THE RICH CIRCUMSTELLAR CHEMISTRY OF SMP LMC 11

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ABSTRACT

Carbon-rich evolved stars from the asymptotic giant branch to the planetary nebula phase are characterized by a rich and complex carbon chemistry in their circumstellar envelopes. A peculiar object is the preplanetary nebula SMP LMC 11, whose Spitzer Infrared Spectrograph spectrum shows remarkable and diverse molecular absorption bands. To study how the molecular composition in this object compares to our current understanding of circumstellar carbon chemistry, we modeled this molecular absorption. We find high abundances for a number of molecules, perhaps most notably benzene. We also confirm the presence of propyne (CH3C2H) in this spectrum. Of all the cyanopolyynes, only HC3N is evident; we can detect at best a marginal presence of HCN. From comparisons to various chemical models, we can conclude that SMP LMC 11 must have an unusual circumstellar environment (a torus rather than an outflow).

Key words: astrochemistry – circumstellar matter – stars: AGB and post-AGB – stars: carbon – stars: individual (SMP LMC 11)

Online-only material: color figures

1. INTRODUCTION

As stars with initial masses between 0.8 and 8–9 M☉ approach the end of their lives, they reach the asymptotic giant branch (AGB) stage. The AGB is characterized by alternate hydrogen and helium shell burning, dredge-up events, and extreme mass-loss rates (up to ∼10−3 M☉ yr−1; Iben & Renzini 1983). This high mass loss causes the star to evolve further, leaving the AGB. When a star leaves the AGB it may become what is known as a preplanetary nebula (pPN) during a relatively short-lived (lasting ∼103–104 yr; Vassiliadis & Wood 1994) transitional period before becoming a planetary nebula (PN).

The material lost by a star during its time on the AGB goes into the circumstellar environment (CSE) before it is dispersed into the interstellar medium (ISM). The CSE is a relatively cool region (with temperatures lower than the effective temperatures of AGB stars, where Teff ≈ 3000 K), which allows the formation of molecules and dust beginning on the AGB and continuing into the (p)PN stages.

One of the first and most stable molecules to form in the CSE is CO. As a result, the relative amounts of carbon and oxygen in the CSE largely determine future chemistry. Stars begin their lives with more oxygen than carbon (C/O < 1), but depending on the initial stellar mass and metallicity, an AGB star may undergo sufficient dredge-up events and become carbon-rich (C/O > 1), resulting in what is known as a carbon star (or a carbon-rich star).

The chemistry of carbon stars can result in an assortment of molecules due to the ability of carbon to form a variety of chemical bonds. For example, more than 60 molecules have been detected in the CSE of the prototypical carbon-rich AGB star IRC+10216 (e.g., Cernicharo et al. 1996).

The carbon chemistry in the CSE of AGB stars and (p)PNe is described as a low-excitation pPN (Sanduleak et al. 1978; Morgan 1984) and has a bipolar outflow (Shaw et al. 2006). It also shows a rather high expansion velocity (122 km s−1; Dopita et al. 1988) with multiple velocity components.

While PAHs are ubiquitous in the universe (including carbon-rich PNe), benzene is not often found in evolved stars; it has been found in just two objects thus far: CRL 618 (Cernicharo et al. 2001b) and SMP LMC 11 (Bernard-Salas et al. 2006, hereafter Paper I). This suggests that it is either difficult to form or that it reacts quickly once formed.

In this paper, we will discuss the latter object, SMP LMC 11, which is a carbon-rich pPN in the Large Magellanic Cloud. It is described as a low-excitation pPN (Sanduleak et al. 1978; Morgan 1984) and has a bipolar outflow (Shaw et al. 2006). It also shows a rather high expansion velocity (122 km s−1; Dopita et al. 1988) with multiple velocity components.

Here we present a detailed analysis of the molecular absorption bands in the mid-infrared spectrum of SMP LMC 11 (first presented in Paper I) and show that our results are inconsistent with current models for the chemistry in evolved carbon-rich CSEs.

