ON IRON MONOXIDE NANOPARTICLES AS A CARRIER OF THE MYSTERIOUS 21 μm EMISSION FEATURE IN POST-ASYMPTOTIC GIANT BRANCH STARS

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ABSTRACT

A prominent mysterious emission feature peaking at $\sim 20.1 \mu m$—historically known as the “21 μm” feature—is seen in over two dozen Galactic and Magellanic Cloud carbon-rich, post-asymptotic giant branch (post-AGB) stars. The nature of its carrier remains unknown since the first detection of the 21 μm feature in 1989. Over a dozen materials have been suggested as possible carrier candidates. However, none of them has been accepted: they either require too much material (compared to what is available in the circumstellar shells around these post-AGB stars), or exhibit additional emission features that are not seen in these 21 μm sources. Recently, iron monoxide (FeO) nanoparticles seem to be a promising carrier candidate as Fe is an abundant element and FeO emits exclusively at $\sim 21 \mu m$. In this work, using the proto-type protoplanetary nebula HD 56126 as a test case, we examine FeO nanoparticles as a carrier for the 21 μm feature by modeling their infrared emission, with FeO being stochastically heated by single stellar photons. We find that FeO emits too broad a 21 μm feature to explain that observed and the Fe abundance required to be locked up in FeO exceeds what is available in HD 56126. We therefore conclude that FeO nanoparticles are not likely to be responsible for the 21 μm feature.

Key words: circumstellar matter – dust, extinction – infrared: stars – stars: AGB and post-AGB – stars: individual (HD 56126)

Online-only material: color figures

1. INTRODUCTION

During the late stages of evolution, low- and intermediate-mass (0.8 $M_\odot < M < 8 M_\odot$) stars undergo a rapid transition phase of several thousand years between the asymptotic giant branch (AGB) phase and the planetary nebula (PN) phase. Objects in this short-lived stage of evolution are known as protoplanetary nebulae (PPNe), a term that is often used interchangeably with “post-AGB stars.”

Dust is a general phenomenon of PPNe, as revealed by its thermal infrared (IR) emission continuum and spectral features. In recent years, much attention has been paid to the so-called “21 μm” feature. This prominent, broad mysterious emission feature, with a peak wavelength at $\sim 20.1 \mu m$ and a FWHM of $\sim 2.2 - 2.3 \mu m$, was first detected in four PPNe (Kwok et al. 1989). To date, it has been seen in 18 Galactic objects (Cerrigone et al. 2011) and 9 Magellanic Cloud objects (Volk et al. 2011), all of which are exclusively PPNe. The 21 μm feature exhibits little shape variation among different sources. The 21 μm sources exhibit quite uniform characteristics: they are metal-poor, carbon-rich F and G supergiants with strong IR excess and over abundant s-process elements (see Jiang et al. 2010).

The carrier of the 21 μm feature remains unidentified, although over a dozen candidate materials have been proposed. Zhang et al. (2009a) examined nine inorganic carrier candidates for the 21 μm feature, including nano TiC, fullerenes with Ti, SiS\textsubscript{2}, doped SiC, a silicon and carbon mixture, SiO\textsubscript{2}-coated SiC, and iron oxides (FeO, Fe\textsubscript{2}O\textsubscript{3} and Fe\textsubscript{2}O\textsubscript{4}). They found that with the exception of FeO nanoparticles, they are all problematic: they either require too much dust material (compared to what would be available in the 21 μm sources) or produce additional features that are not seen in the spectra of the 21 μm sources. As originally proposed by Posch et al. (2004), FeO (iron monoxide or wüstite) nanoparticles seem to be a promising candidate carrier for the 21 μm feature for three reasons: (1) Fe is an abundant element; (2) FeO has a pronounced spectral feature around 21 μm; and (3) except the 21 μm feature, FeO does not have any other notable spectral features. Posch et al. (2004) further argued that FeO nanoparticles could form and survive in the C-rich shells around the 21 μm sources (see Section 4.4.2 and Footnotes 7 and 8 of Zhang et al. 2009a; also see Begemann et al. 1995), provided that they are composed of $< 10^9$ atoms and have a size of $a \lesssim 1$ nm. Iron oxides (particularly maghemite γ-Fe\textsubscript{2}O\textsubscript{3} and magnetite Fe\textsubscript{3}O\textsubscript{4}) have also been suggested as a potential dust component in the interstellar medium (Jones 1990; Draine & Hensley 2013).

