VARIATIONS OF THE MID-INFRARED EMISSION SPECTRUM IN REFLECTION NEBULAE

JESSE BREGMAN
Astrophysics Branch, NASA Ames Research Center, MS 245-6, Moffett Field, CA 94035

AND

PASQUALE TEMI
Astrophysics Branch, NASA Ames Research Center, MS 245-6, Moffett Field, CA 94035; and SETI Institute, Mountain View, CA 94043

Received 2004 April 29; accepted 2004 November 23

ABSTRACT

Using spatial-spectral data cubes of reflection nebulae obtained by ISOCAM, we have observed a shift in the central wavelength of the 7.7 μm band within several reflection nebulae. This band, composed of components at 7.85 and 7.65 μm, shows a centroid shift from 7.75 μm near the edge of the nebulae to 7.65 μm toward the center of the nebulae as the shorter wavelength component becomes relatively stronger. The behavior of the 7.7 μm band center can be explained by assuming either that anions are the origin of the 7.85 μm band and cations the 7.65 μm band, or that the band center wavelength depends on the chemical nature of the polycyclic aromatic hydrocarbons (PAHs). The ratio of the 11.3/7.7 μm bands also changes with distance from the central star, first rising from the center toward the edge of the nebula, then falling at the largest distances from the star, consistent with the 11.3/7.7 μm band ratio being controlled by the PAH ionization state.

Subject headings: infrared: ISM — ISM: lines and bands — ISM: molecules — reflection nebulae

1. INTRODUCTION

The mid-infrared emission bands observed in many environments, including H ii regions, post-AGB (asymptotic giant branch) stars, planetary nebulae, the diffuse interstellar medium (ISM) of galaxies, and reflection nebulae, are still commonly called the unidentified infrared (UIR) bands, even though their association with polycyclic aromatic molecules (PAHs) was made 20 years ago (Leger & Puget 1984; Allamandola et al. 1985) and this identification has since been supported by observations and theoretical calculations. However, identification of the emission bands with a single carrier has not been possible, since the emission bands are likely due to a mixture of PAHs rather than a single molecule. Yet, a wealth of observationally based information about the UIR bands has been collected that, for example, has allowed authors to use them to measure redshifts of galaxies and to differentiate between active galactic nuclei and starburst nuclei (Roche et al. 1991; Genzel et al. 1998).

Trends observed in the detailed UIR emission spectra indicate that the molecules responsible for these bands vary depending on their environment and history. For example, using laboratory spectra, Allamandola et al. (1999) demonstrated that the difference between the emission spectrum of a post-AGB star and the Orion Bar can be explained by varying the PAH mixture in these sources. While a mixture of less stable PAH cations and neutrals could fit the post-AGB spectrum, more stable PAH cations with no neutrals were needed to fit the Orion Bar spectrum. Since the material around the post-AGB star is young and the material in the Orion Bar has been heavily processed, they concluded that processing in the ISM modifies the PAH mixture. Similar conclusions were reached by Hony et al. (2001) and Peeters et al. (2002) on the basis of spectral variations they observed in ISO spectra of a large number of diverse sources.

The spectra of PAH neutrals and ions are quite different, with ions having stronger C—C mode (6—10 μm) emission than C—H mode (10—14 μm) emission, and neutrals having weaker C—C than C—H mode emission. Uchida et al. (2000) and Chan et al. (2001) used this property to determine whether the PAH ionization state changed in reflection nebulae and the diffuse ISM. While the reflection nebulae did show a variation of 40% in the intensity ratio over a wide range of incident UV flux, Uchida et al. (2000) expected a much larger variation if the PAHs changed entirely from ions to neutrals as the UV intensity decreased.

The PAH ionization state is determined by the ratio of the UV field (G0) to the electron density (e.g., Bakes et al. 2001), with PAHs existing primarily as anions for very low values of G0/n_e and as cations for very high values of G0/n_e. At intermediate values, PAHs will exist as a mixture of anions, neutrals, and cations. The ratio of the recombination and ionization rates determines where the transitions from cations to neutrals and anions occur as G0/n_e decreases. Verstraete et al. (1990) have measured the ionization rate for coronene and pyrene, but the recombination rate (cation to neutral) has been measured only for the smallest PAHs (Abouelaziz et al. 1993), and the experimental value is smaller than theoretical values by 1—2 orders of magnitude. Only estimates exist for the physical constants that determine the anion to neutral transition (Le Page et al. 2001). The spectra of anions and cations are very similar from 5 to 14 μm, so that the mid-IR spectrum in regions of very high and very low UV intensities should also be similar.