We begin this paper with a description of the observations and data reduction in Section 2, then we describe the dust continuum in Section 3. We follow this with an inventory of the molecular bands in the spectrum and the method we use to model these bands in Section 4. We then present our results from our model fits in Section 5. Next, we discuss the implications of our results for the evolutionary status, chemical evolution, and geometry of
Finally, we present our conclusions in Section 6. Finally, we present our conclusions (version). The inset shows the 2MASS fluxes with the dust model (dashed gray or dashed blue line in the online version). The Astrophysical Journal.

Figure 1. Spitzer–IRS low-resolution spectrum (SL and LL combined) of SMP LMC 11 (black) and a dust model (dashed gray or dashed blue line in the online version). The inset shows the 2MASS fluxes with the dust model. (A color version of this figure is available in the online journal.)

2. OBSERVATIONS AND DATA REDUCTION

SMP LMC 11 was observed with the Spitzer Space Telescope (Werner et al. 2004) Infrared Spectrograph (IRS; Houck et al. 2004) as part of the Guaranteed Time Observer (GTO) program on 2005 June 6 (program ID 103, AOR key 4947712). Here we present a new reduction of the spectrum with the latest calibration files (pipeline version S18.18). We obtained the basic calibrated data (BCD) files for SMP LMC 11 and processed the data for the short high (SH, $R = 600$, $\lambda$ = 9.9–19.6 $\mu$m), short low (SL, $R = 60$–127, $\lambda$ = 5.2–14.5 $\mu$m), and long low (LL, $R = 57$–126, $\lambda$ = 14.0–38.0 $\mu$m) modes.

We cleaned the data using irsclean with the campaign rogue pixel mask and extracted it in smart v8.2.1 (Higdon et al. 2004); we extracted the SH data using full aperture extraction, and the SL and LL data with the manual optimal extraction mode (Lebouteiller et al. 2010). Next we defringed the LL mode and trimmed the edges of the orders for all modules to remove edge effects. We eliminated flux jumps between the orders by comparing the overlap regions and scaling the orders (for the SH, orders were scaled to match order 20, for the low-resolution data SL2 was scaled to SL1 and both were scaled to the LL data), then we averaged the flux from the two nod positions. Since we were unsure of the reliability of the initial uncertainty estimates, we instead estimated the uncertainties on the flux values by measuring the standard deviation in a featureless region of the SH spectrum between 16.53 and 17.44 $\mu$m; we found a standard deviation of 0.0122 Jy, corresponding to a signal-to-noise ratio (S/N) of 47 in this range.

Finally, to facilitate comparison to molecular models, we shifted the spectrum to the rest frame using a radial velocity of 263.5 km s$^{-1}$ (Morgan & Parker 1998) and the relative motion of Spitzer at the time of the observations ($V_{LSR}$ = 12.5 km s$^{-1}$). The full low-resolution spectrum is shown in Figure 1.

3. THE DUST CONTINUUM

Figure 1 shows the Spitzer–IRS continuum as well as the Two Micron All Sky Survey (2MASS; Skrutskie et al. 2006) H-, J-, and K-band fluxes (Cutri et al. 2003). From those data, it seems clear that there is no appreciable stellar continuum that could contribute to the mid-IR emission. We thus conclude that the flux in the entire IRS spectrum is dominated by dust emission.

The region beyond 17 $\mu$m has a few apparent features near 19 and 21 $\mu$m in the LL data. However, as these features are absent from a quick reduction of the long high (LH, $R = 600$, $\lambda$ = 18.7–37.2 $\mu$m) data, we consider these to be artifacts. Thus, the dust emission does not show clear spectral features, and thus is presumably caused by amorphous carbon dust.

