The Astrophysical Journal Letters, 776:L2 (4pp), 2013 October 10 doi:10.1088/2041-8205/776/1/L2

A SEARCH FOR NEAR INFRARED BANDS OF THE FULLERENE CATION C_{60}^{+} IN THE PROTOPLANETARY NEBULA IRAS 01005+7910

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Received 2013 June 22; accepted 2013 September 1; published 2013 September 23

ABSTRACT

IRAS 01005+7910 is a carbon-rich protoplanetary nebula with a recently reported detection of mid-IR vibrational transitions of the fullerene C_{60} by Zhang and Kwok. We present new high spectral resolution ($R \sim 57{,}000$) observations of this object obtained at the 3.6 m Telescopio Nazionale Galileo, showing the presence of two absorption bands at 9577 and 9632 Å which are consistent with laboratory measurements of the C_{60}^{+} cation. If these two bands were produced by C_{60}^{+} in the material surrounding the central post-asymptotic giant branch star, we estimate that ~1% of carbon could be trapped in this ionized form of fullerenes which would be more abundant than the neutral species in this protoplanetary nebulae. The central star with an effective temperature of $T \geqslant 20{,}000$ K can provide the ionizing photons required. These observations bring further evidence for the presence of fullerenes in protoplanetary nebulae and suggest that a significant production takes place in this late stage of stellar evolution. Mid-IR bands of C_{60}^{+} could be present in the 7–20 μm spectrum of IRAS 01005+7910 and are also likely to be detected in the spectra of planetary nebulae. High-resolution spectroscopy will be required for a reliable determination of the excitation temperatures and the relative abundance of neutral and ionized fullerenes in these objects.

Key words: ISM: lines and bands – ISM: molecules – planetary nebulae: general – stars: abundances – stars: AGB and post-AGB

1. INTRODUCTION

Fullerenes, the third allotropic form of carbon, have been postulated as carriers for diffuse interstellar bands (DIBs; Kroto et al. 1985), mid-infrared emission features in the spectra of planetary nebulae and reflection nebulae (Cami et al. 2010; Sellgren et al. 2010), the UV bump (2175 Å) in extinction curves, and for the anomalous microwave (10–60 GHz) emission in star forming regions and molecular clouds (Iglesias-Groth 2004, 2005). Among the fullerene family, C_{60} is one of the most stable and best characterized molecules in the laboratory. Extensive astronomical searches (e.g., Snow & Seab 1989; Foing & Ehrenfreund 1994; Herbig 1995) eventually led to the C_{60} detection in the planetary nebula Tc1 (Cami et al. 2010) and subsequently in other planetary nebulae (e.g., García-Hernández et al. 2011).

The presence of the fullerene C_{60} in the carbon-rich protoplanetary nebula (PPN) IRAS 01005+7910 has recently been revealed in the analysis of the *Spitzer*/IRS mid-IR spectrum of this object by Zhang & Kwok (2011). The mid-IR bands of this molecule could arise in the cold envelope surrounding the central star of the nebula. This star is classified as spectral type B2 Ie (Hu 2001). Given the low ionization potential of C_{60} (7.61 eV) and the high effective atmospheric temperature of the central star ($T \geqslant 20{,}000$ K; Klochkova et al. 2002) a significant fraction of the C_{60} could be ionized in the surrounding envelope. Indeed, if we take ionization models for polycyclic aromatic hydrocarbons (PAHs) for reference (Bakes & Tielens 1995; Salama et al. 1996), as the ionization potential for C_{60} and 60 atom PAHs are similar, we expect that cationic species are rather abundant in matter near a hot star. Such cationic species would reemit energy absorbed from the nearby star through its four IR modes. Two of these modes have been measured in the laboratory by Fulara et al. (1993) at 7.11 and 7.51 μm, but they are not resolved in the current *Spitzer* data from the 7.0 and 8.45 μm bands of the neutral C_{60} and from other PAH bands populating the region.