A shift of the 7.7 μm band centroid has been observed previously. Bregman (1989) and Cohen et al. (1989) noted that the central wavelength of the 7.7 μm band depended on the type of object. Objects with freshly created PAHs (planetary nebulae) have a band centered near 7.85 μm, while objects with older material (H ii regions and reflection nebulae) have a band centered near 7.65 μm. They noted that the 7.7 μm band often contained contributions from both of these components. Peeters et al. (2002), using higher spectral resolution data from

1 Based on observations with ISO, an ESA project with instruments funded by ESA Member States (especially the PI countries: France, Germany, the Netherlands, and United Kingdom) and with the participation of ISAS and NASA.
The PAH life cycle must be similar to other materials formed around stars and then ejected into the ISM (e.g., silicates). Once ejected into the ISM, PAHs are exposed to the diffuse UV field for about 10^7 yr and chemically modified. They then become part of the material that forms a dark cloud, where all but the most volatile components of the gas, including the PAHs, freeze out to form the ices observed in absorption in the direction of embedded protostellar sources (Sellgren et al. 1995; Brooke et al. 1996; Bregman & Temi 2001). Chemical reactions should occur in the ice (Bernstein et al. 1999, 2002), again modifying the chemistry of the PAHs. As stars burn their way out of the dark clouds, the PAHs become visible as emission from reflection nebula.

In this paper, using ISOCAM spectral images of reflection nebulae, we show that the wavelength of the 7.7 μm emission band varies with position in the nebula in a manner consistent with either variations in the ionization of the PAHs and/or with UV photoprocessing of the PAHs. In regions of the nebulae close to the exciting star, the 7.7 μm band has a weak component at 7.85 μm that becomes stronger relative to the 7.65 μm component with increasing distance from the star. The 11.3/7.7 μm band ratio also varies with increasing distance from the star, first increasing and then decreasing in strength. In § 2 we describe the data reduction of the ISOCAM images to form spatial-spectral data cubes followed by an analysis of the data in § 3 and a discussion in § 4.

2. DATA REDUCTION

A large sample of reflection nebulae was observed with the ISOCAM camera (Cesarsky et al. 1996) on board the ISO satellite (Kessler et al. 1996). For the analysis presented here we selected three reflection nebulae observed in the spectral-imaging mode with the circular variable filter (CVF). The data set is represented by a cube in which the two spatial coordinates are defined by the 32 × 32 Si: Ga infrared array, and the third dimension is the spectral axis obtained by scanning the CVF filter. The CVF is divided in two sections that cover a spectral range from 5.14 to 9.44 μm (CVF1) and from 9.33 to 15.1 μm (CVF2), with a spectral resolution of λ/Δλ ≈ 40.

Two nebulae, vdB 17 and vdB 133, have been recorded by performing a full scan of the two CVFs in both the increasing and decreasing wavelength directions with a scale of 6″ × 6″ per pixel. Each wavelength was observed 11 times for vdB 133 and eight times for vdB 17 in each scan leg, with an elementary integration time per measurement of 2.1 s. The CVF step increment was set to 1 and 2 steps, respectively, for vdB 133 and vdB 17, providing an oversampling factor of 2–4 in both the spectral axes. At the end, the combination of the different parameter set for each observation resulted in a total on-source integration time of 3378 and 1340 s, in each scan direction, for vdB 133 and vdB 17, respectively.

NGC 1333 SVS3 has been recorded with a different set of observing parameters; the pixel scale was set to 1″5, providing a field of view of 48″ × 48″. Combining the 17 exposures taken at each CVF increment with an oversampling factor of 2–4, and a 2.1 s integration time per measurement, the total observing time spent on-source was 2696 s. The spectral scan through the CVF was performed on two noncontiguous sections of the CVF in a single scan direction (long to short wavelengths).

The data were reduced starting from the raw level, the CISP product, using the ISOCAM Interactive Analysis processing package CIA, (ver. 5.0; Ott et al. 1997). To correct the raw data for the dark current we used the dark model (Biviano et al. 2000) that takes into account the observing time parameters and the variation of the dark current both within a single revolution of the satellite and among all the revolutions. Then, the data were deblitched by applying a multiresolution median filter and corrected for the transient response of the detector. We applied the transient correction using the Fouks-Schubert method. Flat fielding was done using dedicated CVF zodiacal measurements that take into account the scattered light pattern that is produced inside the camera from reflections between detector and CVF filters (M. Sauvage 2004, private communication).

3. ANALYSIS

3.1. Wavelength of the “7.7” μm Band

Figure 1 shows spectra from two different locations in the reflection nebulae vdB 133 and NGC 1333 SVS3. There is a clear shift in the centroid of the 7.7 μm emission band between the two locations in each object. Also in both cases, the spectrum with the shorter wavelength emission band is closer to the exciting star than the one with the longer wavelength band. The higher resolution of the NGC 1333 SVS3 spectrum shows that the centroid appears to shift because the 7.7 μm emission band is a combination of two overlapping components, one peaking at approximately 7.65 μm and a second at 7.85 μm, the same components observed by Peeters et al. (2002) and Bregman (1989) in planetary nebulae (7.85 μm) and H ii regions (7.65 μm). The 7.85 μm component is stronger toward the edges of the nebulae, resulting in an apparent shift of the 7.7 μm centroid to longer wavelengths.