Posch et al. (2004) fitted the observed 21 μm emission feature with FeO of steady-state temperatures in thermal equilibrium with the stellar radiation field. However, with fewer than $\sim 1000$ atoms, FeO nanoparticles will be stochastically heated by single stellar photons as their heat capacities are smaller than or comparable to the energy of the stellar photons that heat them (see Section 5). Therefore, they will not attain an equilibrium temperature; instead, they will experience transient “temperature spikes” and undergo “temperature fluctuations” (see Draine & Li 2001). The stochastic heating of FeO nanoparticles by individual stellar photons will result in a distribution of temperatures and consequently, the emission spectra are expected to be broader than that from a single equilibrium temperature.

Zhang et al. (2009a) recognized the stochastic heating nature of FeO nanoparticles in PPNe, but they did not model the IR emission spectra of FeO nanoparticles; instead, they focused on the abundance constraint on Fe. They estimated the amount of Fe required to be locked up in FeO to account for the total emitted power of the 21 μm feature by assuming that FeO nanoparticles emit at the peak temperature to which they are heated upon absorption of a typical stellar photon.

With an aim at examining the hypothesis of FeO nanoparticles as a carrier of the 21 μm feature, we model the
vibrational excitation and radiative relaxation of FeO nanoparticles in a proto-typical PPN—HD 56126 (see Section 4)—and then compare their model emission spectra with the observed 21 μm feature. In Section 2, we discuss the optical properties of FeO. Their heat capacities are discussed in Section 3. In Section 4, we carry out calculations for the temperature probability distribution functions and the emergent IR emission spectra of FeO nanoparticles. Section 5 discusses the results and summarizes the major conclusions.

2. OPTICAL PROPERTIES OF FeO

To model the heating and cooling of FeO in PPNs, we must calculate the absorption cross-sections of FeO from the ultraviolet (UV) to the far-IR. This requires knowledge of the optical properties of FeO. The optical properties of FeO vary with temperature $T$ as the density of free charge carriers decreases with $T$. Since FeO nanoparticles will have a distribution of temperatures, we will consider their refractive indices at a range of temperatures.

Henning et al. (1995) measured the refractive indices of FeO at $T = 300$ K in the wavelength range of $\lambda = 0.2$ μm to $\lambda = 500$ μm. Henning & Mutschke (1997) extended the same measurements to $T = 10, 100, and 200$ K, but for a smaller wavelength range of $\lambda = 2$ μm to $\lambda = 500$ μm.

For $T = 300$ K, we adopt the refractive indices of FeO of Henning et al. (1995) from $\lambda = 0.2 $ μm to $\lambda = 500$ μm (see Figure 1). For $T = 10, 100, and 200$ K, the following synthetic approach is taken: for $\lambda = 2$ μm to 500 μm, we adopt the imaginary parts ($m''$) of the FeO refractive indices of Henning & Mutschke (1997) measured at $T = 10, 100, and 200$ K.