Laboratory spectroscopy of the $C_{60}{}^{+}$ in a neon matrix shows the presence of two electronic bands in the far red optical spectrum at 9583 and 9645 Å (Fulara et al. 1993), which, taking into account the wavelength shift induced by matrix polarisability, could be associated with the bands detected at 9577 and 9632 Å in several diffuse clouds of the interstellar medium (Foing & Ehrenfreund 1994, 1997). The differential shift in wavelength (~0.7%) between these two bands is not unexpected as there is laboratory evidence of such differential wavelength shifts for the near infrared bands of C_{60}, as a function of the matrix gas and of the temperature of the matrix (see Table 1 of Iglesias-Groth et al. 2011). Here we present high-resolution spectroscopy of the central star of the PPN IRAS 01005+7910, which reveals the presence of these two absorption bands. We argue that $C_{60}{}^{+}$ is present in the circumstellar material surrounding the central star of this PPN and provide an estimate of the abundance of this cation and of the ionization fraction of C_{60} fullerenes in the stellar envelope.

2. OBSERVATIONS AND DATA REDUCTION

High-resolution spectra of the central star in the PPN IRAS 01005+7910 were obtained with SARG (Gratton et al. 2001) at the 3.6 m Telescopio Nazionale Galileo (Roque de los Muchachos Observatory, La Palma) in 2011 November. Five spectra were obtained in two consecutive nights at a spectral resolving power of 57,000. The exposure time of each individual spectrum was 1800 s. Hot, fast rotating comparison stars were observed with the same instrument setup on the same nights for the correction of telluric lines. All the spectra were bias-corrected, flat fielded, and corrected for the interorder background signal. The spectral orders were extracted using optimal algorithms and then wavelength calibrated using lines of a ThAr lamp

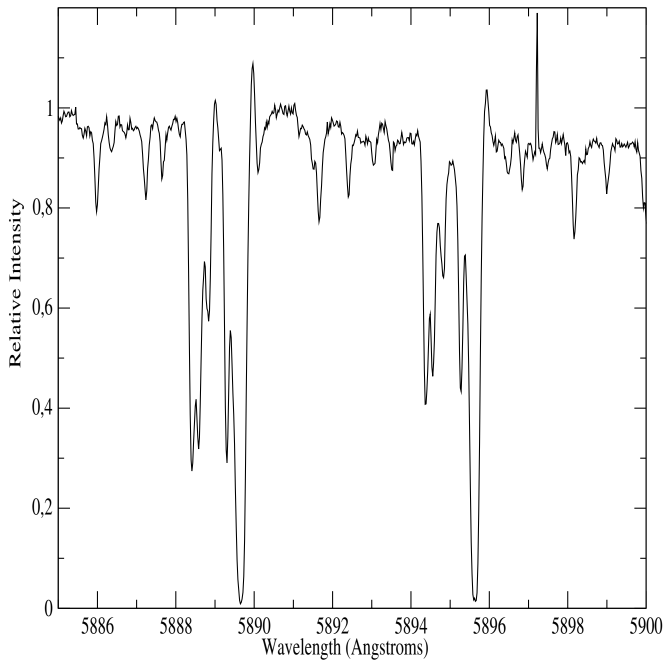

Figure 1. Various components of the Na I doublet.

Table 1
Measurements of the Five Observed Components of Na I and the Two Potential Bands of the C_{60} Cation

λ (Å)	W (mÅ)	FWHM (mÅ)	V_r (km s^{-1}) ($V_r{}^a$)
5889.951	125	0.16	−73.0 (−72^a)
	85	0.15	−63.5 (−66^a)
	62	0.14	−51.1 (−52^a)
	107	0.14	−27.8 (−28^a)
	330	0.31	−8.8 (−11^a)
5895.924	95	0.15	−73.6 (−73^a)
	50	0.14	−63.4 (−65^a)
	55	0.14	−60.1 (−52^a)
	95	0.14	−27.8 (−28^a)
	290	0.30	−8.8 (−10^a)
9577	260 ± 50	2.3 ± 0.3	$-10. \geqslant V_r \geqslant -23$
9632	320 ± 60	2.0 ± 0.3	$-1 \geqslant V_r \geqslant -25$

Note. The superscript "a" corresponds to measurements made by Klochkova et al. (2002).

registered before and/or after the observations of the target. Each of the five individual spectra was corrected for the intense telluric line contamination in the region around 9600 Å and for possible instrumental effects dividing by the spectrum of a brighter, fast rotating star observed in a nearby line of sight. After this correction, individual spectra were checked for potential wavelength shifts and finally combined using a median filter. The final spectrum covered from 5600 to 10000 Å with signal-to-noise ratio per pixel ranged from ∼300 around 6000 Å to ∼30 in the region around 9600 Å. The spectrum of IRAS 01005+7910 reveals numerous photospheric features in emission as well as in absorption corresponding to N II, O II, Al III, Si III, and Si II. The Na I resonance D_{12} lines show five absorption components at our spectral resolution (Figure 1 and Table 1). A previous high spectral resolution study by Klochkova et al. (2002) reports equivalent widths and velocities for these components. The spectral coverage of our new high-resolution spectrum overlaps with the one obtained by these authors in the range 5600–7800 Å. Our spectrum extends farther in the red up to approximately 10000 Å, which allowed us to study the presence of the DIBs at 9577 and 9632 Å.