To explore how the center wavelength of the 7.7 μm band varies within these reflection nebulae, we fitted the spectrum at each point in vdB 133, vdB 17, and NGC 1333 SVS3 with a...
combination of a Gaussian and quadratic extending from 7.0 to 8.3 μm using the gaussfit routine in IDL. The quadratic fits the slope in the data points shortward and longward of the emission band to form a pseudocontinuum that the Gaussian rides on. We use the center wavelength of the Gaussian as the centroid of the emission feature.

3.2. Measuring Feature Strengths

The emission spectra of the reflection nebulae shown in Figure 2 consists of three components, narrow emission features due to PAH molecules, broad features (6–9 and 11–14 μm) due to the overlap of individual emission bands from a collection of PAHs, very large PAHs or PAH clusters, and a continuum rising to longer wavelengths attributed to very small grains (Sellgren et al. 1985; Cesarsky et al. 2000; Bregman et al. 1989). Separating the components is difficult, since the intrinsic band shapes are unknown. However, it is clear from examining the data that the emission at 7, 10, and 15 μm does not decrease as quickly with increasing distance from the exciting stars as the narrow band emission. In the fainter outer regions of the nebulae, incorrect zodiacal light subtraction also contributes to this “continuum.”

Since we are interested in the response of PAH ionization to a changing UV field, we have chosen to only include emission above a continuum level defined by fitting straight line segments between data points centered at 5.8, 7.0, 9.3, 10.0, and 14.9 μm. This procedure removes both the contribution from very small grains and any residual spectral structure in the sky background that could affect the accuracy of the band intensities, primarily in the low-intensity regions of the nebulae.

In vdB 17, we compared band ratios derived by integrating the band intensities of the 7.7 and 11.3 μm bands with peak band intensity ratios. The integrated 7.7 μm band includes all of the flux above the continuum between 6.8 and 9.1 μm, and the integrated 11.3 μm band includes the flux between 10.4 and 11.9 μm. Figure 3 shows a comparison of the 11.3/7.7 μm intensity ratio as a function of distance from the exciting star. Each point is an average of 10 pixels, and the error bars show the standard errors. Both methods produce curves with similar shapes for the 11.3/7.7 μm intensity ratio, and the mean error for both methods is the same (about 3%). The peak band intensities are a factor of 3.35 higher than the integrated band ratios, since the 7.7 μm band is much broader than the 11.3 μm band.

The integrated 7.7 μm band includes a band of unknown origin centered near 8 μm that increases in strength toward the edges of the nebulae, adding to the integrated flux (Uchida et al. 2000). Since both methods produce the same result, we have chosen to use peak intensity ratios to avoid possible contamination by the 8 μm feature.

3.3. Correlation of the Wavelength of the “7.7” μm Band with Other Parameters

For each location in the nebulae, there is a strong correlation between the distance from the exciting star and the wavelength of the 7.7 μm band. This is shown in Figure 4 as a function of the incident UV field, which is also a function of distance from the exciting star. The UV field intensity is generally denoted as $G_0$, where $G_0 = 1$ is the average value of the interstellar UV field and has a value of $1.6 \times 10^{-3}$ ergs s$^{-1}$ cm$^{-2}$. Determining the UV field intensity at each point in a nebula is not necessarily straightforward since there is generally no information about...
the relative positions (in three-dimensional space) of the nebula and the exciting star. In most cases, authors have chosen to use the projected distance on the sky as the true distance for calculating the UV field intensities.

In the case of vdB 17, where the exciting star appears to be centered on the nebula, Uchida et al. (2000) assumed that the exciting star was embedded within the nebula, so that the UV intensity centered on the nebula. Uchida et al. (2000) assumed that the UV intensity would decrease with distance as shown by the dashed line in Figure 5, which does not fit the data. If the star is behind the nebula, the falloff will be even faster. However, if the star is behind the nebula by a distance corresponding to 28°on the sky (2 × 10^17 cm), and the nebula is flat and of uniform density, then the intensity profile can be fitted quite well (Fig. 5, solid line). Using this geometry gives a much smaller range for the intensity profile can be fitted quite well (Fig. 5, solid line). Using this geometry gives a much smaller range than that assumed by Uchida et al. (2000). Both geometries give low values of the absolute magnitude (Fig. 5) and NVSS3. Each point shown is the average of 10 original data points, and the error bars are the standard error in each group of 10.

The wavelength of the 7.7 μm band also correlates well with both visible light (from the Palomar digital sky survey) and at the peak of the 7.7 μm band. The dashed line shows the intensity profile expected for a uniform density sphere with the exciting star at the center, while the solid line shows the intensity profile expected for a star behind a scattering layer.

