Diamonds in space: a brief history and recent laboratory studies

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Abstract. Stardust grains exist in outer space. However, due to their low abundance, structural heterogeneities, and lack of distinct spectroscopic features, unambiguous identification of their chemical composition has been a challenge. Diamond is a notable exception because it is composed of carbon and has several unique physicochemical properties that make the identification possible. Here, we provide a brief review on how diamonds were discovered in space based on the remarkable spectral matching between laboratory spectra and astronomical observations of the infrared emission at 3.43 and 3.53 μm, followed by a discussion of fluorescent nanodiamond as a possible carrier for extended red emission at 600 – 800 nm. Recent evidence to support the latter suggestion is provided.

1. Introduction

Carbon is the fourth most abundant element in the Galaxy. The presence of this element in the form of diamond in space was first proposed by Saslaw and Gaustad [1] in 1969 to account for the observed interstellar extinction curves in the far ultraviolet region of galactic radiation. Little attention was paid to this hypothesis until 1987 when Lewis et al. [2] reported the discovery of small diamond grains (with a mean size of ~3 nm and a concentration up to 400 ppm) in primitive meteorites from outside of the solar system. The search for diamond grains in the interstellar medium was actively pursued in the 1990s [3-6]. Allamandola et al. [3, 4], for example, made one of the first attempts to identify diamond dusts in dense molecular clouds based upon a broad infrared absorption band centered at 2880 cm⁻¹ (3.47 μm), while Hill et al. [5] performed mid-infrared laboratory studies of meteoritic nanodiamonds. However, no satisfactory matches of the spectra were achieved.

An alternative approach of detecting nanodiamonds in space is to examine infrared emission bands from galactic nebulae and circumstellar medium. Among them, the emission from the HD 97048 star deserves special attention. It exhibits two prominent features at 3.43 and 3.53 μm, which are distinctly different than those from other nebulae. In a study of the nature of the emission from HD 97048 and Elias 1, Schutte et al. [7] noticed several anomalies in the observations. First, these two emission bands can be detected only under very special conditions (e.g. close to a hot stellar source). Second, the spatial variation of their intensities is fairly independent of other emission bands in the same frequency region. Third, these two bands always appear together, suggesting that they correlate spatially. An assignment of CVC overtones and the combination bands of highly excited large polycyclic aromatic hydrocarbon (PAH) molecules was proposed for these emission bands [7]. The assignment, however, did not
present a satisfactory interpretation for the origin of these unidentified infrared emission (UIR) bands.

Extended red emission (ERE) is another type of mysterious emission observed in the sky. It has been observed in a wide variety of systems including reflection nebulae, planetary nebulae, HII regions, and the diffuse interstellar medium of our galaxy [8]. ERE was first discovered in 1980 by Schmidt et al. [9] in the spectra of the Red Rectangle nebula. ERE has a wavelength range of 500 − 900 nm and tends to exist in areas with abundant amounts of ultraviolet light, which suggests that it is a product of high-energy photons striking solid materials. No association of ERE with diamond had been made before 2000 except that of Duley [10] who proposed that the sharp emission lines observed at ∼580 nm in the Red Rectangle spectra originate from the electronic transitions of structural defects similar to those found in terrestrial diamonds.

2. Unidentified infrared emission

Working independently, our group initiated a study on infrared spectroscopy and vibrational relaxation dynamics of CH$_x$ (x = 1V3) on diamond nanocrystal and single-crystal surfaces in 1994 [11]. The single-crystal surfaces included H-terminated C(100), C(110), and C(111) (figure 1a). The aim of this project was to elucidate the formation mechanism of diamond by chemical vapor deposition (CVD). We hydrogenated diamond thin films made of 100 nm particles of irregular size and shape (figure 1b) by microwave plasma treatment and then obtained their absorption spectra at 3 − 5 μm with a Fourier transform infrared spectrometer. We observed surprisingly sharp absorption features at 2835 cm$^{-1}$ and 2920 cm$^{-1}$ (figure 1c), which were later confirmed by single crystal experiments to arise from CH stretches on C(111) and C(100) facets [12]. The observation of such distinct and prominent absorption features for the hydrogenated nanodiamonds was attributed to the unique H-etching anisotropy of the diamond substrate [12]. Further studies of the thermal effect on the CH stretching vibrations showed a band redshift of ∼5 cm$^{-1}$ as the sample temperature was raised from 300 K to 1000 K (figure 1d) [13].