3. RESULTS AND DISCUSSION

We confirm that the high-resolution optical spectrum of IRAS 01005+7910 is consistent with that of a high-luminosity early-B type star surrounded by a gaseous envelope (as concluded by Klochkova et al. 2002). The most prominent emission line in our spectrum is Hα with equivalent width $W_\lambda = 10.5$ Å. We also detect emission lines of He I at λλ 5876 and 7065 Å showing both emission and absorption components while the He I 6678 Å line ($W_\lambda = 260$ mÅ) is found in absorption with two dominant components at a heliocentric velocity V_r of −37 and −55 km s^{-1}. Weaker emission lines from Si II at 5978.93 and 6371.37 Å are found with equivalent widths of 130 and 50 mÅ and V_r of −40 and −45 km s^{-1}, respectively. These lines are also reported by Klochkova et al. (2002) with similar strengths and velocities. We report here the detection of emission lines of [S II] at 6717 ($W_\lambda = 17$ mÅ, $V_r = -49$ km s^{-1}) and 6731 Å ($W_\lambda = 31$ mÅ, $V_r = -49$ km s^{-1}). The ratio of these lines suggests electron densities higher than 1000 cm^{-3}. The [N II] λλ 6584 and 6548 Å lines are detected in emission with equivalent widths of 130 and 40 mÅ, and V_r of −58 and −54 km s^{-1}, respectively. For single component lines, the typical uncertainty in velocity is less than 1 km s^{-1}. Typical errors in equivalent widths are of the order of 10% and could be as low as 5% for well behaved single component lines. We also measure many absorption lines of elements with various degrees of ionization (O I, C II, Ne I, N II, O II, Si II, Al III, Fe III). Equivalent widths and heliocentric velocities for these lines will be published elsewhere. In general, we find good agreement with previous observations by Klochkova et al. (2002), although comparison with their results reveals changes in strength and velocity of a large number of lines with time which are consistent with the claimed presence of both the accretion and outflow processes in the object.

The resonance lines of Na I $D_{1,2}$ present a complex structure (see Figure 1) in velocity with at least five components observed at heliocentric velocities of −10, −28, −52, −63, and −73 km s^{-1}, respectively. These velocities are determined with an uncertainty less than 1 km s^{-1}. All Na I components, except the strongest one, show FWHMs in the range 0.14–0.16 Å. This first and strongest absorption component has a broader profile (FWHM = 0.3 Å) which appears to be the result of various unresolved components spanning a velocity range between −15 and −3 km s^{-1}. Radio observations of the CO emission and measurements of Na I lines for stars in nearby lines of sight show a velocity for the interstellar medium in the range −8 to +10 km s^{-1}. We propose that the strongest Na I component is in fact a combination of absorption partly originating in the slowest and optically thin part of the envelope of IRAS 01005+7910 at a velocity of −13 ± 2 km s^{-1} and partly in interstellar medium clouds that would span a velocity range −8 to −5 km s^{-1}. It is difficult to estimate which fraction corresponds to each.

The next Na I component in the spectrum at −28 km s^{-1} is located very close to the systemic velocity proposed by Klochkova et al. (−23 km s^{-1}) and it likely arises in some layers of the envelope of the PPN. We argue that the claimed systemic velocity is rather uncertain as the used convergence method requires very high precision measurements for very weak lines. Uncertainties in the velocities of such weak lines prevent a precise determination of the systemic velocity. The

