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DETECTION OF THE OVERTONE OF THE 3.3 MICRON EMISSION FEATURE IN IRAS 21282+5050

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ABSTRACT

The 1.6–1.8 μm spectrum of the planetary nebula, IRAS 21282+5050, a strong emitter of the unidentified interstellar bands, contains a 0.02 μm wide emission feature centered at 1.680 μm, which is well matched by laboratory spectra of the 0–2 CH stretching mode in polycyclic aromatic hydrocarbons. We identify the new feature as the overtone of the well-known 3.3 μm band. In view of the high excitation required for emission in this band, the identification indicates that the emission is by free molecules rather than molecular moieties in solid dust grains. Modeling of the intensity ratio of the 2–0 to 1–0 band implies that the PAHs emitting in these bands contain about 60 carbon atoms. It is inferred that the $v = 2$–1 hot band of the CH stretching mode occurs at about 3.43 μm and contributes to the long-wavelength shoulder of the 3.40 μm feature. The main 3.40 μm feature probably is due to aliphatic sidegroups on PAH molecules.

Subject headings: infrared: ISM: lines and bands — ISM: molecules — planetary nebulae: individual (IRAS 21282+5050)

1. INTRODUCTION

The well-known unidentified infrared (UIR) emission band at 3.3 μm is generally attributed to the CH stretching mode of aromatic hydrocarbons (Duley & Williams 1981). It has been proposed that these either are in the form of free molecules, especially polycyclic aromatic hydrocarbons (PAHs) (Léger & Puget 1984; Allamandola, Tielens, & Barker 1985), or are in small dust grains (Sakata et al. 1984, 1987; Borghesi, Bussoletti, & Colangeli 1987; Papoular et al. 1989). If the carriers of the 3.3 μm band are free molecules, hot band transitions (e.g., $v = 2$–1, 3–2) are expected to be observable in the 3.4–3.6 μm region (Barker, Allamandola, & Tielens 1987). In several astronomical objects, satellite bands and an emission "plateau" in this wavelength interval are associated with the 3.3 μm feature (Geballe et al. 1985; de Muizon et al. 1986). However, precise identifications for these bands cannot be made easily, as the anharmonicity of the carrier has not been known and emission features due to aliphatic sidegroups such as $-CH_2$ and $-CH_3$ also occur in this region (Jourdain de Muizon et al. 1990), as does the ^{13}CH stretch (at 3.43 μm).

The principal satellite band of the 3.3 μm feature is located at 3.40 μm. If this feature is the 2–1 transition, then a band corresponding to the overtone ($v = 2$–0) transition should occur at about 1.67 μm. Magazzù & Strazzulla (1992), and Siebenmorgen & Peletier (1993) have reported upper limits for the overtone in Hb 5, the Orion Bar, He 2-177, and HD 44179, corresponding to fluxes typically 50 times less than those of the 3.40 μm features. Magazzù & Strazulla suggest that a weak feature at 3.46 μm is the 2–1 band, which, if correct, implies that the overtone occurs at 1.69 μm.

Recent laboratory measurements of several small PAHs at high temperatures (800 K) show that the overtone band is a broad feature (0.025 μm wide) centered at about 1.68 μm (Joblin 1992; Joblin, d'Hendecourt, & Léger 1994 hereafter JHL94). We have searched for this feature in the planetary nebula IRAS 21282+5050. For several reasons this object is one of the best in which to search for the overtone. It has a strong 3.3 μm feature and several prominent satellite bands with relatively high equivalent widths (de Muizon et al. 1986; Nagata et al. 1987; Jourdain de Muizon et al. 1990), as well as other UIR bands in the 5–13 μm region (Cohen et al. 1994). Emission (especially hydrogen recombination) lines are weak. Finally, the $^{12}C/^{13}C$ ratio is very high (Likkel et al. 1988), so that it is unlikely that CH vibrations involving ^{13}C are significant spectral contaminants.

2. OBSERVATIONS AND DATA REDUCTION

Spectra of the IRAS 21282+5050 and calibration stars were obtained on 1992 July 25 (UT) at the United Kingdom 3.8 m telescope, using the facility cold grating spectrometer, CGS4. Skies were clear but the visual seeing was poor (1″–2″) during the observations. The spectrometer employed a 58 × 62 InSb array, a 75 l/mm grating used in first order and optics that provided spectral coverage of 0.2 μm, resolution of 0.0030 μm, and 1″.5 pixels. A 1″.5 wide-slit, oriented NS was used. Spectra were sampled every one-third resolution element. Comparison sky spectra were obtained by nodding the telescope so that each object was measured successively in two rows of the array, separated by 14″ (9 rows). The total exposure time for the spectrum of IRAS 21282+5050 was 24 minutes.

A spectrum of an argon arc lamp provided wavelength calibration accurate to 0.0002 μm. Flux calibration and correction for telluric absorption features were obtained by observations of BS 8025, whose continuum was assumed to be that of a 7300 K blackbody and whose H magnitude was estimated to be 5.35 by comparison to BS 8538. Hydrogen Brackett series absorption lines in its spectrum were removed artificially prior to ratioing.