**Figure 1.** (a) Structure of a hydrogenated diamond C(111) surface. Grey spheres denote carbon atoms and white circles denote hydrogen atoms. (b) Scanning electron microscopy (SEM) image of diamond nanocrystallites used in the laboratory studies. (c) Laboratory absorption spectra of hydrogenated nanodiamond films prepared in different thickness (1 and 8 μm) and treated at different microwave plasma temperatures (1000 and 1300 K). The spectra were acquired at 300 K. (d) Temperature-dependent shifts of the absorption bands of the CH stretching vibrations on C(100) and C(111) facets of hydrogenated nanodiamonds.

In 1997, Geballe [14] provided a high-quality infrared emission spectrum of Elias 1 in the Taurus dark cloud from a ground-based observation. In this emission spectrum, the feature at
2830 cm\(^{-1}\) (3.53 \(\mu\)m) is much better resolved than before, with a full width at half maximum of only 11 cm\(^{-1}\). Two years later, Guillois et al. [6] pointed out an astonishing match of the sharp UIR bands at 3.43 and 3.53 \(\mu\)m of Elias 1 (and also HD 97048) with the absorption bands of CH stretches on hydrogenated nanodiamond surfaces studied in our laboratories (figure 2). They identified these two peculiar emission bands as the CH stretching modes of H-terminated crystalline facets of diamonds, according to our assignments [11–13]. From the spectral redshift of 5 cm\(^{-1}\), a temperature of 1000 K for these circumstellar nanodiamonds was estimated. Careful energy consideration was also given by this research team to understand the nature of the infrared emission process [6, 15].

One may ask: How can the circumstellar nanodiamonds display such distinct vibrational features? This is ascribable to these diamond grains being situated in close proximity to the star, from which they are exposed to intense UV photon fluxes and thus high temperatures can be reached. Such a high temperature and high H-flux condition is reminiscent of that of microwave plasma used in the diamond CVD synthesis. Conceivably, the temperatures reached in these two cosmic environments are sufficiently high to allow hydrogenation and H-etching of the nanodiamond surfaces to occur. The suggestions are indeed supported by the observations of H recombination lines in both Elias 1 and HD 97048 [16].

Figure 2. Comparison between the infrared emission spectrum of Elias 1 and the laboratory absorption spectrum of hydrogenated nanodiamonds measured at 300 K. Note that the absorption spectrum was redshifted by 5 cm\(^{-1}\) in the comparison.

Figure 2 represents one of the best matches ever obtained between laboratory spectra of solid-state candidates and infrared interstellar features. Taking advantage of the brightness of the emission, Habart et al. [17] and Goto et al. [18] were able to acquire spatially resolved spectra of the 3 \(gm\) bands at HD 97048 and Elias 1, respectively. It should be emphasized that CH stretches are the only distinct spectral features that can be clearly identified with nanodiamonds in the infrared. The corresponding CH bending vibrations could not be found in the 6 – 7 \(\mu\)m range [19] because of the weakness of the absorption and, possibly, severe band broadening resulted from vibrational coupling with diamond surface phonons resonant in the same frequency region. The absence of this spectral feature, in contrast to the prominence of the CH bending of PAH [20], represents another unique characteristic of H-terminated nanodiamonds.

The remarkable matches in the peak positions, bandwidths, and profiles of the two emission features at 3.43 and 3.53 \(\mu\)m in figure 2 verify the existence of diamonds in space. Another useful piece of information provided by the observations is the size of the UIR carriers. The information was deduced based on the finding that the 3.53 \(\mu\)m band coincides with the stretching resonance
of CH monolayer on C(111) single-crystal surface [12]. Additionally, they have similar widths. Therefore, these nanodiamonds cannot be too small in size. Analysis of the infrared absorption spectra of meteoritic (∼3 nm) [21] and synthetic (5 – 700 nm) [22] diamonds showed that the sharp 3.53 μm band can emerge only for particles with a mean size greater than 25 nm.

