample cell if the diamond sample is dispersed evenly in the sample cell. $l$ is then the effective path length of the radiation through an equivalent, thin diamond film of the equivalent thickness $l = V_{dia}/A_{cell} = V_{dia}/A_{dia} = \frac{m_{dia}}{\rho_{dia}}/A_{dia}$, so that $\rho_{dia} \cdot l = m_{dia}/A_{dia}$.

$$
\begin{aligned}
\kappa_{UV} &= \frac{2.30258}{m_{dia}/A_{dia}} \log_{10} \cdot \frac{I_0}{I} \\
&= \frac{2.30258}{\left(350 \times 10^{-6}\text{g}\right)/((4.0\text{cm})(1.0\text{cm}))} \cdot \log_{10}\frac{I_0}{I} \\
&= 26315 \cdot \log_{10}\frac{I_0}{I} \quad \text{cm}^2/\text{g}.
\end{aligned} \tag{3}
$$

$$
\begin{aligned}
\kappa_{IR} &= \frac{2.30258}{m_{dia}/A_{dia}} \cdot \log_{10}\frac{I_0}{I} \\
&= \frac{2.30258}{\left(300 \times 10^{-6}\text{g}\right)/(\pi\left(\frac{1.3}{2}\text{cm}\right)^2)} \cdot \log_{10}\frac{I_0}{I} \\
&= 10188 \cdot \log_{10}\frac{I_0}{I} \quad \text{cm}^2/\text{g}.
\end{aligned} \tag{4}
$$

The transmittance, T, is:

$$T = \frac{I}{I_0} \times 100\%,$$

and the absorbance, D, is given by

$$D = \log_{10}\frac{I_0}{I}.$$

Since the transmittance measurement give the monochromatic extinction coefficient (extinction = absorption + scattering) it is necessary to correct for scattering before the monochromatic absorption coefficient can be derived. The measured IR-spectra were corrected for scattering by performing a base-line correction on the measured transmittance spectrum, before it was converted into an absorbance spectrum. In the base-line method a base line is drawn tangent to the spectrum at the wings of the analytical band, and its intersection with a vertical line at the analytical wavenumber is used for $I_0$. No correction for scattering was performed for the UV/VIS measurements, since the amount of scattering in the experiment was very small.

The primary reason for scattering in the measured IR transmittance spectrum is that when the sample is incorporated in
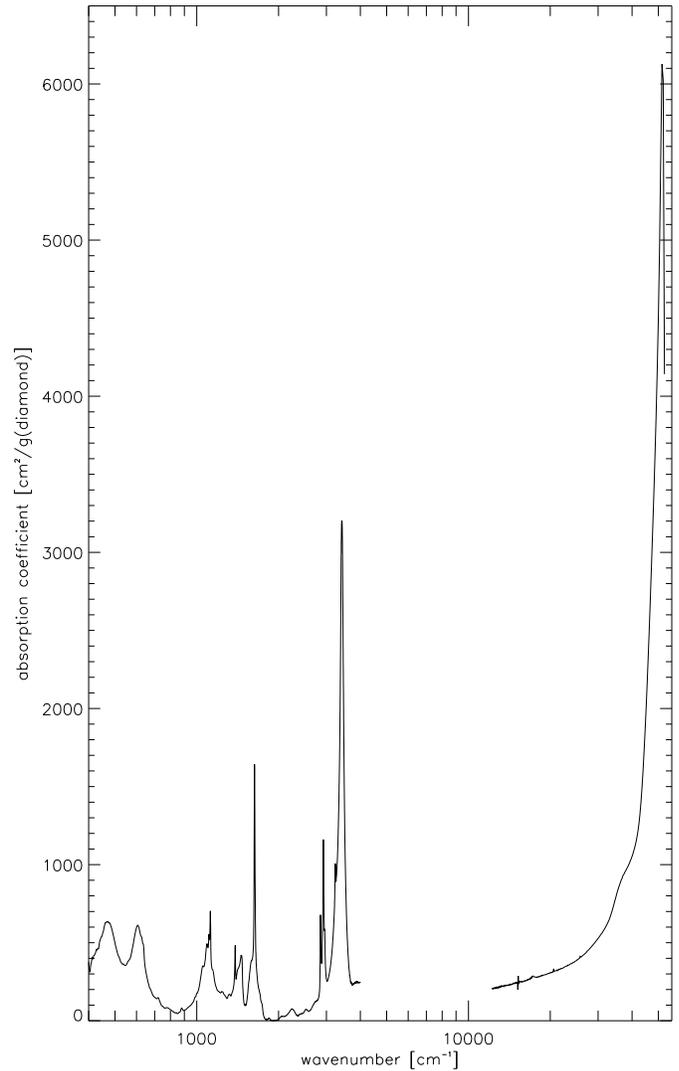


