

*Letter to the Editor***Diamonds in carbon-rich proto-planetary nebulae**H.G.M. Hill<sup>1,2,\*</sup>, A.P. Jones<sup>2</sup>, and L.B. d'Hendecourt<sup>2</sup><sup>1</sup> Muséum National d'Histoire Naturelle, 61 Rue Buffon, F-75005 Paris, France<sup>2</sup> Institut d'Astrophysique Spatiale (CNRS), Université Paris XI - Bâtiment 121, F-91405 Orsay Cedex, France

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**Abstract.** We present the results of a mid-infrared laboratory study of meteoritic nanodiamonds, a natural 'nitro-gen-rich' terrestrial diamond, and a 'nitrogen-poor' diamond before and after irradiation with fast neutrons. Characteristic one-phonon modes, absent in the perfect diamond structure, are evident in the 'nitrogen-rich' and neutron-irradiated diamonds that we analysed. One feature common to these bulk materials occurs at  $\sim 21 \mu\text{m}$ . The precise origin of this feature is unknown, although it may arise from molecular-type vibrations associated with lattice defects created by nitrogen impurities or neutron irradiation. We suggest that interstellar nanodiamonds also possess this feature and that they are the carrier of the unidentified  $\sim 21 \mu\text{m}$  infrared emission feature observed in the dust shells around some carbon-rich proto-planetary nebulae.

**Key words:** Stars: AGB and post-AGB, carbon, circumstellar matter – Interstellar Medium: dust, emission, extinction – Interstellar Medium: general

**1. Introduction**

The  $21 \mu\text{m}$  emission feature seen in the spectra of some carbon-rich proto-planetary nebulae (PPNe) was first observed by Kwok, Volk & Hrivnak (1989). Various materials have been proposed as the carrier of this feature, including; carbon-bearing molecules such as HNC, CNO<sup>-</sup> and NCO (Kwok, Volk & Hrivnak 1989), large PAH clusters/HAC grains (Buss et al. 1990), the iron oxides magnetite, Fe<sub>3</sub>O<sub>4</sub>, or maghemite,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> (Cox 1990), carbamides (Sourisseau, Coddens & Papoular 1992), SiS<sub>2</sub> (Goebel 1993), PAHs (Justtanont et al. 1996), diamond-like materials (Koike et al. 1995), and nanodiamonds (Hill et al. 1997a,b). The particular characteristics of the carbon-rich, PPNe environments that show  $21 \mu\text{m}$  emission feature have been described in detail by Kwok (1993), and indicate that its most likely origin, and that of the associated features, is a refractory carbon-bearing grain.

Nanodiamonds with median radii of 1.3–1.5 nm (Daulton et al. 1996) are present in primitive meteorites in abundances of up to  $\sim 1400$  ppm (Huss & Lewis 1995). These grains contain

an anomalous Xe isotopic component (Xe-HL) considered to be characteristic of the nucleosynthetic processes in supernovae (Lewis et al. 1987). Also, the <sup>15</sup>N depletion and the low C/N ratio in these grains is consistent with carbon-rich stellar environments (Alexander 1997). Clearly, the isotopic composition of nanodiamonds is compatible with their formation in multiple astrophysical environments. However, no persuasive observational evidence for nanodiamonds in an astrophysical setting exists. The presence of a tertiary carbon (C—H) stretching mode at  $3.47 \mu\text{m}$  ( $2885 \text{ cm}^{-1}$ ) was linked to nanodiamonds by Allamandola et al. (1992) but could have other origins (Brooke, Sellgren & Smith 1996).

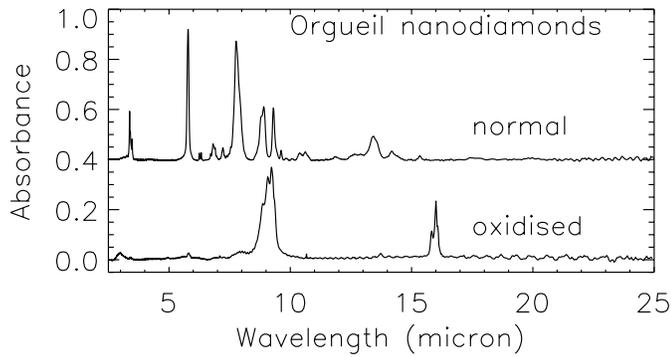
**2. Infrared spectroscopy of diamonds**