4. DISCUSSION

Since the UV intensity changes by 2 orders of magnitude within each reflection nebula, and since the ratio of the UV intensity to the electron density, G0/n_e, determines the PAH ionization state, it is necessary to estimate both G0 and n_e within the nebulae before we can examine whether changes in the PAH ionization as a function of position within the nebulae can account for the observations. In the following sections, we first discuss how we determined G0 and n_e for the nebulae, then model the observations in two different ways.

4.1. Expected Ionization State of the PAHs

The PAH ionization state within a reflection nebula is a function of the ratio of the UV intensity to the electron density. The UV intensity is a function of the nebular geometry and the spectral type of the illuminating star, and the electron density can be determined roughly for these reflection nebulae by estimating the density of the gas within the nebulae. Joblin et al. (1996b) give an electron density of 15 e^- cm^-3 in NGC 1333 SVS3 based on a C/H ratio of 3 × 10^-4, assuming that all of the electrons would come from ionization of neutral carbon, and an estimate of the gas density based on H_2 emission (Joblin et al. 1996a). Owl et al. (2002) derive a density for SVS3 of 2 × 10^4 (n_e = 6 cm^-3) based on a PDR model and far-IR measurements centered at the far-IR peak intensity.

In the reflection nebula vdB 17 (also in the NGC 1333 region), the density can be estimated from the extinction through the nebula. Racine (1968) gives E(B - V) = 0.6 for vdB 17, so that A_v = 1.8 mag. Using the canonical column density value of N_H/A_v = 1.9 × 10^21 cm^-2 mag^-1 gives N_H = 3.4 × 10^21 cm^-2 along the line of sight to the star in vdB 17. We can derive a lower limit to the density by assuming that the nebula is spherical. The nebula has an apparent diameter of 100°, corresponding to 7.5 × 10^17 cm at a distance of 500 pc (Strom et al. 1974). The average density is then 9.1 × 10^3 cm^-3, and the electron density (also assuming that the electrons are from carbon ionization) will be 2.7 cm^-3. We already have stated that the exciting star is 28°behind the scattering nebulousness, so it is very likely that the thickness of the nebula along the line of sight is substantially

![Figure 5](image-url) Figure 5. — Radial brightness profile of a north-south cut through vdB 17 in both visible light (from the Palomar digital sky survey) and at the peak of the 7.7 μm band. The dashed line shows the intensity profile expected for a uniform density sphere with the exciting star in the center, while the solid line shows the intensity profile expected for a star behind a scattering layer.

![Figure 6](image-url) Figure 6. — Correlation of the intensity ratio of the 11.3 and 7.7 μm bands compared to the center wavelength of the 7.7 μm band for vdB 133, vdB 17, and SVS3. Each point shown is the average of 10 original data points, and the error bars are the standard error in each group of 10.
less than 100″, perhaps by an order of magnitude, and that the
electron density is correspondingly higher. Martini et al. (1999)
derive a density of ~1 × 10^4 cm^{-3} (n_e = 3 cm^{-3}) for vdB 17
based on molecular hydrogen line ratios. Warin et al. (1996)
derive a density of 3 × 10^3 to 5 × 10^4 cm^{-3} (n_e = 0.9–15 cm^{-3})
based on CO line observations. Thus, while the electron density
in vdB 17 is uncertain, it is probably in the range of 1–10 cm^{-3},
and we use 1 cm^{-3} for the following discussion.

For vdB 133, Li & Draine (2002) derive an electron density of
0.3 cm^{-3} based on a model fit to the PAH emission spectrum.
We can estimate the average density in the same manner
as we did for vdB 17, using the reddening to the nebula and
its apparent size. Racine (1968) gives E(B − V) = 0.65, the
apparent projected extent of the nebulousity in the infrared is 120″,
and it is at a distance of 1400 pc (Humphreys 1978). Assuming
that the nebula has the same extent along the line of sight as in
the plane of the sky gives an average density of 1.4 × 10^4 cm^{-3}
and n_e = 0.4 cm^{-3}. While both of these values are uncertain,
we do not have any better methods of estimating the density in
vdB 133, and will adopt a value of n_e = 0.3 cm^{-3} for the following
discussion.