**Fig. 5.** The monochromatic absorption coefficient for the presolar diamonds, as derived from the IR and UV/VIS absorbance spectra.

a KBr matrix the size of the KBr grains will force the sample grains to lay around the much larger KBr grains, resulting in some clumping of the sample. The scattering is therefore mainly a matrix effect, and not a property of the diamond that we should expect to observe in stellar environments.

With the measured $I/I_0$, being dimensionless, and $\rho$ and $l$ given in the units described above, the monochromatic absorption for the presolar diamonds comes out in units of cm$^2$ per gram of diamonds which is shown in Fig. 5. We notice that with the correction for scattering, the value of the absorption coefficient at the upper wavenumber of our infrared measurements is almost identical to the value at the low-wavenumber end of the UV/VIS measurements. Further, Mutschke et al. (1995) notice that this spectral region in their measurements of the presolar diamonds from Murchison, is featureless, which is a well known characteristic of terrestrial diamonds, too. A good approximation of the absorption coefficient in the region from $4000\,\text{cm}^{-1}$

to $12200\,\text{cm}^{-1}$ is therefore to approximate it with a constant value, $\kappa = 220\,\text{cm}^2/\text{g}$, which we have also done in the computations of the stellar models and synthetic stellar spectra presented in the next chapter. The full set of data is obtainable on anonymous ftp[1] from *stella.nbi.dk*.

### 4.1. The uncertainty on $\kappa$

The uncertainty of the monochromatic absorption coefficient, $\kappa$, as determined from Eq. (4) and (5) includes the uncertainty in; (1) the estimate of the mass, (2) the assumption that the grains are homogeneously distributed in the sample, and (3) the uncertainty in the measurement of $I/I_0$. Of these three we estimate, that the uncertainty in $m_{\text{dia}}$ is the dominant factor. The mass of our presolar diamond sample for the UV measurements was determined to be $350 \pm 25\,\mu\text{g}$, giving an uncertainty of 7.1% and for the IR measurement to be $300 \pm 45\,\mu\text{g}$ implying an uncertainly of 15%. The overall uncertainty on $\kappa$ as determined from Eq. (4) and (5) is therefore around 15%.

## 5. Synthetic stellar spectra

The knowledge of the monochromatic absorption coefficient for the nano-diamonds allows construction of self-consistent models of the stellar environments in which the diamonds can have formed. We present here self-consistent photospheres and synthetic spectra of carbon stars with simplified diamond condensation. We assume that the diamonds form in the temperature range from 1600 K to 1500 K in such a way that the amount of $C_2H_2$ which transforms into diamond grains increases linearly from 0% at 1600 K to a value at 1500 K which we have set to 0%, 5%, and 10%, respectively, in various models. Models where we induce considerably larger amounts of dust condensation have convergence problems, possibly due to conflicts with our assumption of hydrostatic equilibrium. For temperatures below 1500 K, the condensed fraction of $C_2H_2$ is assumed to be constant (0%, 5%, and 10%, respectively). $C_2H_2$ has been suggested as the primary species for diamond growth by Sharp & Wasserburg (1993) and Krüger et al. (1996), based on full chemical pathway calculations. The condensation temperatures we have adopted are based on the calculation by Sharp & Wasserburg (1993) and by Lodders & Fegley (1995); both of these groups have performed molecular equilibrium calculations to establish the stability fields of C(s), TiC(s) and SiC(s) and other high temperature phases under conditions of different pressures and C/O ratios.