3. THERMAL PROPERTIES OF FeO

FeO nanoparticles consist of several hundred atoms: with a mass density of $\rho \approx 5.7$ g cm$^{-3}$, an FeO grain of spherical radius of $a$ has $N_{\text{atom}} \approx 400(a/\text{nm})^3$ atoms. The vibrational degrees of freedom of FeO nano grains, $3(N_{\text{atom}} - 2)$, are so small that a single stellar photon of energy $\hbar \nu$ is capable of appreciably raising their temperatures from $T_i$ to $T_f$: $\int_{T_i}^{T_f} C(T) dT = h \nu$, where $h$ is the Planck constant, $\nu$ is the photon frequency, and $C(T) \propto N_{\text{atom}}$ is the specific heat of FeO. At low temperatures (i.e., $T \ll \Theta_D$, where $\Theta_D$ is the Debye temperature), the specific heat is proportional to $T^3$:

$$C(T) \propto \frac{12\pi^4}{3} N_{\text{atom}} k (T/\Theta_D)^3,$$

where $k$ is the Boltzmann constant. As a prior, it is not clear if the condition of $T \ll \Theta_D$ will always be met for nano FeO in PPNe. Therefore, we shall not adopt this simple formula for $C(T)$; instead, we will adopt a three-dimensional Debye model with $\Theta_D \approx 430$ K which closely reproduces the experimental specific heat of FeO measured by Grønvold et al. (1993) and Stølen et al. (1996):

$$C(T) = 3(N_{\text{atom}} - 2) k f_3(T/\Theta_D),$$

$$f_3(x) = \int_0^1 \frac{3y^2 dy}{\exp(y/x) - 1}, f_3(x) = \frac{d}{dx} f_3(x).$$

In Figure 2, we show the experimental specific heat of FeO measured by Grønvold et al. (1993) for 298 K $< T < 1250$ K and by Stølen et al. (1996) for 10 K $< T < 450$ K. Also shown are the three-dimensional Debye model fit (with $\Theta_D = 430$ K) and the low-temperature approximation of $C(T) \propto (T/\Theta_D)^3$.

4. RESULTS

Let $\kappa_{\text{abs}}(\lambda) = C_{\text{abs}}(a, \lambda)/m(a)$ be the mass absorption coefficient of FeO at wavelength $\lambda$, where $C_{\text{abs}}(a, \lambda)$ is the absorption cross-section of FeO of size $a$ at wavelength $\lambda$, and $m(a)$ is the mass of FeO of size $a$. For FeO nanoparticles in the IR, $\kappa_{\text{abs}}(\lambda)$ is independent of $a$ since they are in the Rayleigh regime (i.e., $a \ll \lambda$). The IR emissivity per unit mass (in units of $\lambda < 2$ μm, we adopt the imaginary parts $m''$ of FeO of Henning et al. (1995) measured at $T = 300$ K, and then smoothly connect the $m''$ data at $\lambda < 2$ μm to that at $\lambda = 2$–500 μm. The Kramers–Kronig relation is then used to derive the real parts ($m'$) of the indices of refraction of FeO at $T = 10, 100, and 200$ K from $\lambda = 0.2$ μm to $\lambda = 500$ μm. Figure 1 shows the resulting refractive indices ($m = m' + im''$) of FeO at $T = 10, 100, 200$, and 300 K.

We note that, ideally, we should obtain the optical constants of FeO over a much wider wavelength range, from X-rays to millimeter wavelengths. However, the lack of experimental $m''$ data at $\lambda < 0.2$ μm and $\lambda > 500$ μm prevents us from achieving a complete set of ($m', m''$) data. Fortunately, for the present study this is not important: the stellar radiation of PPNe mostly peaks at the visible wavelength range, and FeO nanoparticles mostly emit their energy at $\lambda \sim 20$ μm; therefore, the $m = m' + im''$ data spanning the wavelength range of 0.2 μm to $\lambda < 500$ μm are sufficient for the present study.

