DETECTION OF C\textsubscript{60} IN THE PROTOPLANETARY NEBULA IRAS 01005+7910

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**ABSTRACT**

We report the first detection of buckminsterfullerene (C\textsubscript{60}) in a protoplanetary nebula. The vibrational transitions of C\textsubscript{60} at 7.0, 17.4, and 18.9 \textmu m are detected in the Spitzer/Infrared Spectrograph spectrum of IRAS 01005+7910. This detection suggests that fullerenes are formed shortly after the asymptotic giant branch but before the planetary nebulae stage. A comparison with the observations of C\textsubscript{60} in other sources is made and the implication for circumstellar chemistry is discussed.

**Key words:** infrared: stars – stars: AGB and post-AGB – stars: circumstellar matter

**Online-only material:** color figures

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1. INTRODUCTION

Fullerenes, together with other forms of carbon such as graphite, diamonds, and carbynes, are expected to be the important components of the interstellar medium (Henning & Salama 1998). The most stable fullerene is buckminsterfullerene (C\textsubscript{60}) which has a soccer-ball-like structure (Kroto et al. 1985). Fullerenes have been proposed as possible carriers of diffuse interstellar bands (e.g., Kroto et al. 1985; Léger et al. 1988), the origin of which is a long-standing mystery (see Herbig 1995, for a review). Foing & Ehrenfreund (1994) found that the laboratory spectrum of C\textsubscript{60} in argon and neon matrices shows approximate matches with two diffuse interstellar bands in the near-infrared spectra of stars. Possible formation processes of fullerenes in space that have previously been discussed include condensation in supernova gas, shock-induced decomposition of hydrogenated amorphous carbon (HAC) grains, cold interstellar gas-phase chemistry, etc. (See Moutou et al. 1999; Sellgren et al. 2010, and references therein.) The carbon-rich, hydrogen-poor circumstellar envelopes, such as Wolf–Rayet (WR) stars and R Coronae Borealis (RCB) stars, have also been proposed as favorable sites for the synthesis of fullerenes (Cherchneff et al. 2000; Goeres et al. 1992). However, none of these theoretical predictions have been confirmed observationally.

The search for fullerenes in space started soon after their laboratory discovery (Cherchneff et al. 1995). Kwok et al. (1999) noted a faint feature at 17.85 and 18.90 \textmu m in the ISO-SWS spectrum of IRAS 01005+7910. Unlike the other sources in our sample, IRAS 01005+7910 does not show the 21 \textmu m feature and its central star has a higher temperature (~21,500 K), suggesting the central star has a higher temperature (~21,500 K), suggesting...
that it is a PPN about to enter the PN stage (Zhang et al.
2010). Hu (2002) classified it as a B2 Ie star with
magnitude of 10.85. Its hydrogen Balmer lines show P Cygni profiles.
Through a study of the high-resolution spectrum, Klochkova
et al. (2002) concluded that it is a carbon-rich PPN with a
luminosity log(L/L⊙) = 3.6 at a distance about 3 kpc.

2. DATA

The study makes use of the infrared spectra retrieved from
the Spitzer Heritage Archive (SHA).1 The observations were
conducted with the Infrared Spectrograph (IRS; Houck
et al. 2004) on the Spitzer Space Telescope (Spitzer; Werner
et al. 2004) in 2004 and 2006. We have carried out a systematic
search for C60 in the 10 PPNs studied by Zhang et al. (2010)
and found that among the studied sample IRAS 01005+7910
is unique in clearly exhibiting the C60 features. The spectra
of IRAS 01005+7910 were obtained with the short-wavelength
low-resolution module (SL; 5–14.5 μm) as part of the program
30036 (PI: G. Fazio), and the short-wavelength high-resolution
module (SH; 9.5–19.5 μm) as part of the program 93 (PI: D.
Cruikshank). Details of the data processing have been
described elsewhere (e.g., Hrivnak et al. 2009; Cerrigone
et al. 2009) and are not repeated here. However, no ob-
ervation utilizing long-wavelength high-resolution module
(LH; 18.7–37.2 μm) was made for IRAS 01005+7910.