Since it is precisely this dust emission that is then absorbed by molecular bands (especially in the 10–17 $\mu$m region, see Figure 1), we require some idea about the properties of this dust continuum before we can model the molecular bands. A single blackbody curve cannot properly reproduce the overall shape of the dust continuum, suggesting that there is some stratification in the dust layers. From our point of view, we can see through the outer (and colder) dust layers up the point where the dust becomes optically thick; at that point, the dust temperature is $T_d^{\text{max}}$. We thus approximated the dust emission by a weighted sum of blackbody spectra at temperatures between $T_d^{\text{max}}$ and an arbitrarily chosen minimum temperature $T_d^{\text{min}}$ of 25 K in steps of 25 K. Assuming optically thin dust in radiative equilibrium with the hottest (optically thick) dust, we then determined the appropriate weights for each temperature bin consistent with a constant-velocity outflow at a constant mass-loss rate (i.e., we determined the mass in each layer). We find that the best model is one with a maximum dust temperature of about 425 K (see Figure 1). However, even in such a case, we overestimate the dust emission at the longer wavelengths; this suggests that there is less cold dust than expected for a constant-velocity outflow at a constant mass-loss rate. Nonetheless, the cold dust does not matter much for the analysis of the molecular bands; for the modeling presented in this paper, we assume that the molecules are absorbing 425 K blackbody radiation.

We also note that our dust temperature estimate is higher than that in Paper I, but our estimate should be more reliable than their graybody fit.

4. MOLECULAR BANDS

4.1. Molecular Inventory

Superposed on the dust emission are many absorption features due to various molecular species (see Figure 2). We will restrict our discussion to wavelengths shorter than 17 $\mu$m, where most of the absorption occurs.

Here, we describe the molecular bands in detail and determine the physical conditions by modeling these bands. Acetylene ($C_2H_2$) is often the dominant molecular absorber in the infrared spectra of carbon-rich pPNe. In the spectrum of SMP LMC 11, $C_2H_2$ provides by far the strongest absorption. The $Q$-branch for the $v_5$ bending mode is obvious as a very deep absorption feature at 13.7 $\mu$m; additionally, the $P$- and $R$-branches of $C_2H_2$ cause much of the broad and deep absorption that is obvious between 12 and 16 $\mu$m (see Figure 1). Such broad and deep $C_2H_2$ absorption is also seen in some other carbon-rich objects, such as the carbon star IRAS 04496–6958 (Speck et al. 2006), for example. In addition, acetylene exhibits a much weaker combination band ($v_4+v_5$) at 7.5 $\mu$m which is blended with other features in the spectrum of SMP LMC 11.
Figure 2. Normalized SL and SH spectra for SMP LMC 11 from 6 to 16.6 μm with our best-fit models and residuals. The combined best fit is shown offset above the spectrum in dark gray (red in the online version). The individual best fits for each molecule are offset above this in light gray (blue). The residuals are shown offset below the spectrum and the dot-dashed lines indicate the error ranges.

(A color version of this figure is available in the online journal.)

Larger acetylene chains are less commonly observed in the CSE of pPNe (Fonfría et al. 2011). In the spectrum of SMP LMC 11 though diacetylene (C₄H₂) is another major contributor to the molecular absorption in the spectrum. The ν₈ bending mode of this species appears at 15.9 μm and the ν₆ + ν₈ combination band is clearly visible at ~8 μm. Small amounts of the corresponding ν₁₁ bending mode of triacetylene (C₆H₂) might be present in the red wing of the 15.9 μm feature.

In contrast, HCN—which often shows up in carbon star spectra alongside the C₂H₂ band at 14 μm—at best barely contributes to the absorption in this spectrum. It is thus surprising that HC₅N is present and shows a clear and deep absorption at 15.03 μm from its bending mode. There is no evidence for any longer cyanopolyynes; for instance, there is no absorption at 15.57 μm from the ν₇ band of HC₅N.

Nearly unique for pPNe (with one other detection thus far in CRL 618; see Cernicharo et al. 2001b), the spectrum also shows significant benzene absorption (as noted in Paper I). It has its deepest absorption at 14.85 μm, where the ν₁ bending mode absorbs more than 15% of the total continuum flux. Additionally, strong absorption is clearly present at the wavelengths where other strong benzene bands are expected: another bending mode (ν₁₄) at 9.6 μm and a ring stretching and deforming mode (ν₁₃) at 6.72 μm.

In the blue wing of the C₄H₂ band, near 15.78 μm, some additional absorption could be due to the ν₈ bending mode of propyne (CH₃C₂H, also sometimes called methylacetylene) at 15.78 μm, as suggested in Paper I. Furthermore, there is also some absorption visible in the spectrum from the ν₄ band of CH₄ at 7.7 μm as well as the ν₃ band of C₂H₄ at 10.53 μm. Finally, we could not determine the origin of the absorption feature near 10.38 μm, although we suspect a molecular origin for this feature.