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erg s$^{-1}$ cm$^{-1}$ g$^{-1}$) from FeO nanoparticles of size $a$ located at a distance of $r$ from the illuminating star is

$$j_{\lambda}(r, a) = \kappa_{\text{abs}}(\lambda) \int_0^\infty dT \ 4\pi B_{\lambda}(T) \ dP(r, a, T)/dT,$$

(3)

where $B_{\lambda}(T)$ is the Planck function of temperature $T$ at wavelength $\lambda$, $dP(r, a, T)$ is the probability that the temperature of a FeO nanoparticle of size $a$ at a distance of $r$ from the illuminating star will be in $[T, T + dT]$. The total IR emissivity per unit mass from FeO nanoparticles of size $a$ is obtained by integrating over the entire dust shell

$$j_{\lambda}^{\text{tot}}(a) = \int_{r_{\text{min}}}^{r_{\text{max}}} dr \ j_{\lambda}(r, a) \ 4\pi r^2 \ dn(r)/dr,$$

(4)

$r_{\text{min}}$ and $r_{\text{max}}$ are, respectively, the inner and outer edge of the dust shell, and $dn(r)/dr$ is the FeO dust spatial distribution. The power output per unit mass in the 21 $\mu$m band is calculated by integrating $\Delta j_{\lambda}^{\text{tot}}(a)$ over the entire band, where $\Delta j_{\lambda}^{\text{tot}}(a)$ is the continuum-subtracted $j_{\lambda}^{\text{tot}}(a)$

$$P_{21\mu m}(a) = \int_{21\mu m \text{ band}} \Delta j_{\lambda}^{\text{tot}}(a) \ d\lambda.$$

(5)

The FeO mass $M(\text{FeO})$ required to account for the observed 21 $\mu$m emission is

$$M(\text{FeO}) = E_{21\mu m}^{\text{obs}} / P_{21\mu m}(a),$$

(6)

where $E_{21\mu m}^{\text{obs}}$ (in unit of erg s$^{-1}$) is the total power emitted from the 21 $\mu$m feature. Let $M_{\text{H}}$ be the total H mass in the shell. The Fe abundance (relative to H) required to be locked up in FeO is

$$[\text{Fe}/\text{H}]_{\text{FeO}} = M(\text{FeO}) / [\mu_{\text{FeO}} M_{\text{H}}],$$

(7)

where $\mu_{\text{FeO}} = 72$ is the molecular weight of FeO.
We take HD 56126, a proto-typical 21 μm source, as a test case. HD 56126 (≡ IRAS 07134 + 1005), a bright post-AGB star with a spectral type of F0-5I and a visual magnitude of ∼8.3, is one of the four 21 μm sources originally discovered by Kwok et al. (1989). Mid-IR imaging of this object at 11.9 μm shows that its circumstellar dust is confined to an area of 1′.2–2′.6 from the star (Hony et al. 2003). Detailed modeling of its dust IR spectral energy distribution suggested a distribution function—confined to an area of 1′.2–2′.6 from the star, (Hony et al. 2003). The necessity to model the stochastic excitation of FeO nanoparticles. Draine et al. (2001) to treat the stochastic heating of FeO nanoparticles. The necessity to model the stochastic excitation of FeO nanoparticles in the dust shell around HD 56126 will be justified in Section 5. For FeO dust of given size a at a given distance of r from the star, P(r, a, T)—the temperature probability distribution function—is calculated from the “thermal-discrete” method. We first consider spherical dust and use the Mie distribution function—is calculated from the “thermal-discrete” method developed by Draine et al. (2001) to treat the stochastic heating of FeO nanoparticles. We also note that for a ∼1 μm, P(r, a, T) roughly peaks at T ∼ 100 K (although the distribution function P is still appreciably broad for a < 3 nm), implying that the absorbed photon energy of FeO will be mostly radiated away at T ∼ 100 K. This justifies the choice of the (m′, m″) data of FeO at T ∼ 100 K.