Our computed model photospheres are based on an improved version (Jørgensen et al. 1992) of the MARCS code (Gustafsson et al. 1975). It assumes hydrostatic equilibrium and local thermodynamic equilibrium (LTE), but includes effects of sphericity and uses an opacity sampling (OS) treatment of molecular opacities from approximately 60 million spectral lines (Jørgensen 1994). Such models have proven to reproduce

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[1] Use userid anonymous, type your e-mail address as password, type then "cd pub/scan". You now find the data in the file "diamonds.dat", and a description of how to use them in the file "diamonds.tex".
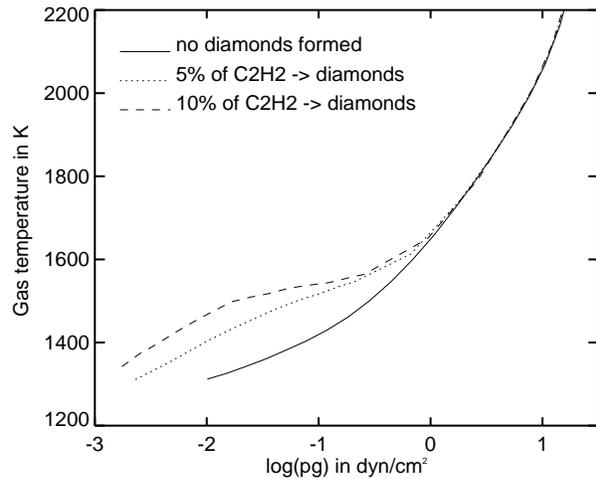


**Fig. 6.** The gas temperature versus total gas pressure for three carbon star model atmospheres with $T_{\text{eff}}$ = 2600 K, log(g) = 0, C/O = 1.17, M = $M_\odot$, and Z = $Z_\odot$. The full drawn line represent a model where no dust is allowed to form. The two other curves represent models where $C_2H_2$ gradually (linearly in temperature) solidifies to diamonds in the temperature range from 1600 K to 1500 K. The maximum degrees of completeness (for T≤1500 K) of the $C_2H_2$ consumptions are 5% and 10%, for the dotted and the dashed curves, respectively.

well the observed spectral features of carbon stars (Lambert et al. 1986; Jørgensen 1989; Jørgensen & Johnson 1991). Full line opacities of CO, $C_2$, CN, CH, $C_2H_2$, $C_3$, HCN, and presolar diamonds were included. The model calculations were performed with the following parameters: C/O = 1.17, 1.35, 2.00; $T_{\text{eff}}$ = 2600 K, 2700 K, 2800 K; log(g) = 0.0, Z = $Z_\odot$, and M=$M_\odot$.

Fig. 6 shows the temperature versus gas pressure structure of a model atmosphere of $T_{\text{eff}}$ = 2600 K, log(g) = 0, Z = $Z_\odot$, C/O = 1.17, without diamond formation, and with 5%, and with 10%, respectively, of the $C_2H_2$ transformed into diamond over a region of the atmosphere from 1600 K to 1500 K. The result of the inclusion of the diamond opacity into the model calculation, is a heating of the upper layers of the photosphere for a given value of the gas pressure. This is a consequence of the larger absorption coefficient of diamond than of $C_2H_2$ in the wavelength region just long-ward of the Planck maximum (at $1 - 2\,\mu\text{m}$). As a result of this heating the model with diamond included produce a slight increase (compared to the model without diamond) in the spectral flux of the central part of the $3\,\mu\text{m}$ ($C_2H_2$) band as well as of the spectral region of the diamond features themselves. The effect is, however, too small to make a clear identification of possible stellar extrasolar diamonds likely on this basis. It should also be mentioned that the effect of reducing the intensity of the $3\,\mu\text{m}$ spectral feature due to the photospheric heating, is smaller than the effect caused by reducing the adopted gravity of the model atmosphere within observationally determined limits (Jørgensen 1989), so this indirect measure of the diamond absorption is not applicable either.