4.2. Modeling the Molecular Absorption

We modeled the molecular absorption using the same methods that are used to build the SpectraFactory database (Cami et al. 2010). These model calculations start from line lists detailing the frequencies and intensities of the individual molecular transitions.

Line lists for C₂H₂ (including the H₁³CCH isotopologue), HCN, CH₄, and C₂H₄ are taken from the HITRAN 2008 database (Rothman et al. 2009); the line lists for C₄H₂, C₆H₆, HC₃N, and CH₃C₂H are from the GEISA database (Jacquinet-Husson et al. 2008).

As we could not find reliable line lists for all species or bands, we calculated some line lists from molecular constants and pgopher v 7.1.108 (Western 2010). The GEISA line list for benzene contains only data for the fundamental ν₁ band. Thus, in order to model benzene absorption at the shorter wavelengths in the SL data, we calculated line lists for the ν₁₃ and ν₁₄ bands using molecular constants from Dang-Nhu & Pliva (1989). Similarly, the GEISA line list for C₄H₂ does not contain data for the transitions of the ν₆ + ν₈ combination band at ~8 μm; we thus calculated a line list using molecular constants found in Arié & Johns (1992), Guelachvili et al. (1984), and Khelifi et al. (1995). Finally, we calculated a C₆H₂ list using data from McNaughton & Bruget (1991).

From these line lists, we calculated optical depths assuming a population in local thermodynamic equilibrium and a Gaussian intrinsic line profile with a width of 10 km s⁻¹, which is typical of outflows of evolved stars. We carried out radiative transfer through isothermal, plane-parallel molecular slabs in front of a 425 K blackbody background (see Section 3) and smoothed and rebinned the resulting models to match the resolving power of the observations—600 for the SH module and 90 for the SL data.
We compared the resulting models to the observations (normalized by a cubic spline continuum) and calculated $\chi^2$, the reduced $\chi^2$ statistic. However, we note that there may be some systematic errors as well. For instance, it is important to realize that the current line lists for C$_2$H$_2$ do not allow us to reproduce the broad and deep absorption in the 12–16 $\mu$m range (see Speck et al. 2006, for a discussion).

To find the best model, we calculated models at different temperatures ranging from 200 to 400 K with a step size of 25 K, and similarly at column densities between $N = 10^{15}$ and $N = 10^{19}$ cm$^{-2}$ in steps of $\log N = 0.1$ and then calculated the $\chi^2$ value for each model. For wavelength ranges containing absorption due to several species, we properly treated line overlap by summing the optical depth profiles for each contributing molecule prior to performing the radiative transfer calculations when we fit several species simultaneously. We thus simultaneously modeled the absorption of the C$_2$H$_2$ isotopologues and HCN between 12 and 14 $\mu$m and similarly also combined C$_4$H$_2$, C$_6$H$_2$, CH$_3$C$_2$H, and CH$_3$N in the 15–16.5 $\mu$m range. We fit benzene to the spectrum between 14.2 and 15.5 $\mu$m and C$_2$H$_4$ from 10.5 to 11 $\mu$m. Where overlap appeared across the modeled regions, we added the optical depth values determined from earlier fits to the new regions (e.g., the best-fit optical depths for C$_2$H$_2$ and HCN were added to the optical depth for the C$_4$H$_2$, C$_6$H$_2$, HC$_3$N, and CH$_3$C$_2$H fits) and then performed the radiative transfer calculations. We expect that small errors may be introduced using this method, but due to the small difference in temperature between the layers, this effect should not be large.

Using the results from fitting the SH observations, we predicted the absorption in the SL data for benzene, C$_2$H$_2$, and C$_4$H$_2$. The CH$_4$ absorption was fit by itself between 7.5 and 7.9 $\mu$m, but the optical depth profiles for the $v_h + v_g$ band of C$_2$H$_2$ as well as the C$_3$H$_2$ band at 7.5 $\mu$m as determined in the SH data were added to the total optical depth profile prior to calculating the radiative transfer calculations for the CH$_4$ fits.