Figure 3 shows the temperature probability distribution functions P(r, a, T) for spherical FeO of radius a = 1 μm at a distance of 1′.20, 1′.46, 1′.77, 2′.14, and 2′.60 from the star. The P(r, a, T) distribution functions are broad, confirming that nano FeO undergoes temperature excursions in PPNe (otherwise P(r, a, T) should be strongly peaked and approximated by a delta function). At a larger distance from the star, P(r, a, T) becomes broader because of the reduced starlight intensity which leads to a smaller photon absorption rate and therefore enhances the single-photon heating effect. We also note that for a ≥ 1 nm, P(r, a, T) roughly peaks at T ∼ 100 K (although the distribution function P is still appreciably broad for a < 3 nm), implying that the absorbed photon energy of FeO will be mostly radiated away at T ∼ 100 K. This justifies the choice of the (m′, m″) data of FeO at T ∼ 100 K. Figure 3 also shows the IR emissivity per unit mass j_λ(r, a) of spherical FeO of radius a = 1 nm at 1′.20 and 2′.60, as well as that integrated over the entire shell j_λ^tot(a). It is apparent that the model feature, with a FWHM of 21 μm, is too broad to explain the 21 μm feature of HD 56126, which has a FWHM of ∼2.2 μm (see Footnote 1 of Zhang et al. 2009a). For illustration, in Figure 4, we compare the model spectrum of FeO of a = 10 Å with the 21 μm emission spectra observed in four C-rich PPNe (Volk et al. 1999): IRAS 04296 + 3429, IRAS 22272 + 5425, IRAS 23304 + 6147, and IRAS 07134 + 1005 (i.e., HD 56126), with each spectrum normalized to its peak value. Figure 4, in linear abscissa and ordinate, clearly shows that the FeO model results in too broad a 21 μm feature to explain the observed one, while observationally, the 21 μm feature in all sources has a FWHM of 21 μm.
of FeO of a functions and the IR emission spectra for FeO nanoparticles narrowly peaked at its “equilibrium” temperature of $21 \mu m$ results are obtained for spherical grains. For nonspherical grains, FWHM ($\gamma$ see Figure 5), implying that the single-photon heating effect becomes more pronounced for the $a = 1 nm$ FeO, its photon absorption rate is also just one-fourth of that of the $a = 1 nm$ FeO, and therefore, the single-photon heating effect becomes more pronounced for the $a = 5 Å$ FeO. In contrast, the $a = 2 nm$ FeO, with a heat capacity eight times that of the $a = 1 nm$ FeO, the $P(r, a, T)$ distribution function is more narrowly peaked at its “equilibrium” temperature of $T = 120 K$ (see Figure 5), implying that the single-photon heating effect becomes less significant for larger FeO dust. The criterion for single-photon heating will be discussed in detail in Section 5.

The model $21 \mu m$ feature from the $a = 5 Å$ FeO, with a FWHM $\gamma = 3.6 μm$, is also too broad compared to that of the observed feature. To account for the $21 \mu m$ emission feature observed in HD 56126, the $a = 5 Å$ FeO requires $M(FeO) = 2.78 \times 10^{29} g$ and $[Fe/H]_{FeO} = 9.70 \times 10^{-6}$. For the $a = 2 nm$ FeO, the corresponding numbers are $21 \mu m \approx 3.7 μm$, $M(FeO) \approx 2.54 \times 10^{29} g$, and $[Fe/H]_{FeO} \approx 8.87 \times 10^{-6}$.

5. DISCUSSION

We have seen in Section 4 that FeO nanoparticles emit strongly at $21 \mu m$. However, the model $21 \mu m$ feature (with a FWHM of $\gamma = 3.6–3.7 μm$) is much broader than the observed feature (with a FWHM of $\sim 2.2 μm$). The Fe abundance required to be locked up in FeO ($[Fe/H]_{FeO}$) exceeds the available abundance $[Fe/H]_{s}$ by a factor of $\sim 2.6–3$. These results are obtained for spherical grains. For nonspherical grains, the model $21 \mu m$ feature would be even broader. We have calculated the IR emission spectra for FeO nanoparticles with a distribution of spheroidal shapes with $dP/dL_{∥} = 12L_{∥}^{1-(1-L_{∥})^{2}}$.