Fig. 7 shows the diamond spectrum, normalised to the true continuum, for the model from Fig. 6 where 10% of the $C_2H_2$ has transformed into diamonds. This spectrum is essentially the

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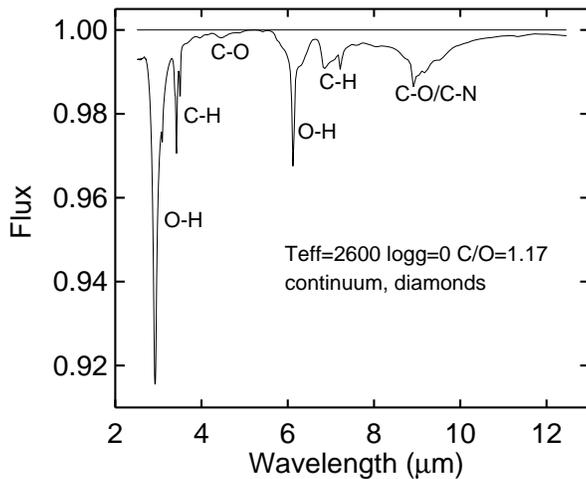


**Fig. 7.** The absorption spectrum from 2 to 12 $\mu$m (5,000 to 800 cm$^{-1}$) of presolar diamonds in a carbon star atmosphere (model as in Fig. 6, with 10% condensation), calculated based on the measured presolar diamond absorption coefficient shown in Fig. 5. Our assignments (from Table 1) are indicated along with the spectrum.
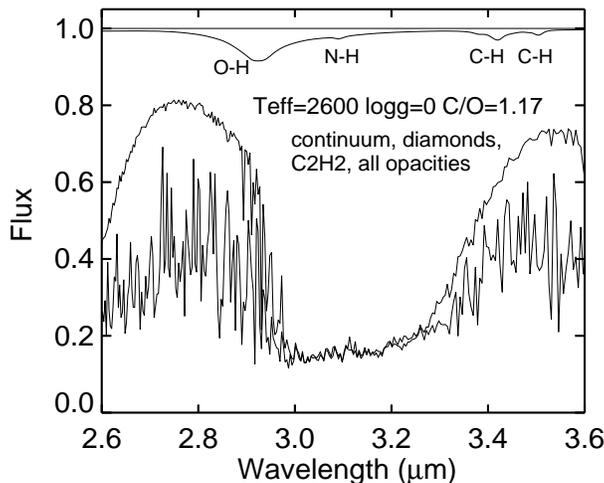


**Fig. 8.** Same as Fig. 7 (although limited to the spectral region 2.6 $\mu$m − 3.6 $\mu$m). In addition to the continuum and the diamond spectrum, also the C$_2$H$_2$ spectrum, and the full self-consistent synthetic spectrum based on all included opacity sources, are shown.

monochromatic absorption coefficient modified by the radiation field and the partial pressures through the atmosphere. The same features as in Fig. 3 are therefore seen here too. Some of these may be artifacts caused by the extraction procedure, as discussed above, but all the measured spectral features are shown here for completeness.

It is seen that the strongest spectral feature (at $\approx$ 3 $\mu$m) from our measurements of the presolar diamonds gives rise to a reduction of the model spectral flux of 8%. In Fig. 8 is seen that the left over C$_2$H$_2$ in the same model gives rise to a flux reduction of between 20% and 80% in the 3 $\mu$m spectral region. When also the other molecules in this region are taken into account, the outcome of synthetic spectrum computations based on a

fixed model structure, is almost identical spectra independent of whether the diamonds are included in the spectra or not. In addition, the 3 $\mu$m diamond feature is likely to be an artifact of the chemical extraction procedure, as discussed above, so that the real intrinsic diamond spectral features may be even weaker. Also at 6 and 9 $\mu$m, where the total molecular absorption is weaker than at 3 $\mu$m, the diamond features are weak compared to the molecular spectral features.

Generally, grain nucleation (as opposed to grain growth) is the bottle neck in stellar dust formation. Polycyclic Aromatic Hydrocarbons (PAH) are often assumed to be the molecular nucleation seeds for dust growth in carbon stars. In hydrodynamic model atmospheres, however, the time scales for PAH formation are too long compared to the dynamical time scales, and in the corresponding hydrostatic photospheres the gas temperature is too high for PAH formation (Helling et al. 1996). The relatively modest opacity, and higher condensation temperature of the diamonds than that of the PAH molecules, may cause nucleation of diamond grains at relatively high atmospheric densities, where the velocity field is still negligible (hence, the hydrostatic approximation is acceptable here). If nucleation of diamond dust (as oppose to PAH) can act as seeds for grain growth in carbon stars, the long dynamical time scales in the region of diamond condensation may therefore contribute to the solution of the nucleation problem mentioned above.