We have analysed nanodiamonds extracted from the Orgueil (CI1) meteorite (Hill et al. 1997b) in order to search for intrinsic diamond features that could lead to their unambiguous detection in astronomical objects. In common with other research in this field (e.g. Lewis et al. 1987; Mutschke et al. 1996) we found that our IR nanodiamond spectra contain many features, such as those at: 3.4–3.5, 5.8, 6.9, 7.8, 8.9, 9.3 and  $13.4 \mu\text{m}$  (Fig. 1). These are attributable to adsorbed species introduced during laboratory extraction (Hill et al. 1997b).

Nanodiamonds have a large surface area to volume ratio, an active surface chemistry, and all intrinsic IR nanodiamond features are extremely weak. We have therefore undertaken analyses on a bulk terrestrial diamond sample rich in nitrogen (type IaA), and also on a diamond poor in nitrogen (type IIa) that was irradiated with fast neutrons to introduce lattice defects. The spectrum of a type IaA diamond cube of  $\sim 3 \text{ mm}$  dimensions is presented in Fig. 2a. This type of diamond contains nitrogen as an impurity at  $\sim 0.1\%$  atomic concentration which is present as pairs of atoms ('A' aggregates) characterised by distinctive one-phonon bands at wavelengths  $> 7.3 \mu\text{m}$  (Davies 1977).

It is well established that irradiation by energetic particles can introduce defects into the lattice structure of diamonds (Smith & Hardy, 1960) and that the induced absorption features can closely resemble those due to nitro-gen-related impurities (Morelli, Perry & Farmer 1993) suggesting that a defect centre is the source of both. We therefore undertook an irradiation ex-

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**Fig. 1.** Mid-IR spectra of nanodiamond residues extracted from the Orgueil meteorite. The ‘oxidised’ sample received prolonged oxidation, with respect to the ‘normal’ sample, resulting in the suppression of most features; we attribute the remaining broad band centred at  $9\ \mu\text{m}$  to surface-bonded ether and carbonyl species and the  $16\ \mu\text{m}$  feature to the presence of chlorine from acid used in the extraction process. All spectra were recorded at room temperature with a Bruker IFS 66V Fourier transform infrared spectrometer.

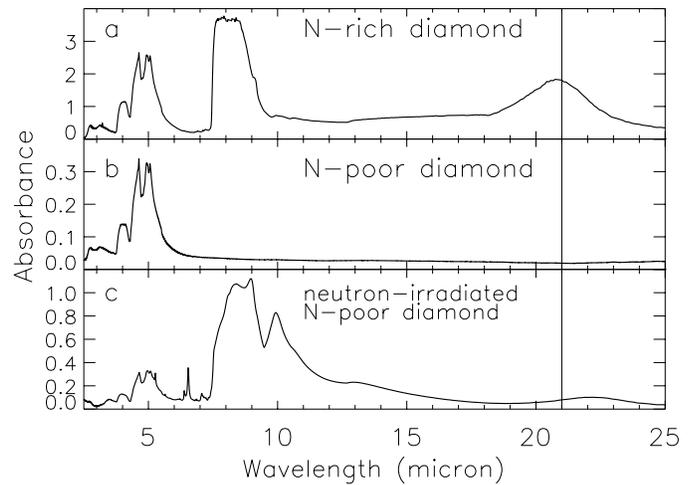
periment in order to introduce defects into a natural diamond poor in nitrogen. The spectra of a type IIa circular diamond window (radius 3 mm and thickness 0.5 mm), were recorded before and after the irradiation (Figs. 2b and 2c).

The IR spectrum of the nitrogen-poor type IIa diamond (Fig. 2b) is modified following neutron irradiation (Fig. 2c) and new features appear at  $8.3$ ,  $9.0$ ,  $10.0$  and  $22.0\ \mu\text{m}$  in the one-phonon region. These features are similar to those seen in the nitrogen-rich diamond spectrum (Fig. 2a). Like nitrogen impurities, irradiation-induced point defects in bulk diamond modify the lattice structure of perfect diamond and hence the translational symmetry and electric dipole selection rules (Smith & Hardy 1960). This permits normally ‘forbidden’ (one-phonon) IR modes to become active (Morelli, Perry & Farmer 1993). It is also possible that molecular-type vibrations in this wavelength region may be activated at lattice defect sites. This appears to be the first time that a  $\sim 21\ \mu\text{m}$  absorption band has been reported in both natural and irradiated diamonds.