Figure 6. Upper panel: the temperature probability distribution functions of (1) spherical FeO (red) and (2) spheroidal FeO with a distribution of shapes (black) of radius $a = 1 nm$ in HD 56126 at $1.20$ from the star. Lower panel: the IR emissivity per unit mass of (1) spherical FeO (red) and (2) spheroidal FeO with a distribution of shapes (black) of radius $a = 1 nm$ at $1.20$ from the star. Also shown is the observed $21 \mu m$ emission feature of HD 56126 (blue dashed line; Volk et al. 1999) which is scaled to that of spherical FeO. The $21 \mu m$ feature arising from the spherical $a = 1 nm$ FeO (with a FWHM of $21 \mu m \approx 3.5 μm$) is much narrower than that of spheroidal FeO with a distribution of shapes (for which the FWHM is $21 \mu m \approx 5.6 μm$).

(Ossenkopf et al. 1992), where $0 < L_{∥} < 1$ is the so-called “depolarization factor” parallel to the grain symmetry axis (for spheres $L_{∥}=1/3$); this shape distribution peaks at spheres and drops to zero for the extreme cases $L_{∥} → 0$ (infinitely thin needles) or $L_{∥} → 1$ (infinitely flattened pancake). As shown in Figure 6, the model $21 \mu m$ emission feature arising from FeO nanoparticles with such a distribution of spheroidal shapes is much broader than that of spherical FeO.

In calculating the absorption cross-sections of FeO, we use the optical constants of $T = 100 K$. As shown in Figure 9 of Posch et al. (2004), the absorption profile of the $21 \mu m$ band broadens if one adopts the optical constants of $T = 200, 300 K$, while it essentially remains unchanged from $T = 100 K$ to $T = 10 K$. Although small, $P(r, a, T)$ is positive at $T > 200 K$ for $a < 1 nm$ (see Figures 3 and 5). Therefore, if we adopt the $(m', m)$ data of $T > 200 K$ for FeO warmer than 200 K, we would expect a broader $21 \mu m$ emission feature. Nevertheless, we note that the $21 \mu m$ feature of nano FeO calculated in this work is based on the dielectric functions of bulk FeO material (see Section 2). It is not clear how the dielectric functions near the $21 \mu m$ resonance wavelength range will be affected when FeO becomes nano-sized.

For a small metallic grain, the imaginary part of its dielectric function is expected to be larger compared to that of its bulk counterpart, as a consequence of the so-called electron mean free path limitation effect (see Section 6 in Li 2004). For FeO, which is a semiconductor (Seagle et al. 2009; Schrettle et al. 2012), the number density of free charge carriers is lower than

$E_{FeO}^{abs} \approx 1.0 \times 10^{36} erg^{-1}$ for the $21 \mu m$ emission feature of HD 56126 (Hony et al. 2003) and $M_{a} \approx 0.20 M_{⊙}$ for the circumstellar envelope of HD 56126 (Zhang et al. 2009b), we calculate a total FeO mass of $M(FeO) \approx 2.38 \times 10^{29} g$ which is required to account for the $21 \mu m$ emission feature. The Fe abundance required to be locked up in FeO is $[Fe/H]_{FeO} \approx 8.31 \times 10^{-6}$, exceeding what is available in HD 56126 ($[Fe/H] \approx 3.24 \times 10^{-6}$; van Winckel & Reyniers 2000) by a factor of $\sim 2.6$.