If diamonds are the nucleation seeds of other dust grains, then we should of course expect that the presolar diamonds were part of agglomerates or part of heterogeneous larger grains when they left the parent stellar atmosphere, rather than being pure diamonds (but our considerations above about the photospheric spectra would still apply, since the small, high-temperature diamond seeds will form as individual grains in the pseudo-hydrostatic, denser photosphere before the agglomeration). Such larger grains may, however, have been destroyed in the interstellar space or in the solar nebula. If they survived all the way to being included in the carbonaceous chondrites, they would unfortunately most likely be dissolved during the present chemical extraction procedure, and the development of a more gentle extraction procedure could therefore add important new information about the origin of the presolar diamonds.

## 6. Discussion and conclusion

The obtained spectra of the presolar diamonds show many features which are mostly dominated by O–H, C–H and C–N features. The O–H features does probably not originate from when the nano-diamonds were formed in a carbon/hydrogen rich environment, but is rather an artifact originating from the very rough chemical treatment that is used to extract the diamonds, but the C–H, C–N and N–H (if the nitrogen inclusions are situated at the surface) bonds could very well be responsible for the features we should expect to detect if diamonds are present in a stellar environment.

This mean that the UV/VIS features around 217 and 270 nm (paired N in diamond), the feature around 3200 cm$^{-1}$ (N–H), the features around 2900 cm$^{-1}$ (C–H) and 1100 cm$^{-1}$ (C–N/C–

C/interstitial N) and the features around $350\,\mathrm{cm}^{-1}$ (C–N–C) and $125\,\mathrm{cm}^{-1}$ (unidentified) are all promising features when trying to establish the presence of nano-diamonds.

Knowledge of the monochromatic absorption coefficient is necessary in order to include grains in model atmosphere calculations and in synthetic spectrum calculations, which are needed for comparison with high-resolution observed spectra. In the models presented here the diamond spectrum is weak compared to the molecular spectral features, indicating that an observational identification of diamonds not will be straight forward. The effect on the atmospheric structure is however substantial, and nano-diamonds could play an important role in the grain nucleation process.

We have presented here the computed spectrum as it would look like if the diamonds form in carbon stars (under the simplified assumptions described above). Our measured monochromatic absorption coefficient (which is available from the authors) can likewise be used by other authors, doing models of other objects, for predicting the spectrum from such objects.

Beside carbon stars, the other possible candidates for the diamond formation includes novae (Clayton et al. 1995), carbon rich Wolf-Rayet stars (Tielens 1990; Arnould et al. 1993), and young expanding supernova remnants with dust originating from the deeper layers of the star (Clayton 1989; Clayton et al. 1995).

Until now, the observational searches for presolar diamond grains have focused on the interstellar medium. One of the most encouraging results is the present identification by Allamandola et al. (1992) of an absorption band in four dense molecular clouds (proto stars) at $3.47\,\mu m$ ($2882\,\mathrm{cm}^{-1}$), which they attributed to a tertiary C–H stretching mode, and tentatively interpreted as due to hydrogenate nano-diamonds. We notice that this absorption band is in the exact right region to be a mix of the two absorption features we observe at $2927\,\mathrm{cm}^{-1}$ and $2856\,\mathrm{cm}^{-1}$, present in our infrared spectrum of the presolar diamonds. Other searches for diamonds in interstellar space have, however, mainly reached negative results (Sandford et al. 1991 and references therein), and for this there might be at least three reasons; one is that the presence of functional groups attached to the surface of the grains will alter the absorption features. The second reason is that the nano-diamonds might be included in other dust grains, if they work as the nucleation seed, the third reason is that the stellar grains are likely to be covered with ices while in interstellar space. The possible interstellar diamond spectrum is therefore expected to be quite different (or absent if the grain mantle or ice cover is sufficiently thick) from the obtained laboratory spectrum.

Diamonds is the major known presolar component in meteorites, but their origin is still a puzzle. We have presented here data, and preliminary analysis based on these data, which might make it possible to identify their place of origin. An observational identification of the stellar source of the presolar grains would lead to improved understanding of the upper layers of stellar atmospheres, grain formation, the mass loss process, and of the detailed chemical evolution of our Galaxy.

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