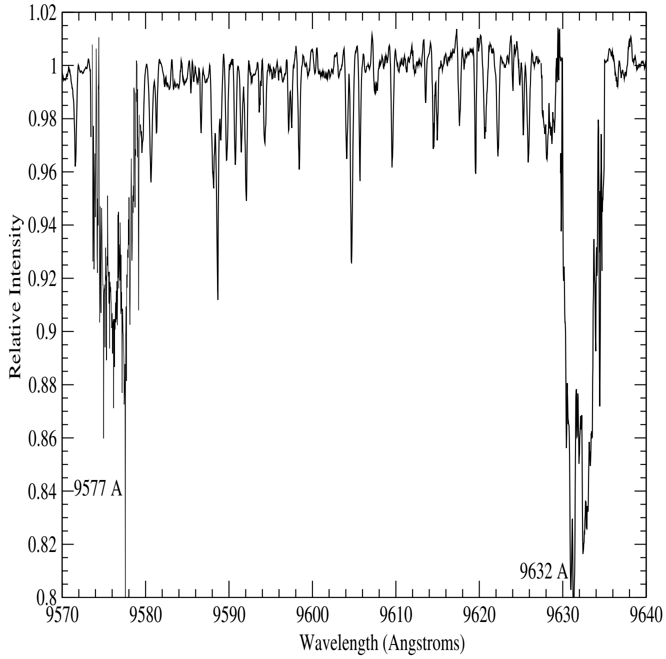

Figure 2. Two near IR bands in the spectrum of IRAS 01005+7910, attributed to the cation of C_{60}, corrected for telluric lines. In the core of the 9632 Å band we see structure potentially produced by residual contamination of a stellar Mg II line.

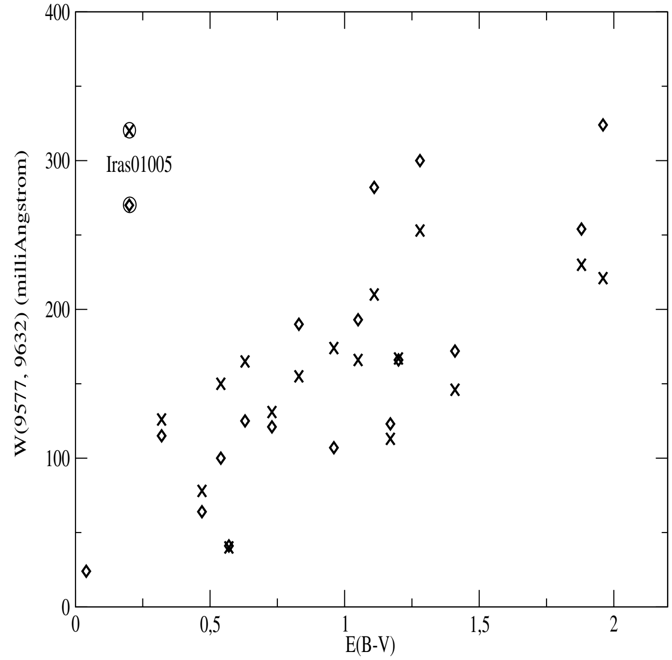

Figure 3. Measurements of the equivalent widths of the 9577 and 9632 Å bands as a function of extinction for various lines of sight of the ISM (data from Galazutdinov et al. 2000; Jenniskens et al. 1997: diamonds and crosses are for the 9577 and 9632 bands, respectively) and for IRAS 01005+7910 (encircled diamond and cross; This work). Typical 1σ errors are in the range 10%–30% of the measured equivalent widths.

remaining higher-velocity components of the Na I D lines are possibly formed in the circumstellar envelope ejected during the asymptotic giant branch (AGB) phase.

Our spectrum of IRAS 01005+7910 contain several DIBs. Among the most intense are the following: 5780 Å (W_λ = 100 mÅ, $V_r = -14$ km s^{-1}), 5797 Å (W_λ = 47 mÅ, V_r = -17 km s^{-1}), and 6613 Å (W_λ = 69 mÅ, $V_r = -6$ km s^{-1}). Compared with the typical strengths reported by Jenniskens et al. (1997) in several lines of sight, these DIBs appear to be rather weak and consistent with $E(B-V)$ 0.2 and $A_V = 0.6$. Jenniskens & Desert (1994) noted that DIBs are significantly fainter in dense molecular clouds with strong UV irradiation, therefore a higher extinction cannot in principle be ruled out for our star. The band at 5780 Å is known to be more resistant to strong UV fields than the 5797 DIB. The ratio of the bands 5780/5797 in the envelope of the PPN compares well with the ratios found in ζ type clouds discussed by Krelowski et al. (1995) and may suggest not very different physical conditions. Based on the average ratio between the equivalent width of the Na D lines and the 5780 Å band (see, e.g., Table 2 of Jenniskens & Desert 1994) in various lines of sight of the interstellar medium, we expect equivalent widths for this band about 20% larger than the equivalent width of the Na D lines. We instead observe a value 70% smaller. This suggests that the carrier of the 5780 Å band is severely affected by the UV radiation of the central star in this PPN and that material at $V_r = -14$ km s^{-1} (where the observed DIB appear) may have been ejected and remain relatively close to the object. However, given the velocities of the observed bands, it is also possible that they originate in an intervening interstellar medium (ISM) cloud unrelated to IRAS 01005+7910.