Using the value of G_0 for SVS3 given by Joblin et al. (1996a)
and those given by Uchida et al. (2000) for vdB 17 and vdB 133,
we can calculate G_0/n_e as a function of distance in the nebulae.
Figure 7 shows the 11.3/7.7 μm band ratio as a function of G_0/n_e
for the three nebulae. Each data point is an average of 10 pixels
and the error bars show the standard error of each group of 10.
A constant value of 0.5 has been added to the SVS3 data for
display purposes since it overlaps the data from the other two
nebulae. Qualitatively, the observed trend is as expected for the
11.3/7.7 μm band ratio since as G_0/n_e increases, PAHs should
transition from anions through neutrals to cations. Bakes et al.
(2001) show that the strength of the 7.7 μm band is a slowly
changing function of G_0/n_e, with a value 30% larger at G_0/n_e = 10
than at G_0/n_e = 1 × 10^4. Their result is also consistent with
our observation that the 7.7 μm band tracks the scattered light
intensity in vdB 17 (Fig. 5), which requires that most of the
observed variation in the 7.7 μm band intensity be due to re-
emission of absorbed radiation rather than abundance vari-
ations. The 11.3 μm band is strongest in neutral PAHs, so that
the observed peak in the 11.3/7.7 μm band ratio at G_0/n_e = 100
can be interpreted as the value of G_0/n_e where there is a max-
imum in the abundance of neutral PAHs. This is about a factor
of 4 lower than calculated by Bakes et al. (2001), which can
simply be the result of Bakes et al. using too large a value for the
PAH^{+} recombination coefficient. Chan et al. (2001) also prefer-
a low value for the recombination coefficient based on their
measurements of relative PAH band intensities in the diffuse
ISM. Thus, as G_0/n_e decreases from 1000 to 100, the cation-to-
neutral ratio drops. Below G_0/n_e = 100, anions are forming and
the 11.3/7.7 μm band ratio decreases. If this interpretation is
correct, then it appears that PAHs transition almost directly
from cations to anions with only a narrow range of G_0/n_e where
neutral PAHs are present, and that the abundance of neutral
PAHs is never very high. This could also explain why the PAH
emission spectrum does not change very much from object to
object, as the anion and cation spectra are very similar in the
mid-IR. However, even if the abundance of neutral PAHs is
never very high, they can contribute significantly to the 11–14 μm
emission, since these bands are much stronger in neutral PAHs
than in PAH ions.

Figure 8 shows the 7.7 μm centroid plotted as a function of
G_0/n_e, where each point plotted is the average of 10 pixels.
The coincidence of the vdB 133 and SVS3 curves and the near
coincidence (within a factor of 2 in G_0/n_e) of the vdB 17 curve
can be explained if the process that causes the band centroid to
shift is a chemical equilibrium process. An example of such a
process is detailed in the next section.

4.2. Modeling the PAH Emission Process 1: The Wavelength
of the 7.7 μm Band as an Indicator
of the Anion/Cation Ratio

To explain the observed behavior, we can construct a simple
model in which we assume that anions have an emission band at
7.85 μm while cations have an emission band at 7.65 μm. Then
we calculate the ionization balance between anions and neutrals
and cations separately assuming ionization equilibrium. Following
Verstraete et al. (1990), the ionization balance between neutrals and cations can be expressed as

\[ n_a r_a G_0 = n_+ n_e k_+ \]  

(1)

where n_a is the number of neutral PAHs, r_a is the ionization rate
coefficient for neutral PAHs, n_+ is the number of singly ionized
PAHs, n_e is the electron density, and k_+ is the recombination
coefficient for singly ionized PAHs. The ionization balance
between anions and neutrals can be described by a similar equation.
Rearranging the equation gives an expression for the fraction of PAHs that are singly ionized \((f_+)\):

\[
f_+ = \frac{G_0}{G_0 + n_e k_+},
\]

where \(K_+ = k_+/r_n\). The fraction of anions \((f_-)\) is

\[
f_- = \frac{n_e}{n_e + G_0 K_-},
\]

where \(K_- = r_-/k_0\), \(r_-\) is the rate for removing an electron from anionic PAHs, and \(k_0\) is the attachment rate for electrons to neutral PAHs. The centroid of the 7.7 \(\mu\)m band \((\lambda_c)\) is then

\[
\lambda_c = \frac{7.65 f_+ + 7.85 f_-}{f_+ + f_-}.
\]

For a PAH molecule with 80 carbon atoms, Verstraete et al. (1990) give \(r_n = 3.2 \times 10^{-8} \text{ s}^{-1}\). Using this value, we then adjusted \(k_+\) and the ratio \(r_-/k_0\) until the 7.7 \(\mu\)m centroid calculated as a function of \(G_0/n_e\) fitted the data (Fig. 9, solid line). The fit requires a value for \(k_+\) of 3.2 \(\times\) 10\(^{-6}\) cm\(^3\)s\(^{-1}\), a factor of 2 less than that given by Verstraete et al. (1990), and a value of 1.8 \(\times\) 10\(^{-2}\) cm\(^3\) s\(^{-1}\) for \(r_-/k_0\), a factor of 3 less than the estimate given by Le Page et al. (2001). Using these parameters, we calculated \(f_+\) and \(f_-\) as a function of \(G_0/n_e\), and the neutral fraction \((f_0)\) as \(1 - f_+ - f_-\).