3. RESULTS

Figure 1 shows that the Spitzer/IRS spectrum of
IRAS 01005+7910 is dominated by a thermal dust continuum,
the 11.5 μm SiC emission, the AIBs at 6.2, 7.7–7.9, 8.6, 11.3,
and 12.7 μm, and the 15–20 μm plateau feature. The AIB and
the broad plateau emission features have been previously de-
tected and discussed by Cerrigone et al. (2009) and Zhang et al.
(2010). In this paper, we report the detection of the C60 features
at 7.04 ± 0.05, 17.4 ± 0.05, and 18.9 ± 0.04 μm. The fourth
expected C60 feature at the 8.5 μm feature is badly blended with
the AIB 8.6 μm feature. These C60 features have a width of
0.31 ± 0.05 μm, much broader than the spectral resolution. The measured widths of the C60 features are similar to those seen
in other PNs (see Table 1, García-Hernández et al. 2010). These
C60 features are not found in any other PPNs in our sample. This
suggests that these features likely share a common origin, and
thus strengthens the identification of C60 as their carrier.

The continuum was fitted, using the feature-free spectral
regions, and was subtracted from the observed spectrum. As
the features in PPN spectra are usually broad and blended with
each other, we conducted a spectral decomposition using the
IDL package PAHFIT developed by Smith et al. (2007) in order
to accurately measure the feature fluxes. Drude profiles are
assumed for the AIBs and C60 features. The actual profile of
the 15–20 μm plateau, where C60 17.4 and 18.9 μm features are
superimposed, is poorly known. We have assumed two broad
Gaussian profiles having a width of 1.3 μm and peaked at
16.1 and 17.5 μm for the plateau. (This causes only slight
uncertainty in the flux measurements since the C60 features
are much narrower than the plateau.) For the fitting, we have
taken into account the AIBs at 6.2, 6.4, 6.6, 6.8, 7.4, 7.6,
7.9, 8.3, 8.6, and 16.5 μm. Figures 2 and 3 give the zoom-
in view of these C60 features and the fitting results. From the
fitting results, we derived fluxes of (3.0 ± 0.3) × 10−15 W m−2,

Figure 1. Spitzer/IRS spectrum of IRAS 01005+7910 compared to the IRS
spectra of two other known C60 sources (NGC 7023 from Sellgren et al. 2010
and Tc 1 from Cami et al. 2010). The vertical dotted lines mark the wavelengths
of the C60 lines at 7.0, 8.5, 17.4, and 18.9 μm. The dashed line represents a
fit to the continuum. The other prominent features at 6.2, 7.7, 8.6, 11.3, and
12.7 μm are AIBs.

(1.2 ± 0.5) × 10−15 W m−2, and (2.9 ± 0.5) × 10−15 W m−2 for
the C60 7.0, 17.4, and 18.9 μm features, respectively. The errors
of the fluxes were estimated using the full covariance matrix of
the least-squares parameters. Sellgren et al. (2010) found that
the C60 17.4 μm transition in the spectrum of NGC 7023
is partially blended with an AIB feature. If this is also the case
for IRAS 01005+7910, the estimated strength of the 17.4 μm
feature would be the upper limit.

Hrivnak et al. (2000) presented the ISO-SWS spectrum of
IRAS 01005+7910 covering a wavelength range of 2.4–
45.4 μm. Due to the lower sensitivity of the ISO-SWS compared
to the IRS, the C60 features are completely overwhelmed
by the noise in the ISO spectrum. However, a strong feature at
30 μm is detected by ISO, and its presence was subsequently
confirmed by the Spitzer/IRS spectrum (Cerrigone et al. 2009;
Zhang et al. 2010). This seems to support the finding by García-
Hernández et al. (2010) that all the C60 sources exhibit the 30 μm

1 http://sha.ipac.caltech.edu/applications/Spitzer/SHA/
feature. However, this correlation only applies to circumstellar sources as the Spitzer archive spectra of the reflection nebulae NGC 2023 and NGC 7023 (program 40276, PI: K. Sellgren) do not show the 30 μm feature. The 30 μm feature is commonly seen in carbon-rich AGB stars, PPNs, and PNs (Forrest et al. 1981; Volk et al. 2002), and has been attributed to solid magnesium sulfide (MgS; Goebel & Moseley 1985). However, the identification of MgS as the carrier of the 30 μm feature is debatable as this feature is only detected in carbon-rich sources. Recently, Zhang et al. (2009) found that the MgS dust mass in circumstellar envelopes is not enough to account for the observed feature strength. Therefore, carbonaceous compounds might be more likely to be the carrier of the 30 μm feature.