Clearly, nanodiamond particles will have properties somewhat different from bulk diamond. However, in view of the dearth of published work on the optical properties of diamonds with radii of the order of one nanometre, defective bulk diamonds provide a useful model for the spectroscopic properties of nanodiamonds. We suggest that ‘imperfect’ interstellar nanodiamonds should exhibit bands in the one-phonon region due to: i) their tiny dimensions, ii) the likely presence of substituted nitrogen, and iii) defects such as vacancies and interstitial atoms incorporated during the growth process or subsequent irradiation.

### 3. Astrophysical implications

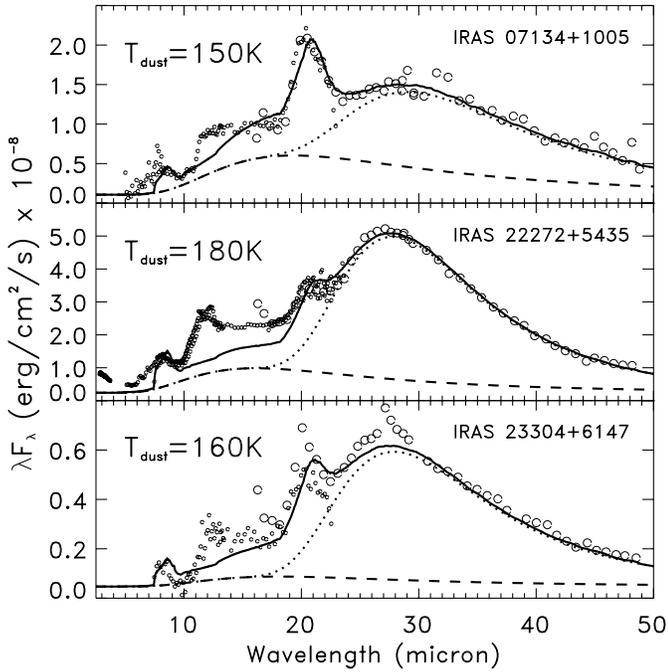
The  $21\ \mu\text{m}$  emission feature is only seen in particular circumstellar environments (carbon-rich PPNe), which suggests that the carrier is excited only under restricted physical conditions or is a transient species. The energy distributions of these objects



**Fig. 2a–c.** The mid-IR spectra of bulk diamonds: type IaA (‘nitrogen-rich’) diamond **a**, type IIa (‘nitrogen-free’) diamond before **b** and after neutron irradiation **c**. Note that the type IaA diamond spectrum **a** is saturated in the  $\sim 7.5\text{--}8.5\ \mu\text{m}$  region. The spectrum of the type IIa diamond **b** shows only the ‘perfect’ diamond two and three phonon modes. Following irradiation new features appear at  $\sim 8.3$ ,  $9.0$ ,  $10.0$  and  $22.0\ \mu\text{m}$ , which are similar to those in the ‘nitrogen-rich’ diamond **a**. The vertical line marks the  $21\ \mu\text{m}$  wavelength position. The irradiation was carried out at the OSIRIS facility at CEA Saclay (fast neutron fluence =  $3.1 \times 10^{18}\ \text{cm}^{-2}$ ).

show double-peaked IR emission with similar amounts of energy in the photospheric and circumstellar components (Kwok, Volk & Hrivnak 1989), consistent with detached dust shells with temperatures of order  $T \sim 200\ \text{K}$  (Hrivnak & Kwok 1991).