Given the PAH ionization state as a function of \(G_0/n_e\), we can also calculate the 11.3/7.7 \(\mu\)m ratio as a function of \(G_0/n_e\) if we know the intrinsic 7.7 and 11.3 \(\mu\)m band strengths for anions, neutrals, and cations. The intrinsic band strengths are the average for the entire PAH population weighted by the abundance of each PAH, and will depend on the PAH mix present in each object and on the spectrum of the exciting UV field. For this calculation, we assume that the PAH mix does not change within an object, and that the intrinsic band strengths are the same as those calculated by Bakes et al. (2001). Then, the 11.3/7.7 \(\mu\)m ratio is

\[
\frac{I_{11.3}}{I_{7.7}} = \frac{0.59 f_- + 4.0 f_0 + 1.2 f_+}{1.2 f_- + 0.62 f_0 + 1.6 f_+}
\]

and is shown as the solid line in Figure 10 along with the data from the reflection nebulae. In addition, the dashed line shows the effects of reducing the intrinsic 11.3 \(\mu\)m band intrinsic strength by 20%. The agreement between the model and the data is fairly good, especially since we did not adjust any of the intrinsic band strengths to create a better fit (for example, a small decrease in the intrinsic 11.3/7.7 \(\mu\)m band ratio for cations would result in a better fit for points with \(G_0/n_e\) greater than 200 and a small increase for neutrals would give a better fit near \(G_0/n_e = 100\)). The three points plotted at the lowest values of \(G_0/n_e\) do not fit the model very well, but we have made the assumption here that the density is constant within the entire nebula and that there is no UV extinction internal to the nebula.

4.3. Modeling the PAH Emission Process 2: The Wavelength of the 7.7 \(\mu\)m Band as an Indicator of PAH Processing

A second model that could fit the data assumes that the position of the 7.7 \(\mu\)m band depends on the physical nature of the emitting PAHs rather than on the ionization state of the PAHs. Hony et al. (2001) suggested that PAH molecules are eroded by exposure to the interstellar UV field, and these physical changes are reflected in the relative strengths of the C–H out-of-plane bending modes. It is possible that the same physical changes cause the 7.7 \(\mu\)m band to shift from 7.85 \(\mu\)m, as observed in planetary nebulae, to 7.65 \(\mu\)m, as observed in H II regions. The outer regions of reflection nebulae, where the band centroid is closer to 7.85 \(\mu\)m, would contain a larger fraction of less eroded PAHs than the regions closer to the exciting star where the UV intensity is higher.

The molecular clouds from which reflection nebulae are born are formed from the gas and dust of the ISM, and in the scenario we are considering here, the PAHs leaving these clouds have a 7.7 \(\mu\)m band centered near 7.85 \(\mu\)m. We can determine the wavelength of the 7.7 \(\mu\)m band for PAHs entering these clouds by examining the spectra of PAHs in the diffuse ISM. Mattila et al. (1996) used the ISOPHOT spectrometer (PHT-S) to take spectra of the galactic plane along lines of sight that avoided bright IR emission and optically bright stars. We averaged spectra taken at \((l, b)\) of \((-45^\circ, 0^\circ), (-30^\circ, 0^\circ), (-15^\circ, 0^\circ), (-15^\circ, 1^\circ), (-5^\circ, 0^\circ), and (+30^\circ, 0^\circ), all regions with obvious PAH emission, to produce the spectrum shown in Figure 11. Using these data, we determined the position of the 7.7 \(\mu\)m band in the diffuse ISM, finding that its centroid occurs at 7.67 \(\mu\)m, the same wavelength (within the precision possible with the low resolution spectra from ISOPHOT) as found in H II regions and reflection nebulae, implying that material entering H II regions...
and the dark clouds from which reflection nebulae form have 7.7 μm bands near 7.65 μm. In this model, PAHs are chemically altered during the time that the PAH molecules reside within the dark cloud, and molecules are formed that are similar to the fresh PAHs observed around planetary nebulae. It is these chemically altered molecules that have a strong 7.85 μm band and are most abundant at positions in the reflection nebulae that are farthest from the exciting stars, and thus have suffered the least amount of cumulative UV exposure. Nearer to the exciting stars, the PAHs are processed as they are during residence in the ISM, and the 7.65 μm band becomes more prominent. Figure 4 shows that as the UV field intensity increases, the centroid shifts to shorter wavelengths. For vdB 133, the band centroid shift occurs as $G_0$ increases from 20 to about 100, but then remains constant at about 7.65 μm for larger values of $G_0$, while in SVS3, the transition to a constant value occurs at about a $G_0$ of 700. This is the behavior expected if the PAHs are fully reprocessed by the UV exposure for intensities above $G_0 = 100$ (for vdB 133, or 700 for SVS3) since once all the material is converted to the form with a strong 7.65 μm band, it will not appear to shift any further. The behavior in vdB 17 mirrors that in vdB 133. If the above explanation is correct, then we expect that the UV exposure that PAHs experience before they are ejected into the ISM plus the exposure within the ISM should be comparable to the exposure they suffer in these reflection nebulae. Assuming a residence time in the ISM of $1 \times 10^7$ yr, and where by definition $G_0 = 1$, the total UV exposure can be expressed as the product of these two values, or $1 \times 10^7$ in units of $G_0$ yr. The UV exposure of a PAH before it is ejected from a planetary nebula is more difficult to estimate. PAHs are likely formed during the mass-loss phase of carbon-rich stars and then modified by exposure to UV radiation to produce the PAH spectrum characteristic of planetary nebulae. The 7.85 μm component is usually stronger than the 7.65 μm component in planetary nebulae, but there is a wide range observed in the ratio of the two components. For example, in BD +30°3639 the 7.85 μm component is dominant while in NGC 7027, the two components are almost of equal strength (Peeters et al. 2002). The emitting PAHs are at the edges of the ionized region (within the surrounding photodissociation region), and if they have experienced the same UV field for the lifetime of the nebulae, then the total UV exposure in the two objects is similar ($\sim 5 \times 10^7 G_0$ yr). However, the actual exposure is certainly less than this value since in the past the ionized region was smaller and the PAHs that are now visible were shielded by material closer to the central star. Thus, the PAHs that are present in the ISM likely have a cumulative UV exposure of a few times $10^7 G_0$ yr.