3. RESULTS

The resultant spectrum of the central 1″.5 of IRAS 21282+5050 contains weak and unresolved Brackett series

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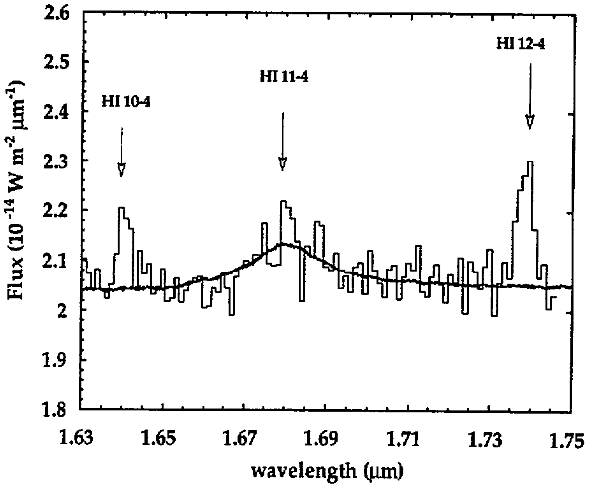

FIG. 1.—The 1.63–1.75 μm spectrum of IRAS 21282+5050 and a laboratory absorption spectrum of the 0–2 CH stretch in gas-phase pyrene ($C_{16}H_{10}$) at 800 K (Joblin 1992; JHL94). The astronomical spectrum (*thin line*) is the sum of the two spectra obtained at 1".5 N and 1".5 S of the central object. In addition to the broad 1.68 μm feature, the spectrum also shows hydrogen recombination lines (Brackett lines) at 1.641, 1.681, and 1.737 μm. Noise may be estimated by point-to-point variations.

lines in emission and marginal evidence for a broader emission feature centered roughly at the wavelength of Br 11–4 at 1.681 μm, all superposed on a bright continuum. At positions 1".5 north and 1".5 south of the center, the continuum is much weaker and all of the above features, especially the broad emission, are more prominent. Figure 1 shows the sum of the spectra at these two positions. The broad emission feature is centered at 1.680 μm (5950 cm^{-1}), is above the continuum by about 5%, and extends from roughly 1.668 to 1.692 μm. The integrated intensity above the continuum is 1.44×10^{-17} W m^{-2}. After subtracting the contribution of Br 11–4, determined by averaging the observed strengths of Br 10–4 (1.641 μm) and Br 12–4 (1.737 μm), the flux in the feature is 0.8×10^{-17} W m^{-2}. Alternatively, if the observed strength of Br 11–4 (above a smooth fit to the feature) is subtracted, the flux is 1.1×10^{-17} W m^{-2}. For the remainder of this *Letter* we adopt $0.9 \pm 0.2 \times 10^{-17}$ W m^{-2} for the flux of the broad feature in Figure 1.

The low signal-to-noise ratio and the uncertainty in removing the contribution of Br 11–4 limit the ability to determine accurately the shape of the broad feature in IRAS 21282+5050. It appears, however, that the emission feature is not as strongly peaked as either the 3.3 or 3.40 μm UIR features.

We note that a weak and broad emission feature centered at 1.677 μm is present in the spectrum of HD 44179 published by Siebenmorgen & Peletier (1993). Those authors doubt its reality. However, in view of its close proximity in wavelength to the emission feature detected in IRAS 21282+5050, it may be that the emission feature in HD 44179 is real.

4. DISCUSSION

4.1. *Identification*

The 0–1 and 0–2 CH stretching bands in small free PAHs have been observed in the laboratory to occur near 3.28 and 1.68 μm (Joblin 1992; JHL 1994). In these laboratory experiments the molecules were evaporated in an oven and thermally excited at temperatures $T \leq 800$ K. At such temperatures the $v = 1$ and 2 levels are only slightly populated, and hence emission from them and $v = 1$–2 absorption were not detected. However, the fundamental and overtone absorption bands (0–1 and 0–2) were detected. In Figure 1 the laboratory absorption spectrum of gas-phase pyrene ($C_{16}H_{10}$) at 800 K is shown in the spectral region of interest; the agreement with the feature in IRAS 21282+5050 is good. Although the precise wavelengths of the 1–0 and 2–0 CH stretching bands depend on the structure (size) and excitation of the particular molecule, similarly good fits can be obtained with other PAHs at somewhat different temperatures. We conclude that the 1.68 μm feature in IRAS 21282+5050 is the 2–0 CH stretch.