Similarly, we have calculated the $P(r, a, T)$ distribution functions and the IR emission spectra for FeO nanoparticles of $a = 5 Å$ and $a = 2 nm$ (see Figure 5). Compared to that of FeO of $a = 1 nm$, the $P(r, a, T)$ distribution function for $a = 5 Å$ is much broader and is appreciably large even at $T > 300 K$. This is because for the $a = 5 Å$ FeO (with only $\sim 50$ atoms), its heat capacity is only one-eighth of that of the $a = 1 nm$ FeO and therefore it can be heated to a much higher temperature by the same stellar photon. On the other hand, with a cross-section only one-fourth of that of the $a = 1 nm$ FeO, the single-photon heating effect becomes more pronounced for the $a = 5 Å$ FeO. In contrast, the $a = 2 nm$ FeO, with a heat capacity eight times that of the $a = 1 nm$ FeO, the $P(r, a, T)$ distribution function is more narrowly peaked at its “equilibrium” temperature of $T = 120 K$ (see Figure 5), implying that the single-photon heating effect becomes less significant for larger FeO dust. The criterion for single-photon heating will be discussed in detail in Section 5.

The model $21 \mu m$ feature from the $a = 5 Å$ FeO, with a FWHM $\gamma \approx 3.6 μm$, is also too broad compared to that of the observed feature. To account for the $21 \mu m$ emission feature observed in HD 56126, the $a = 5 Å$ FeO requires $M(FeO) \approx 2.78 \times 10^{29} g$ and $[Fe/H]_{FeO} \approx 9.70 \times 10^{-6}$. For the $a = 2 nm$ FeO, the corresponding numbers are $21 \mu m \approx 3.7 μm$, $M(FeO) \approx 2.54 \times 10^{29} g$, and $[Fe/H]_{FeO} \approx 8.87 \times 10^{-6}$.

$^6$ The mass of the circumstellar envelope of HD 56126 is not precisely known. Hony et al. (2003) derived a circumstellar envelope mass of $M_{a} \approx 0.16–0.44 M_{⊙}$, depending on the assumed gas-to-dust ratio ($\sim 220–600$). Meixner et al. (2004) derived a much smaller mass of $M_{a} = 0.059 M_{⊙}$ based on the CO $J = 1–0$ line emission images. Zhang et al. (2009b) derived $M_{a} \approx 0.20 M_{⊙}$, a value which is intermediate between the estimation of $M_{a} = 0.16–0.44 M_{⊙}$ of Hony et al. (2003). We therefore adopt $M_{a} \approx 0.20 M_{⊙}$.

$^7$ Zhang et al. (2009a) derived $[Fe/H]_{FeO} \approx 5.76 \times 10^{-7}$ by assuming that FeO emits at the peak temperature which it reaches upon absorption of a typical stellar photon. They adopted a Debye temperature of $\Theta_{D} \approx 850 K$ which is higher than $\Theta_{D} \approx 430 K$ derived here by a factor of $\sim 1.9$. For a given stellar photon, this would overestimate the FeO temperature by a factor of $\sim 1.5^{1/3} \approx 1.36$ and therefore underestimate the required FeO mass by a factor of $\sim 1.36^{1/3} \approx 6.2$. 
that of metals by several orders of magnitude (see Henning & Mutschke 1997). Therefore, the small size effect on the dielectric function caused by the limitation of the electron mean free path is expected to be less significant for FeO than for metals.

We also note that the thermal properties of nano FeO may differ from that of bulk material (see Section 3). The specific heats of some small metal particles are reported to be strongly enhanced over their bulk values (see Section 6 in Li 2004). It is not clear how the Debye temperature \( \Theta_D \) of nano FeO would compare to that of bulk FeO. If nano FeO is like palladium (with \( \Theta_D \approx 273 \) K for bulk palladium and \( \Theta_D \approx 175 \) K for nano palladium of \( a = 1.5 \) nm), the stochastic heating effect will be less substantial. However, we also note that the specific heats of nano silicon crystals and nanocrystalline diamonds do not differ much from their bulk values (see Section 6 in Li 2004).