To determine the UV exposure of PAHs in the reflection nebulae, it is necessary to estimate the age of the nebulae. Both vdB 17 and SVS3 are in the NGC 1333 complex, which includes a star cluster with an age of $(1-2) \times 10^6$ yr (Lada et al. 1996). Joblin et al. (1996a) adopted an age of $1 \times 10^5$ yr for SVS3. The reflection nebulae must be somewhat younger than the stars since they formed only after the stars broke out of the dark cloud. Also, there is no reason why both nebulae should have the same age. SVS3 is more compact than vdB 17 and probably has a higher density, perhaps indicating that it is younger. Using $1 \times 10^5$ yr for the age of SVS3 gives a range for the cumulative UV exposure of the PAHs of $1 \times 10^4$ to $1 \times 10^5$ for $G_0 = 100 - 10,000$, with the PAHs showing no change in the 7.7 μm centroid position above $G_0 = 700$, corresponding to a UV exposure of $7 \times 10^4 G_0$ yr. For vdB 17, an age of $1 \times 10^5$ yr gives an exposure of from $2 \times 10^4$ to $2 \times 10^5 G_0$ yr for $G_0 = 20 - 200$, and an exposure 10 times higher if the age is $1 \times 10^6$ yr. In both of these objects, the cumulative UV exposure of the PAHs is comparable to the UV exposure of PAHs in the diffuse ISM. The near coincidence of vdB 17 and vdB 133 in Figure 4 then implies that these two objects have similar ages.

Figure 12 shows two model fits to the 7.7 μm centroid as a function of $G_0/n_e$. If UV processing of the PAHs causes the wavelength shift, then the shift could be linear with $G_0/n_e$ time) if it is due to an irreversible reaction (dotted line) such as loss of side groups (Joblin et al. 1996a). However, in this case the co-alignment of the curves when plotted versus $G_0/n_e$ would not be expected unless density is linearly related to the age of the nebulae. If the shift is due to a reversible reaction (i.e., loss of H), then it should scale as $G_0/n_e$ and follow the solid curve. Thus, while this curve may not fit as well as a linear fit, the co-alignment of the data from the three nebulae is a consequence of the equilibrium reaction process. In this plot, the vdB 17 data has been shifted to larger $G_0/n_e$ by about a factor of 2, which is equivalent to lowering the density by a factor of 2.

4.4. Comparison of the Models

Changes in the ionization balance of PAHs provides a good explanation for the changing ratio of the 11.3 to 7.7 μm features, and this explanation is supported by models (Bakes et al. 2001) and from fitting laboratory spectra to astronomical...
Joblin et al. (1996a) showed that the 3.4 μm band is due to -CH₃ side groups on PAH molecules that are lost upon exposure to UV radiation with a corresponding decrease in the 3.4/3.3 μm band intensity ratio. Thus, Figure 13 shows that chemical evolution of PAH molecules and the ionization state of the molecules can be well correlated. We conclude that the present data does not rule out either explanation.

5. CONCLUSIONS

We have observed a shift in the central wavelength of the 7.7 μm band within three reflection nebulae. Previous observations had established that the 7.7 μm band has a strong component near 7.85 μm in fresh PAH material (e.g., around planetary nebulae), while PAHs that have been exposed to the UV of the ISM for long periods (e.g., H II regions, diffuse ISM) are dominated by a band near 7.65 μm. In the reflection nebulae studied here, the wavelength of the feature occurs at longer wavelengths at points distant from the exciting stars in the nebulae, and at progressively shorter wavelengths for points closer to the stars. We also observe that the 11.3/7.7 μm band ratio changes as a function of $G_0/n_e$ in a manner consistent with changes in PAH ionization.

The shift of the 7.7 μm band position can be explained either as a result of changes in the anion to cation ratio (assuming that anions have a strong band at 7.85 μm and cations have a strong band at 7.65 μm) or as an indicator of UV processing of the PAH mixture. In the second scenario, PAHs enter a dark cloud with a 7.65 μm band center and are chemically processed on grain surfaces, causing a shift of the band to 7.85 μm. Upon exposure to UV radiation, the PAHs are modified back to the form they had in the diffuse ISM, and the band shifts back to 7.65 μm.