We have calculated the emission spectra for type IaA nitrogen-rich nanodiamonds by multiplying the absorbance given in Fig. 2a by a Planck function at the temperature  $T_{dust}$ . We have also included a dust continuum at the same temperature ( $T_{dust}$ ) and a gaussian profile for the  $30\ \mu\text{m}$  band which has been attributed to MgS (Goebel & Moseley 1985). Three calculated dust emission spectra are shown in Fig. 3 along with the observational data (Omont et al. 1995 and references therein). The width and position of the nanodiamond  $21\ \mu\text{m}$  emission band is in good agreement with the observed bands in these PPNe. Note that significant emission from the  $5$  to  $8\ \mu\text{m}$  diamond features (Fig. 2) will only occur for  $T_{dust} > 300\ \text{K}$ , i.e. temperatures greater than those typical of PPNe dust shells ( $150\text{--}300\ \text{K}$ , Kwok 1993). We note that some of the emission observed in the  $11\text{--}15\ \mu\text{m}$  region (Fig. 3) could also be due to nanodiamonds where part of the surfaces may have relaxed to  $\text{sp}^2$  carbon configurations (Blake et al. 1988). Clearly, other grain components such as MgS, PAHs and hydrogenated amorphous carbons must be present in these dust shells in order to explain all of the observed dust emission features. This implies that in carbon-rich PPNe nanodiamonds, PAHs, hydrogenated amorphous carbon and MgS grains are probably formed contemporaneously. An understanding of this co-formation scenario awaits a detailed grain nucleation model.



**Fig. 3.** A comparison of the IR spectra of three PPNe (data points, Omont et al. 1995 and references therein) with the calculated emission spectra of our type IaA diamond (solid line) superimposed on a dust continuum (dashed line) and a gaussian profile for the 30  $\mu\text{m}$  feature (dotted line), see text for details. Note in particular the excellent agreement of the width of the  $\sim 21 \mu\text{m}$  emission band in these spectra, the band at 8  $\mu\text{m}$  and a contribution to the continuum between 10  $\mu\text{m}$  and 20  $\mu\text{m}$ .

It is well-known that diamond materials absorb strongly only in the ultraviolet region at wavelengths  $< 300 \text{ nm}$  (Davies 1977). The central stars in these three PPNe have spectral types F5–G5 and therefore only emit weakly in the UV region. In order to estimate the ‘mean’ size of the nanodiamonds in these objects we need only consider the absorption of photons with wavelengths  $< 300 \text{ nm}$  (4–5 eV), *i.e.* where diamond absorbs strongly. Assuming average emission temperatures of 150–180 K (Fig. 3) and the bulk diamond heat capacity (Lide 1992), we estimate radii of 1–2 nm, with  $\sim 10^3 - 5 \times 10^3$  carbon atoms per particle. The derived nanodiamond dimensions are in excellent agreement with those of meteoritic nanodiamonds which have median radii of 1.3–1.5 nm (Daulton et al. 1996). To derive these sizes we treated the nanodiamonds as transiently-heated particles following the formalism of Léger & d’Hendecourt (1987). This mechanism is identical to the one developed by Désert, Boulanger & Puget (1990) to account for the mid-IR emission in the diffuse ISM from the so-called very small grains (VSGs). On this basis, we propose that nanodiamonds are a reasonable contender for the VSG IR emission component in the ISM.

Two of the PPNe which we consider (Fig. 3) have been observed and modelled by Meixner et al. (1997); IRAS 07134+1005 and IRAS 22272+5435. Using their data we can determine the column mass in the dust shells, *i.e.*,  $(\text{Nm})_{\text{dust}} =$

$(M_{\text{shell}} R_{\text{dg}})/(\pi r^2)$ , where  $M_{\text{shell}}$  is the mass of the dust shell,  $R_{\text{dg}}$  is the dust to gas mass ratio and  $r$  is the source size. Using the observed and derived parameters ( $M_{\text{shell}}$ ,  $R_{\text{dg}}$  and  $r$ ) from Meixner et al. we find that for both of these sources  $(\text{Nm})_{\text{dust}} \sim 2 \times 10^{-4} \text{ g cm}^{-2}$ . From the observations presented by Omont et al. (1995) we have calculated that the energy in the 21  $\mu\text{m}$  emission feature in these sources,  $E_{21}$ , is  $\sim 10^{-9} \text{ erg s}^{-1} \text{ cm}^{-2}$ . Then, using the measured mass absorption coefficients for meteoritic nanodiamonds in the UV,  $\kappa_{\lambda}$  (Mutschke et al. 1996), we calculate the mass of diamonds in these sources that absorb the energy  $E_{21}$  in the UV by solving the following equation for the diamond mass;