Finally, we note that ideally we should have justified why, in the first place, it is necessary to consider the stochastic heating of nano FeO. It is now well recognized that a grain undergoes stochastic heating by single stellar photons if (1) its heat content is smaller than or comparable to the energy of a single stellar photon (Greenberg 1968), and (2) the photon absorption rate is smaller than the radiative cooling rate (Draine & Li 2001). The photon absorption timescale—the mean time \( \tau_{abs} \) between photon absorptions—for a nano FeO of size \( a \) is given by

\[
\tau_{abs}^{-1} \equiv \int_0^\infty C_{abs}(a, \lambda) \frac{1}{h \nu} d\lambda. \tag{8}
\]

where \( \nu \) is the frequency of light, \( h \) is the Planck constant, and \( \frac{1}{h \nu} \) is the starlight energy density. The mean photon energy \( \langle h \nu \rangle_{abs} \) absorbed by the FeO dust of size \( a \) is

\[
\langle h \nu \rangle_{abs} \equiv \tau_{abs} \int_0^\infty C_{abs}(a, \lambda) \frac{1}{h \nu} d\lambda. \tag{9}
\]

The radiative cooling time for a FeO grain of size \( a \) containing a vibrational energy of \( \langle h \nu \rangle_{abs} \) is

\[
\tau_{cooling} \approx \frac{\langle h \nu \rangle_{abs}}{\int_0^{\lambda_{min}} C_{abs}(a, \lambda) 4\pi B_{\lambda}(T) d\lambda}, \tag{10}
\]

where \( \lambda_{min} \equiv h c / \langle h \nu \rangle_{abs} \) and \( T_p \) is determined by its heat content \( E(T_p) = \int_0^{T_p} C(T) dT = \langle h \nu \rangle_{abs} \).

For nano FeO of \( a < 30 \) nm in the dust shell around HD 56126, the mean absorbed photon energy is \( \langle h \nu \rangle_{abs} \approx 4.45 \) eV, independent of dust size \( a \). This is because in the UV/visible wavelength range nano FeO is in the Rayleigh regime and its absorption properties are independent of size \( a \). In Figure 7(a) we show \( \tau_{abs} \) and \( \tau_{cooling} \) of FeO dust in the HD 56126 dust shell, at a distance of \( r = 1.77 \) from the central star which is intermediate between the inner boundary and the outer boundary of the shell. It is apparent that \( \tau_{abs} \propto a^{-2} \) rapidly
attain an equilibrium temperature of $T_{\text{ss}}$, which would be attained by FeO dust of $a \approx 1 \mu m$. FeO dust this small will have $\tau_{\text{abs}} \propto T_{\text{ss}}$ at $T_{\text{ss}} \approx 10^6 K$, the temperature probability distribution function $dP/dT$ is like a delta function, implying that it will attain an equilibrium temperature of $T_{\text{ss}} \approx 10^6 K$. According to Posch et al. (2004), the size of the FeO dust which could form and survive in the C-rich shells around the $21 \mu m$ sources should not exceed $\sim 1 \mu m$. FeO dust this small will have $\tau_{\text{abs}} \gg \tau_{\text{cooling}}$ (see Figure 7(a)), and $E(T_{\text{ss}}) \propto \langle h\nu \rangle_{\text{abs}}$ at $T_{\text{ss}} \approx 10^6 K$ (see Figure 7(b)), and therefore will be stochastically heated by single stellar photons. To summarize, we have examined the hypothesis of FeO nanoparticles as a carrier of the mysterious $21 \mu m$ emission feature seen in C-rich PPNe. The temperature probability distribution functions and the resulting IR emission spectra have been calculated for these stochastically heated nano-sized grains. We find that they emit too broad a $21 \mu m$ feature to explain the observed one and the Fe abundance required to be locked up in FeO exceeds what is available. This, combined with the special conditions required for the formation of FeO nanoparticles in C-rich environments (see Section 3.3 of Posch et al. 2004; Duley 1980), leads us to conclude that probably FeO nanoparticles are not responsible for the $21 \mu m$ feature.

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