### 5. RESULTS

The best fits for the SH and SL data are shown in Figure 2; the corresponding parameters are listed in Table 1. As can also be seen from the residuals in Figure 2, our models reproduce the observations quite well ($\chi^2 \approx 0.84$ over the entire fitting region). Our best fits indicate that the molecules are found in a range of temperatures from 250 to 375 K; however, some of the temperature stratification may be artificial due to the large uncertainties on our temperature determinations.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$\log N$</th>
<th>$T$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_2$H$_4$</td>
<td>17.30$^{+0.05}_{-0.50}$</td>
<td>350$^{+50}_{-50}$</td>
</tr>
<tr>
<td>C$_2$H$_2$</td>
<td>18.10$^{+0.05}_{-0.05}$</td>
<td>375$^{+25}_{-50}$</td>
</tr>
<tr>
<td>H$_3$CCCH</td>
<td>16.90$^{+0.10}_{-0.10}$</td>
<td>375$^{+25}_{-50}$</td>
</tr>
<tr>
<td>HCN</td>
<td>16.50$^{+0.50}_{-1.50}$</td>
<td>375$^{+25}_{-50}$</td>
</tr>
<tr>
<td>C$_4$H$_6$</td>
<td>17.80$^{+0.40}_{-1.00}$</td>
<td>350$^{+50}_{-50}$</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>17.10$^{+0.05}_{-0.05}$</td>
<td>325$^{+12.5}_{-25}$</td>
</tr>
<tr>
<td>C$_2$H$_2$</td>
<td>17.00$^{+0.05}_{-0.05}$</td>
<td>325$^{+12.5}_{-25}$</td>
</tr>
<tr>
<td>CH$_3$C$_2$H</td>
<td>16.40$^{+0.10}_{-0.05}$</td>
<td>325$^{+12.5}_{-25}$</td>
</tr>
<tr>
<td>CH$_3$N</td>
<td>16.40$^{+0.10}_{-0.05}$</td>
<td>325$^{+12.5}_{-25}$</td>
</tr>
</tbody>
</table>

5.1. Benzene

To fit the $v_4$ bending mode of benzene at 14.85 $\mu$m, we require a high column density ($\log N = 17.80$) consistent with the deep absorption in the spectrum. Our model reproduces the depth of the absorption feature well, but does not match the width and profile shape. This discrepancy is probably due to the absence of hot bands in our molecular model. Hot bands are generally slightly offset compared to the fundamental mode, and thus tend to broaden the absorption band. At the relatively high temperature of benzene found here, we certainly expect some contribution from the hot bands; at 300 K, only 54% of the molecules should be in the ground state (Kauppinen et al. 1980). However, hot bands are not included in the GEISA line list for benzene. As a result, our model fit is much narrower than it should be.

Using the benzene parameters found from fitting the $v_4$ band, we predicted the appearance of the bands at 9.6 and 6.7 $\mu$m. As seen in Figure 2, while there are absorption features at these wavelengths consistent with benzene, our predictions do not fit these bands particularly well. At 9.6 $\mu$m, we can see that the predicted absorption is much deeper than the observed band, although the band shape is similar.

The feature at 6.7 $\mu$m is more unusual: while there is an overall absorption feature in the spectrum of SMP LMC 11 at this wavelength, the feature is much broader than our model and shows what could be a small emission bump right at the central wavelength of the benzene absorption. Just as for the 14.85 $\mu$m band, the broader observed feature could be a consequence of the absence of hot bands in our model. Indeed, we note that the absorption in the spectrum appears to be approximately twice as broad as in the model, with a similar red degraded wing (see Figure 3). Thus, we consider benzene the carrier for the overall absorption feature at 6.7 $\mu$m. The nature of the small emission bump is not clear. If this is a real emission feature, it seems unlikely that it would be due to benzene, since we do not see any similar emission at the other benzene absorption bands.