In spite of an imperfect correction of the prominent telluric lines, the inspection of the spectral region around 9600 Å revealed the presence of two broad absorption bands at approximately 9577 and 9632 Å (see Figure 2). The wavelengths and separations appear consistent with those measured in the diffuse interstellar medium by Foing & Ehrenfreund (1994), Jenniskens et al. (1997), and Galazutdinov et al. (2000). We measure a wavelength difference between these two bands at 55 ± 3 Å, FWHMs of ~2.2 ± 0.3 Å and determine heliocentric velocities in the range −10 to −25 km s−1. This large uncertainty is due to the difficulty of determining the center of the bands, and to the structure in the core of the second band which may be due to a residual Mg II 9631.89 Å stellar line. The equivalent widths resulted $W_\lambda = 270 \pm 40$ mÅ and $W_\lambda = 320 \pm 60$ mÅ for the 9577 and 9632 Å bands, respectively. The measured ratio compares well with measurements by Foing & Ehrenfreund (1997) and Galazutdinov et al. (2000) in lines of sight of the interstellar medium. The extreme UV stability of the 9577 and 9632 carrier molecule is very remarkable, as noted by Foing and Ehrenfreund. We plot in Figure 3 the equivalent widths of the bands 9577/9632 measured in various lines of sight of the ISM as a function of extinction $E(B-V)$. The point corresponding to the PPN IRAS 01005+7910 largely deviates from the general trend outlined by the ISM observations. This is strongly against these bands emerging in the general ISM, in an intervening cloud unrelated to the star. On the contrary, it supports that the carrier of these bands is located in the surrounding envelope of the central star. The ratio of the equivalent widths of the bands at 9577/9632 and the 5780/5797/6613 DIBs is also much higher in IRAS 01005+7910 than in typical clouds of the ISM.

Assuming that the 9577 and 9632 Å bands originate in the circumstellar envelope and that the carrier is indeed C_{60}^+, and adopting a log gf = 0.006 (Fulara et al. 1993), we infer from the band strengths an abundance of the cation N(C_{60}^+) = 0.5 × 10^{14} cm^{-2}. From the $E(B-V)$ we estimate N(H) ~ 1 × 10^{21} cm^{-2} and therefore n(C_{60}^+)/n (H) = 0.5 × 10^{-7}, which is equivalent to 0.05 ppm, a value very similar to the meteoritic fullerene abundance and to the value inferred by Iglesias-Groth (2004) for the abundance of the fullerene C_{60} in the ISM if these molecules were responsible of the UV bump in the extinction curves. Assuming the solar carbon abundance of C/H = 2.5 × 10 $^{-4}$, we obtain a fraction of 1.2% ± 0.4% of carbon is locked in the form of C_{60}^{+} in the envelope of the PPN.

The absorption of UV photons by C_{60}^{+} will also cause IR emission due to the vibrational decay of the molecule. Four active IR modes at 7.1, 7.5, 17.3, and 18.9 μm are expected (Fulara et al. 1993). Zhang & Kwok (2011) studied the *Spitzer* mid-IR(7–20 μm) spectrum of IRAS 01005+7910 and claimed detection of several active modes of C_{60} with fluxes of the various bands in the range 1–3 × 10^{-15} W m^{-2}, but they do not explicitly identify potential bands from the cation. Their decomposed mid-IR spectrum (see their Figure 2) is interpreted as a combination of active IR modes of the neutral fullerene (7.0, 8.5, 17.4, and 18.9 μm) and also several strong bands of PAHs. They found that the 7 μm band provides the largest contribution to the flux emitted by neutral fullerenes. Using the strength ratio of the mid-IR bands of C_{60} to the emission of the aromatic infrared bands, Zhang and Kwok estimated the percentage of carbon locked in C_{60} molecules in IRAS 01005 to be 0.06% ± 0.02% (a similar value was obtained by Sellgren et al. 2010 in the reflexion nebula NGC 7023). We argue that the IR modes of the ionized species of C_{60} can also contribute to the observed mid-IR emission spectrum of the PPN. Since the ionized species could be as abundant as the neutral ones, their potential contribution to the mid-IR spectrum should be taken into account in the fullerene abundance analysis.