In order to establish a connection between the 30 μm feature with the C60 features, more C60 sources need to be discovered.

In Figure 1, we compare the Spitzer/IRS spectra of IRAS 01005+7910 with two other C60 sources, NGC 7023 (Sellgren et al. 2010) and Tc 1 (Cami et al. 2010). All three sources have a strong infrared excess, and IRAS 01005+7910 and Tc 1 have a very red (low color temperature) continuum. IRAS 01005+7910 and NGC 7023 show strong AIB features, which are absent in Tc 1. The fact that IRAS 01005+7910 does not show the narrow atomic lines as seen in the spectrum of Tc 1 is consistent with the object being a PPN and its central star is not hot enough to ionize the surrounding envelope. After subtracting the continuum, we found that the spectral shape of IRAS 01005+7910 is similar to that of NGC 7023. Cami et al. (2010) also detected a few weaker C60 features in Tc 1, which are not seen in IRAS 01005+7910 and NGC 7023. Assuming that all the sources have the same C70/C60 strength ratio, the C70 features in IRAS 01005+7910 should be well below the detection limit.

### 4. DISCUSSION

The relative intensities of the C60 lines reflect the excitation conditions of the molecule. Assuming a thermal distribution of the vibrational states, Cami et al. (2010) determined the excitation temperature of Tc 1 to be ~330 K, and suggested that the C60 molecules are in a solid state. Similar temperature values were also derived in the PNs studied by García-Hernández et al. (2010). Using a similar procedure as Cami et al. (2010) and García-Hernández et al. (2010), we have constructed a vibrational diagram for IRAS 01005+7910 from the observed fluxes of the three C60 lines (Figure 4). An excitation temperature of 460 ± 50 K is derived.

The C60 line ratios in IRAS 01005+7910 are $I_{7.0}/I_{18.9} = 1.0 ± 0.3$ and $I_{17.4}/I_{18.9} = 0.4 ± 0.2$, which are very close to the values found by Sellgren et al. (2010) in NGC 7023 ($I_{7.0}/I_{18.9} = 0.82 ± 0.12$ and $I_{17.4}/I_{18.9} = 0.42 ± 0.02$). Since the central star of IRAS 01005+7910 has a similar temperature as NGC 7023 (~17,000 K), it is possible that the C60 molecules in IRAS 01005+7910 and NGC 7023 are excited in a similar manner. Sellgren et al. (2010) suggest that C60 molecules in
Laboratory measurements show that the wavelengths of gas-phase C₆₀ bands shift with temperature (Frum et al. 1991; Nemes et al. 1994). The positions of the four infrared bands ν₂₅, ν₂₆, ν₂₇, and ν₂₈ shifts from 6.97, 8.40, 17.41, and 18.82 at 0 K to 7.11, 8.55, 17.53, and 18.97 at 1000 K, respectively. Our measurements show that the wavelengths of all C₆₀ bands in IRAS 01005+7910 lie inside these ranges. Assuming that the frequencies of the C₆₀ bands have a linear dependence on the temperature, we can estimate the temperature as 100–600 K. The observed widths of the C₆₀ features are about 0.3 μm (see Section 3), which correspond to a wavenumber width of ~60 cm⁻¹ and ~10 cm⁻¹ for the 7 and 17.4/18.9 μm bands, respectively. These values can be compared with the laboratory measured widths of about ~13 cm⁻¹ of gas phase C₆₀ (Frum et al. 1991), suggesting that a gas-phase origin of the molecule cannot be ruled out.

We estimate the abundance of C₆₀ following the same method of Sellgren et al. (2010) by calculating the total strength ratios between the C₆₀ and AIB features and assuming that the carrier of the AIB features to contain 6% ± 2% of interstellar carbon (Cerrigone et al. 2009). The strength ratio of C₆₀ to AIB emission is 0.01 in the observed wavelength range of IRAS 01005+7910, resulting in a percentage of carbon in C₆₀ of 0.06 ± 0.02%. This value is slightly lower than those obtained in NGC 7023 (Sellgren et al. 2010) and the PN SMP SMC 16 (García-Hernández et al. 2010), but a factor of 25 lower than that of Tc 1 estimated by Cami et al. (2010).