$$E_{21} = \int_{\lambda_0}^{\lambda_{\infty}} 4\pi B_{\lambda}(T_{\text{eff}})(1 - e^{-\tau_{\lambda, \text{D}}})\Omega_{*} \left( \frac{\Omega_{\text{shell}}}{4\pi} \right) d\lambda, \quad (1)$$

where  $4\pi B_{\lambda}(T_{\text{eff}})$  is the emission from the central star,  $\Omega_{*}$  is the solid angle subtended by the star at the dust shell where the radiation is absorbed,  $\Omega_{\text{shell}}$  is the solid angle subtended by the observed dust shell emission at  $\sim 12 \mu\text{m}$  (Meixner et al. 1997),  $\tau_{\lambda, \text{D}} = F_{\text{D}} \times (\text{Nm})_{\text{dust}} \times \kappa_{\lambda}$ , and  $F_{\text{D}}$  is the fraction of the total dust mass in the AGB shell in nanodiamonds. In this calculation we have made the reasonable assumption that all of the UV energy absorbed by the nanodiamonds is re-emitted in the 21  $\mu\text{m}$  feature at  $T_{\text{dust}}$ , and since  $T_{\text{dust}} \leq 200 \text{ K}$  this precludes significant emission at wavelengths shorter than 21  $\mu\text{m}$  (Fig. 3). Using Eq. (1) we estimate that nanodiamonds constitute  $\sim 13\%$  and  $\sim 3\%$  of the dust mass in IRAS 07134+1005 and IRAS 22272+5435, respectively. The major source of error in the diamond mass determination is the factor of two uncertainty in the distances to these sources (Meixner et al. 1997), but this does not affect our derived diamond mass fractions.

To date the 21  $\mu\text{m}$  emission feature has not been seen in the dust shells around AGB stars, the PPNe precursor phase. The non-observation of this feature in AGB dust shells could be related to the nucleation/formation of nanodiamonds only in the PPNe phase. This scenario will need theoretical investigation. The 21  $\mu\text{m}$  emission feature has not been reported in the diffuse ISM. This may simply be due to a lack of observational data at these wavelengths. In this respect ISO may yield some information, although the Short Wavelength Spectrometer (SWS) instrument may lack sensitivity in this spectral region. A search for this feature in carefully selected SWS fields is therefore warranted.

Finally, nanodiamonds should exhibit active surface chemistry in the ISM, resulting in the formation of IR active species such as CH, CH<sub>2</sub>, CO, NH, *etc.* However, bands due to these species generally occur at wavelengths  $< 10 \mu\text{m}$  and will therefore not show up in emission in the spectra of PPNe where nanodiamond temperatures are of the order of 150–180 K.

#### 4. Conclusions

Our spectra of nanodiamonds contain many IR features which originate from non-specific adsorbates. We therefore conclude that the use of these data is without value in the search for nanodiamonds in the spectra of astronomical objects. We strongly

emphasise that the spectral features observed in ‘laboratory’ nanodiamonds primarily reflect their last chemical treatment. Intrinsic diamond features will be weak at best and should only show up in emission in circumstellar, and interstellar regions, if at all. Nevertheless, as we show, the analysis of bulk diamonds, especially ‘defective’ ones, provides a useful tool in the prediction of the intrinsic spectroscopic properties of nanodiamonds.

The IR properties of bulk diamonds are sensitive to lattice defects such as those arising from nitrogen impurities, vacancies and disorder, and we note that they consistently display a feature at  $\sim 21 \mu\text{m}$  in the samples that we have analysed. This feature reproduces the shape and the width of the emission feature observed in some carbon-rich PPNe. We postulate that nanodiamonds possess a similar feature. This idea is strongly supported by our diamond irradiation experiment in which nanometre-sized defects are introduced into the lattice by fast neutron irradiation.

We tentatively estimate that 3–13% of the total dust mass in PPNe may be in the form of nanodiamonds in the cases of the IRAS sources 07134+1005 and 22272+5435. Since we predict that the  $21 \mu\text{m}$  feature is a characteristic of nanodiamonds, we suggest that a search for this feature using ISO data would be very timely, especially in the diffuse ISM.

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