5.2. Acetylene Chains

The C$_2$H$_2$ absorption at 13.7 $\mu$m is the deepest and broadest absorption feature in the spectrum. Accordingly, we find the highest column density for this feature ($\log N = 18.10$) of the molecular bands we fit. Since we ignored the deep and broad absorption between 12 and 16 $\mu$m, which is at least partly due to C$_2$H$_2$, this is clearly a lower limit of the true column density. In addition to the main isotopologue, we detect a fairly high column density of H$_3$CCCH ($\log N = 16.90$) yielding an $N_{12C-H}_2/N_{13C-H}_2$ ratio of 16 and a $^{12}$C/$^{13}$C ratio of 33. This is in the low end of the range for carbon-rich objects as determined by Milam et al. (2009), who found $^{12}$C/$^{13}$C ratios between 25 and 90. However, since we underestimate the column density of the main isotopologue, this is most certainly an absolute lower limit to the $^{12}$C/$^{13}$C ratio. Similarly, from the column densities of C$_2$H$_3$ and C$_2$H$_4$, we find a ratio of C$_2$H$_2$/C$_4$H$_2$ of 10, which would again be a lower limit.

We find that the identification of the $v_4$ band of C$_6$H$_2$ in this spectrum is uncertain. Using reasonable defringing techniques, the apparent absorption feature near 16.1 $\mu$m disappears (see Figure 4). Further, when the molecular constants from McNaughton & Bruget (1991) are used to calculate a model line list, we find that the calculated band center appears 0.02 $\mu$m longer of the apparent absorption in the spectrum. A comparison between our calculated model and the previously identi-
We do not detect any absorption at the position of the bending mode of HC3N at 15.57 μm. Since the band strengths for the bending modes of HC3N (268.2 cm\(^{-2}\) atm\(^{-1}\); Bénilan et al. 2007) and HC13N (245.1 cm\(^{-2}\) atm\(^{-1}\); Jolly et al. 2007) are fairly similar and since the modes should have a similar profile, this suggests that HC3N is simply not present in SMP LMC 11. From the measured equivalent width of the band (0.007 μm) and the S/N of ~85 in this part of the spectrum, we estimate an upper limit of log \(N = 15.4\) to the column density for HC3N, yielding a lower limit to the HC3N/HC13N ratio of 10.

5.4. Other Species

Our best-fit model shows a clear contribution from CH3C2H at a relatively high column density, blended with the C3H2 absorption band. Again, we performed an F-test and found that in this case, adding CH3C2H does indeed significantly improve the fit: we find \(F = 53\) and the probability of observing this \(F\) value with the addition of a random factor is \(\sim 10^{-8}\)%. This absorption cannot be due to isotopologues of C3H2 either, as these absorb at longer wavelengths than the main isotopologue peak (at 15.95 and 15.93 μm for H13CCCCH and HC13CCCH, respectively; Jolly et al. 2010). We thus conclude that CH3C2H is indeed present in the spectrum of SMP LMC 11. Note that this species was also observed in the pPN CRL 618 at millimeter wavelengths, and that it was suggested to contribute to the absorption at infrared wavelengths too (Cernicharo et al. 2001a). Here, however, we find a higher column density.
Finally, we also find good fits and fairly high column densities for the CH$_4$ absorption at 7.7 μm and the C$_2$H$_4$ absorption at 10.53 μm.

Judging from the residuals and low overall χ^2, we have accounted for most of the molecular absorption. Thus, any additional molecular bands apart from those already noted must be either weak or perhaps shallow and broad.

6. DISCUSSION

The rich molecular spectrum of SMP LMC 11 seems to offer a unique astrophysical laboratory to study chemical pathways in carbon-rich environments, including the formation of benzene. Indeed, although the CSE of SMP LMC 11 shares some properties with CRL 618—the only other pPN in which benzene is detected—there are some significant differences that offer clues to the conditions required for the efficient formation of benzene and other carbonaceous molecules.

6.1. Circumstellar Geometry

The first aspect we consider is the geometry of the CSE and the physical conditions of the material within. The continuum emission in the Spitzer–IRS observations is due to dust and provides the background intensity against which the molecular gas absorbs. Thus, the molecular gas is either mixed in with the dust or located further from the star. Additionally, the dust must be optically thick at infrared wavelengths to explain the overall shape of the combined SL and LL spectrum. Moreover, optically thick dust is consistent with the featureless shape of the dust continuum which can be represented reasonably well with blackbody curves (see also Section 3).