In fact, the strong feature at 7.5–7.6 μm resulting in the decomposition made by Zhang and Kwok of the observed broad emission between 7.0 and 8.0 μm in IRAS 01005+7910 may have a relevant contribution from the 7.5 μm band of the cation C_{60}^{+}. It is also possible that there is a band at 7.1 μm contributing to the observed flux rise in the spectrum. The bands at 17.3 and 18.9 μm attributed to C_{60} could also be contributed by the modes of the ionized species. To the best of our knowledge, the molar absorptivity of the mid-IR bands of the fullerene cation and its dependence with temperature are not known. It is therefore not possible to make an accurate prediction of what will be the strength of these lines. It is likely that these lines are formed in regions with higher excitation temperature than 460 K as determined by Zhang and Kwok for the excitation of neutral C_{60}.

We may speculate that the if the molar absorptivity of the cation bands in the mid-IR follow the temperature behavior of the C_{60} band (Iglesias-Groth et al. 2011) at higher temperatures we may expect an increasing relevant role of the 7.5 μm band with respect to 7.1 μm. It is extremely important to extend the molar absorptivity measurements to C_{60}^{+} in a wide range of temperatures as these molecules may in fact be the dominant fullerene species in objects like protoplanetary and planetary nebulae where the central star is a strong source of ionizing photons. In this respect we note the presence of a weak feature at 7.5 μm in the spectrum of Tc 1 (see, e.g., Figure 1 of Zhang & Kwok 2011) which could be associated to C_{60}^{+}. Abundance estimates of fullerenes and excitation temperatures in planetary nebulae and reflection nebulae may require to consider the contribution of the cation bands to the observed features at 7.0, 17.3 and 18.9 μm.

4. CONCLUSIONS

We recorded the spectrum of the PPN IRAS01005+7910 between 5500 and 10,000 Å with resolving power of 57,000. Two broad bands are detected at 9577 and 9632 Å which are consistent in strength and wavelength with laboratory gas phase transitions of C_{60}^{+}. We argue that these bands and other DIBs identified in the spectrum originate in the slowest optically thin part of the protoplanetary envelope. From their strength, we infer that ∼1% of carbon in the envelope is in the form of ionized C_{60} and that the cation abundance is much higher than that of the neutral fullerene species. It appears that ionized fullerene species in this PPN are significantly more abundant than in neutral form, which is consistent with the predictions of ionization models of PAHs (Bakes & Tielens 1995; Salama et al. 1996) for irradiated clouds near a hot star.

We propose that the mid-IR bands of the cation could be present in the *Spitzer*/IRS spectrum analyzed by Zhang & Kwok (2011). In particular, the 7.5 μm band of C_{60}^{+} could contribute significantly to the prominent band detected between 7.3–7.6 μm. Other cation bands at 7.1, 17.3, and 18.9 μm could also be present in this spectrum but are not resolved from the mid-IR bands of the neutral molecule which have very similar wavelengths. This set of mid-IR bands is frequently used nowadays to determine the abundance of C_{60} in planetary nebulae and reflection nebulae. We caution that the derived abundances and excitation temperatures may have to be revised if indeed there is a significant contribution of cations to the formation of these bands. Accounting for the ionized species of fullerenes appears necessary in nebulae where there is a nearby source of ionizing photons. This may also rise the estimated values for the fullerene abundance in planetary nebulae. Laboratory measurements of the molar absorptivity of the C_{60}^{+} would be very valuable.

Our results reinforce the evidence for fullerene C_{60} in the PPN IRAS 01005+79 and suggest that fullerene abundances in the post-AGB phase can reach values similar to those found in meteorites. Given the large outflows of material in this phase of stellar evolution and the resistant nature of fullerenes, the late stage evolution of intermediate mass stars appears a potential major source of fullerene production in the Galaxy.

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