3. Extended red emission

In 2005, our group launched a new project to study the photoluminescence properties of nanodiamonds. The work was motivated by the findings that diamond can emit bright red photoluminescence from nitrogen-vacancy (NV) defects, which are potentially useful as photostable fluorophores for bioimaging applications [23]. The NV center in diamond is a crystallographic defect consisting of a nitrogen atom and a nearest-neighbour lattice vacancy (figure 3a). It can exist in two different forms: NV⁰ (neutral) and NV⁻ (negatively charged). They both can be synthesized by bombarding synthetic diamond nanocrystallites (containing ∼100 ppm N) with a high-energy (e.g. 3 MeV) proton beam from a particle accelerator, followed by annealing at elevated temperatures (e.g. 1000 K). Photoluminescence occurs as a response to excitation by green light (figure 3b). These two colour centers are characterized by the sharp zero-phone lines (ZPLs) at 575 nm and 638 nm, accompanied by broad phonon sidebands peaking at 610 nm and 680 nm, for NV⁰ and NV⁻ respectively (figure 3c) [24]. Particles subjected to the irradiation and annealing treatment are called fluorescent nanodiamonds (FNDs). The typical concentration of NV centers in FND is 1 – 10 ppm with a photoluminescence quantum yield of 10 – 90% [25].

![Figure 3](image-url)

Figure 3. (a) Structure of a nitrogen-vacancy (NV) center in diamond. Black spheres denote carbon atoms in a unit cell. (b) Bright-field (left) and epifluorescence (right) images of FNDs and their aggregates on a glass slide. Scale bar: 10 gm. (c) Photoluminescence spectra of single NV⁰ and NV⁻ centers in nanodiamonds.

The laboratory studies of the photoluminescence properties of FNDs brought our attention to the ERE of reflection and planetary nebulae. Without much effort, we found a striking resemblance between the astronomical spectrum of the planetary nebula NGC 7027 [26] and the laboratory spectra of FNDs deposited on a glass slide (figure 4a) [27]. The close similarity between these two spectra led us to posit that nanodiamonds are the source of this red emission. The hypothesis had immediate backing: NGC 7027 is rich in carbon [28]. It was also supported by the fact that nitrogen atoms are abundant in the universe and they can be easily incorporated into the diamond lattice during synthesis. As vacancies in diamonds are created in laboratory by high-energy proton irradiation under vacuum, which can similarly occur in space, the FNDs are expected to form in the cosmic environments where ERE is observed.

Next, we compared the photoluminescence spectra of FNDs with the ERE bands of the Red Rectangle nebula, an object emitting ERE with exceptional strength. The high quality of its
spectra allows for a stringent test of the theory that FND is a possible carrier of ERE. A notable feature of the Red Rectangle is that the spectral profile of the ERE varies substantially with distance from the central star HD 44179. The peak wavelengths of the spectra shift from 635 nm at 10" south to 660 nm at 6" south within the same object (figure 4b) [29, 30]. To account for the difference in the spectral profile, we consider that there exist two types of NV centers in FND: NV$^0$ and NVV. Spectra can thus be synthesized with data given in figure 3c for these two centers at different ratios. With the fluorescence intensity ratios of NV$^0$:NVV = 1:0 and 3:2, we can indeed properly reproduce the ERE bands at different offset distances (figure 4b).

Figure 4. (a) Comparison between the observed ERE spectrum of NGC 7027 and the laboratory fluorescence spectrum of FND excited with 510 – 560 nm light. (b) Comparison between the observed ERE spectra of the Red Rectangle at 10 south and 6 south of HD 44179 and the laboratory fluorescence spectra of FNDs with different contents of NV$^0$ andNVV. The fluorescence intensity ratios of NV$^0$:NVV in samples FND1 and FND2 are roughly 3:2 and 1:0, respectively.

4. Conclusion
We have developed two spectroscopic approaches (infrared absorption and visible photoluminescence) to characterize nanodiamonds in laboratories and to assist their identification in space. The first approach is a proven success. However, only 2 star systems (Elias 1 and HD 97048) have been found so far to exhibit clear fingerprints of hydrogenated nanodiamonds in the infrared region. ERE is an appealing alternative to the 3.43- and 3.53-μm emission bands because it has been observed in a wide variety of dusty environments. The Red Rectangle is an ideal testing ground in this context and a proper explanation for the variation in the ERE spectra at different offset distances from the star HD 44179 is still lacking. To understand better this object as well as other ERE features in the galaxies, further studies of the thermal effect on the photoluminescence spectra of NV centers in the diamond grains are needed.

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Huan Cheng Chang giving his talk.
Left: Masatoshi Ohishi  Right: Masaaki Otsuka