It is clear that the physical conditions in the CSE of SMP LMC 11 are somewhat different from those in CRL 618: the CSE of SMP LMC 11 is denser and warmer than that of CRL 618. We find a typical dust temperature of 425 K, whereas the dust and molecular gas temperatures in SMP LMC 11 are more typical of a late AGB star than a pPN for which dust temperatures are often seen around binary systems containing an evolved star such as the Red Rectangle (see, e.g., Burton & Geballe 1986). Such massive, vertically extended and long-lived disks are often seen around binary systems containing an evolved star such as the Red Rectangle (see, e.g., Jura et al. 1995; Waters et al. 1998), for example. However, it is not clear what the primary cause for the higher temperatures in SMP LMC 11 is. This could simply indicate that the torus is closer to the central star than for CRL 618, either because the CSE is younger, or because it is expanding more slowly than that of CRL 618 (which is expanding at a rate of 20 km s$^{-1}$; see, e.g., Herpin & Cernicharo 2000). However, one could also attribute the different temperatures to differences in the optical thickness of the dust between the two objects. In either case, the molecular excitation seems constrained to a fairly small range in temperatures.

6.2. The Chemistry in SMP LMC 11

In terms of the molecular composition, the most striking difference between SMP LMC 11 and CRL 618 is the much stronger absorption that we find for benzene. The center of the benzene band at 14.85 μm is about three times deeper in SMP LMC 11 than in CRL 618. It may be somewhat surprising then that we find a column density that is 130 times larger than that found for CRL 618 (Cernicharo et al. 2001b); however, we believe that this difference is due to the fact that we used more recent line lists. Additionally, not only is benzene itself much more abundant in SMP LMC 11, it is also enhanced compared to many other species, especially compared to acetylene. If we take the lower limit for the column density of C$_2$H$_2$ at face value, we find that there is about twice as much C$_2$H$_2$ as there is benzene; for CRL 618, the ratio found between these molecules was about 40 (Cernicharo et al. 2001b).

The relative abundances of the acetylene chains might offer some hints about the chemistry leading to efficient benzene formation. Woods et al. (2002, 2003) found that the interstellar benzene formation route (McEwan et al. 1999) was not efficient in environments such as CRL 618. Instead, they proposed a much more efficient route in such environments starting from acetylene and HCO$^-$. The same model also predicts high column densities of C$_2$H$_2$ and C$_6$H$_2$ that are similar to one another. In fact, this matches the abundances in CRL 618 to within a factor 4–6. In the spectrum of SMP LMC 11, however, we cannot reliably establish the presence of C$_6$H$_2$ in the spectrum. This suggests that there is yet another formation route to benzene in these warm and dense environments, or possibly some additional reactions that need to be considered. These reactions might involve fast and efficient ring-closing reactions that deplete C$_6$H$_2$ or an additional route to benzene formation that starts...
from the abundant $C_2H_2$ and $C_4H_2$ which then decreases the
efficiency of the formation of $C_6H_2$.

It is equally interesting to consider the benzene loss reactions.
Chemical models for environments comparable to those studied
here show that the main destruction route for benzene is a further
reaction with CN to form benzonitrile ($C_6H_2CN$; Woods et al.
2003). This molecular species has strong absorption bands at
13.2 and 14.4 $\mu$m, which we do not observe in the spectrum of
SMP LMC 11. Although the CN in these reactions is expected
to originate from the photodissociation of HCN, which is again
at best marginally present in the spectrum of SMP LMC 11.
Benzene destruction could thus be inhibited by the absence of
the CN parent species.

The cyanopolyynes also present an interesting case. As shown
in Cherchneff & Glassgold (1993), for example, the primary
routes to the formation of cyanopolyynes in pPNe environments
are through reactions between members of the acetylene family
and the CN radical, which itself is produced from HCN in
photochemical reactions. Reactions between CN and $C_2H_2$ then
result in $HC_3N$, while reactions with $C_2H_2$ yield $HC_5N$. Since
both $C_2H_2$ and $HC_5N$ are abundant in the spectrum of SMP
LMC 11, we would thus expect fairly large abundances of
the longer cyanopolyynes as well. However, while we clearly
detect a strong absorption band due to $HC_3N$, we do not find
much evidence for the parent molecule, HCN, nor for the
longer cyanopolyynes. $HC_5N$, for instance, should have a strong
bending mode at 15.57 $\mu$m (Beniljan et al. 2007) which does not
appear in the spectrum (see Figure 2).