With the detection of C₆₀ in circumstellar envelopes, the next question is how they are formed. In the laboratory, C₆₀ can be effectively produced from the vaporization of graphite in a hydrogen-poor environment. Cami et al. (2010) proposed that fullerenes are produced only in hydrogen-poor envelopes created by a late AGB thermal pulse. However, García-Hernández et al. (2010) argued that C₆₀ can be synthesized under hydrogen-containing environment. As shown in Figure 1, the spectrum of IRAS 01005+7910 exhibits both hydrogen-containing AIBs and C₆₀ features, supporting the latter hypothesis. García-Hernández et al. (2010) also suggested that both C₆₀ and PAHs are the products of decomposition of HACs. In this scenario, photochemical processing can lead to dehydrogenation of the dust grains and form PAHs and C₆₀ molecules (Scott et al. 1997). On the other hand, the dehydrogenation of dust grains can also induce the formation of H₂ in the grain surfaces (e.g., Fleming et al. 2010). The strongest H₂ line in the observed wavelength range is the 0–0 S(0) transition at 28 μm. This line is not detected in the spectrum of IRAS 01005+7910 (Hrivnak et al. 2000; Cerrigone et al. 2009; Zhang et al. 2010). Moreover, we have detected H₂ in two PPNs with no detectable C₆₀ (Zhang et al. 2010). Because of this lack of correlation between the presence of H₂ and C₆₀, we are unable to give additional support for the idea that the formation of C₆₀ is the result of dehydrogenation of HACs.

Our detection suggests that fullerenes can be formed in the PPN stage. So far, there is no definite detection of C₆₀ in AGB stars. Although Clayton et al. (1995) noted a possible emission feature centered at 8.6 μm in the spectrum of the bright AGB star IRC+10216, the other C₆₀ features were not detected in the ISO-SWS spectrum (Cernicharo et al. 1999). The circumstellar spectra of AGB stars are dominated by silicates or silicon carbide emission features (Kwok et al. 1997). Although there are a small number of AGB stars exhibiting AIBs, the AIBs mainly emerge in the post-AGB phase. Is it possible that the formation of C₆₀ is related to the emergence of the AIB features? Sellgren et al. (2010) found that the C₆₀ and AIB emissions in NGC 7023 have different spatial distributions and attributed this to the effect of UV excitation. It can be argued that the C₆₀ and AIB carriers are already present in the AGB phase of evolution but are not excited until the stars evolve to the PPN phase. However, comparisons between the spectra of AGB stars, PPNs, and PNs suggest a sequence of molecular synthesis, with acetylenes forming in the late AGB phase, leading to the formation of diacetylenes, triacetylenes, and benzene in the PPN phase (Kwok 2004). Since these molecules are detected in absorption, the question of excitation does not arise. Since benzene is the first step toward the synthesis of aromatic materials, we can say with confidence that aromatic compounds only form after the AGB. If C₆₀ molecules are synthesized during the AGB, they should be detectable with absorption spectroscopy.

5. CONCLUSIONS

The detection of C₆₀ in a PPN as reported in this paper, together with the detection of this molecule in five PNs, confirms that the late stages of stellar evolution is a phase of active molecular synthesis. Beginning with simple diatomic molecules, such as CO, CN, and C₂, dozens of gas-phase organic molecules have been seen in the stellar winds from AGB stars. The formation of acetylene during the late AGB phase is believed to lead to the formation of benzene in the post-AGB phase of evolution. This also coincides with the first detection of vibrational modes of aromatic and aliphatic compounds. From this study, we now learn that gas-phase C₆₀ molecules may also form during the same epoch. As the number of C₆₀ detection increases, we would be in better position to study the relationships between C₆₀ and the carriers of other spectral features, such as the AIBs, and 21 and 30 μm features.

The detection of C₆₀ in the outflows from evolved stars also raises the possibility of the molecule being detected in the diffuse interstellar medium as the molecule is stable and should be able to survive journeys through the interstellar medium (Foing & Ehrenfreund 1994). The fact that a large variety of presolar grains (e.g., SiC) have been detected in meteorites (Zinner 1998) raises the possibility that presolar C₆₀ can be incorporated into comets and asteroids and be detected in meteorites. In fact, C₆₀ and C₇₀, as well as higher fullerenes, have been detected in the Allende meteorite (Becker et al. 1999). The evidence for stellar synthesis of C₆₀ in the late stages of stellar evolution as presented in this paper therefore adds further support to the idea of chemical enrichment of the Solar System by stellar molecular products.

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