We wish to thank Lou Allamandola, Max Bernstein, Doug HUDGINS, and Greg Sloan for their helpful comments.

REFERENCES

Abouelaziz, H., Gomet, J. C., Pasquerault, D., Rowe, B. R., & Mitchell, J. B. A. 1993, J. Chem. Phys., 99, 237
Allamandola, L. J., Hudgins, D. M., & Sandford, S. A. 1999, ApJ, 511, L115
Allamandola, L. J., Tielens, A. G. G. M., & Barker, J. R. 1985, ApJ, 290, L25
Bakes, E. L. O., Tielens, A. G. G. M., & Bauschlicher, C. W., Jr. 2001, ApJ, 556, 501
Bernstein, M. P., Esilis, J. E., Dworkin, J. P., Sandford, S. A., Allamandola, L. J., & Zare, R. N. 2002, ApJ, 576, 1115
Bregman, J. D., & Temi, P. 1996, A&A, 315, L32
Brooke, T. Y., Sellgren, K., & DePoy, D. L. 1999, ApJ, 526, 772
Cesarsky, C. J., et al. 1996, A&A, 315, L32
Chas, D., & Guibert, E. 1996, ApJ, 459, 209
Cesarsky, C. J., & et al. 1996, A&A, 315, L32
Derek, D., Lequeux, J., Ryter, C., & Girin, M. 2000, A&A, 354, L87
Chan, K. W., et al. 2001, ApJ, 546, 273
Cohen, M., Tielens, A. G. M., Bregman, J., Witteborn, F. C., Rank, D. M., Allamandola, L. J., Wooden, D., & Jourdain de Muizon, M. 1989, ApJ, 341, 246
Genzel, R. et al. 1998, ApJ, 498, 579
Hony, S., Van Kerkhoven, C., Peeters, E., Tielens, A. G. G. M., Hudgins, D. M., & Allamandola, L. J. 2001, A&A, 370, 1030
Humphreys, R. M. 1978, ApJS, 38, 309
Joblin, C., Tielens, A. G. G. M., Allamandola, L. J., & Geballe, T. R. 1996a, ApJ, 458, 610
Joblin, C., Tielens, A. G. G. M., Geballe, T. R., & Wooden, D. H. 1996b, ApJ, 460, L119
Kessler, M. F., et al. 1996, A&A, 315, L27
Lada, C. J., Alves, J., & Lada, E. A. 1996, AJ, 111, 1964
Leger, A., & Puget, J. L. 1984, A&A, 137, L5
Le Page, V., Snow, T. P., & Bierbaum, V. M. 2001, ApJS, 132, 233
Li, A., & Drain, B. D. 2002, ApJ, 572, 232
Martini, P., Sellgren, K., & DePoy, D. L. 1999, ApJ, 526, 772
Mattila, K., Lemke, D., Haikala, L. K., Laureijs, R. J., Leger, A., Lehtinen, K., Leinert, C., & Mezger, P. G. 1996, A&A, 315, L353
Ott, S., et al. 1997, in ASP Conf. Ser. 125, Astronomical Data Analysis Software and Systems VI, ed. G. Hunt & H. E. Payne (San Francisco: ASP), 34
Peeters, E., Hony, S., Van Kerkhoven, C., Tielens, A. G. G. M., Allamandola, L. J., Hudgins, D. M., & Bauschlicher, C. W. 2002, A&A, 390, 1089
Racine, R. 1968, AJ, 73, 233
Roche, P. F., Aitken, D. K., Smith, C. H., & Ward, M. 1991, MNRAS, 248, 606
Sellgren, K., Allamandola, L. J., Bregman, J. D., Werner, M. W., & Wooden, D. H. 1985, ApJ, 299, 416
Sellgren, K., Brooke, T. Y., Smith, R. G., & Geballe, T. R. 1995, ApJ, 449, L69
Sloan, G. C., Bregman, J. D., Allamandola, L. J., Hayward, T. L., Devito, B., Geballe, T. R., & Woodward, C. E. 1997, BAAS, 29, 787
Strom, S. E., Grasdalen, G. L., & Strom, K. M. 1974, ApJ, 191, 111
Uchida, K. I., Sellgren, K., Werner, M. W., & Houdashelt, M. L. 2000, ApJ, 530, 817
Verstraete, L., Leger, A., d’Hendecourt, L., Deforouche, D., & Dutil, O. 1990, A&A, 237, 436
Warin, S., Castets, A., Langer, W. D., Wilson, R. W., & Pagani, L. 1996, A&A, 306, 935
Witt, A. N., & Schild, R. E. 1986, ApJS, 62, 839
Young Owl, R. C., Meixner, M. M., Fong, D., Haas, M. R., Rudolph, A. L., & Tielens, A. G. M. 2002, ApJ, 578, 885