Such abundance patterns are very different from those ob-
erved in CRL 618 and cannot be accommodated by the
chemical models for these environments (e.g., Cherchneff &
Glassgold 1993; Woods et al. 2003). Even if one were to con-
sider that HCN could be completely depleted by $HC_3N$ forma-
tion, one would expect to see efficient formation of $HC_3N$ as
well since this involves the same mechanism and large amounts
of $C_2H_2$ are available for this process. This observation then
suggests that for the cyanopolyynes, some of the chemical path-
ways that are possible in pPNe environments might be missing
from the models.

6.3. Pathways to PAHs?

The formation of benzene is often studied in the context of
PAHs, for which they are the basic unit. In the formation
pathways for PAHs, the formation of benzene is considered
to be the bottleneck (see, e.g., Allamandola et al. 1989). We
searched for any features due to neutral naphthalene and pyrene
(two of the smallest PAHs consisting of two and three aromatic
rings, respectively) but did not find any evidence for these
species. However, since PAH formation cannot occur at the
low temperatures in SMP LMC 11—typically 900–1100 K is
required (Frenklach & Feigelson 1989; Allamandola et al. 1989;
Cherchneff et al. 1992), this should not be surprising.

It is interesting to consider what might happen to the benzene
as the central star and CSE evolve further. All other things
being equal, the increasingly hot central object would heat up
the CSE. If the torus expands (as is the case for CRL 618),
then the circumstellar material will become diluted and more
transparent, which would clearly increase the importance of
photochemistry. It is not immediately clear what the result of this
increased photochemistry would be, but it is certainly possible
that the conditions created are ideal for further processing of
the circumstellar benzene into PAHs. If so, this might represent
an important PAH formation pathway, provided that the torus
contains enough mass to represent a significant carbon reservoir.
Note that for objects like the Red Rectangle, the circumbinary
disks are indeed found to be massive. However, in that particular
object, PAHs are clearly found in the bipolar outflows (Waters
et al. 1998) and not in the torus.

Although the molecular composition of the CSE of SMP
LMC 11 is certainly unique thus far, we do not believe
that the environment represented by this object is necessarily
exceptional. CRL 618 is the only other source where benzene is
detected, and it also shows different abundances for the polyynes
and the cyanopolyynes. However, the two environments are very
similar in many of their physical properties. Given the short
expected timescales for the evolution from the tip of the AGB
to the PN phase, it is reasonable to expect the evolution of
CSEs to be fast. The two objects could then represent cases
where either the initial conditions (of the torus, for example)
were slightly different or, alternatively, they could represent
slightly different steps in the evolution of the torus. It would
certainly be interesting to study how the physical conditions of a
(slowly expanding) dense torus change in this short evolutionary
phase and how the chemistry in this environment will evolve.

7. CONCLUSIONS

We presented an analysis of the rich molecular absorption in
the Spitzer–IRS spectrum of SMP LMC 11. We have compared
it to chemical models for carbon-rich pPNe and to CRL 618,
the only other pPN in which benzene is detected to date. The
geometrical configuration in both objects is fairly similar and
includes a dense, warm torus of material in which a
rich molecular gas resides. However, the absolute and relative
chemical abundances of the carbonaceous species in SMP LMC
11 do not match models and are also quite different from those
in CRL 618. In particular, benzene is very abundant, making SMP
LMC 11 an important environment to consider in the study of
benzene and possibly also in PAH formation. Current chemical
models can reproduce some of the molecular absorption, but
not all of it. In particular, the absence of $C_2H_2$ and $HC_5N$ seems
to require additional ring-closing reactions that deplete
those species. Alternatively, new chemical pathways have to be
found for the formation of $C_2H_2$ and $HC_5N$ that do not result in
abundant formation of $C_6H_2$ and $HC_5N$. We encourage a more
detailed study of the chemical pathways which could explain
these anomalies.

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