For pyrene the peak of the 0–1 CH stretch was measured at 3046 cm^{-1} (3.283 μm), which does not correspond exactly to the peak emission in IRAS 21282+5050 (3036 cm^{-1}, 3.294 μm; Jourdain de Muizon et al. 1990). Thus pyrene at 800 K is not the principal carrier of the UIR bands in IRAS 21282+5050, as it has neither the observed 1–0 frequency nor the correct anharmonicity. The different anharmonicities (140 cm^{-1} for pyrene, 120 cm^{-1} for the carrier of the features in IRAS 21282+5050) are not surprising, because anharmonicity is size dependent and the calculated size of the interstellar carrier is considerably larger than pyrene (see below). Future laboratory spectra of larger PAHs will help to put further constraints on the size of the emitting species.

In the harmonic approximation the 2–0 transition is forbidden in symmetric molecules. It has been argued recently that any broad emission features found near 1.7 μm will not be due to the CH overtone, but instead will be due to combination bands (Duley 1994). However, the CH stretching mode is highly anharmonic, and its overtone band will be perturbed into activity even for highly symmetric molecules. For example, extensive laboratory studies of benzene have conclusively demonstrated that its band at 1.674 μm is due to the CH overtone (Reddy, Heller, & Berry 1982). The integrated intensity of this transition agrees well with the above-described laboratory studies, lending further support to the assignment of the laboratory band to the CH stretch overtone.

4.2. *Constraints*

The detection of the overtone of the CH stretch in IRAS 21282+5050 provides new constraints on the carriers of the UIR bands. One fundamental question has been whether the UIR features are emitted by free molecules or by molecules in dust particles. Equilibrium dust grain temperatures at the distance from the central source where the 2–0 emission is detected are too low for the $v = 2$ level of the CH stretch, 6000 cm^{-1} above the ground state, to be significantly populated (see Cohen & Jones 1987 for estimates of the luminosity of and distance to IRAS 21282+5050). In addition, following the absorption of a single UV photon by a dust grain, even a small fractional population of the $v = 2$ level requires extreme localization of excitation during the time interval between absorption and radiative relaxation, which is untenable. Thus, the measured strength of the 1.68 μm band cannot be easily reconciled with the dust grain hypothesis. However, for properly sized free molecules, significant population of the $v = 2$ level will occur following UV absorption, as discussed below. Thus, subject to this size constraint, the detection is consistent with the emitting molecules being free.

The size of the emitting molecules is determined by the intensity ratio of the 1.68 and 3.3 μm bands. Assuming that the flux in the overtone feature is 4×10^{-16} W m^{-2} (i.e., the

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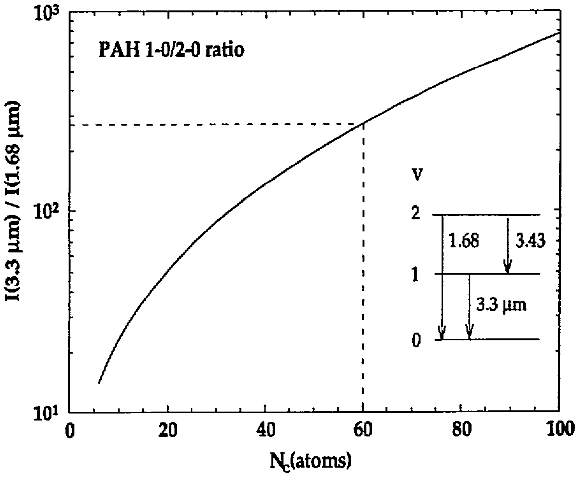

FIG. 2.—Calculated intensity ratio of the fundamental (3.3 μm) to the overtone (1.68 μm) band as a function of the number of carbon atoms in the molecule (see text). The emitting PAH is assumed to have 10 eV of internal energy. The insert is a level diagram of the relevant transitions.

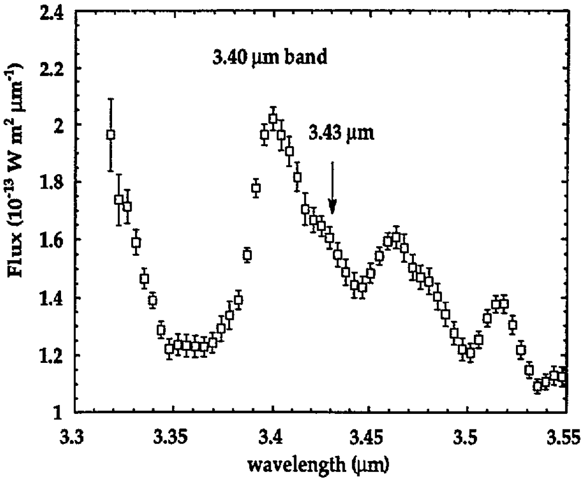

FIG. 3.—"Satellite" bands of the 3.3 μm feature in the spectrum of IRAS 21282+5050, from Jourdain de Muizon et al. (1990). The bulk of the 3.40 band is attributed to aliphatic $-CH_3$ sidegroups (Joblin 1992; JHL94); the shoulder at 3.43 μm is expected to include the 2–1 hot band of the CH stretch (this *Letter*).

surface brightness is constant over the central 3 × 3 grid of 1″.5 pixels) and using the 3.3 μm flux in a 5″ aperture (Jourdain de Muizon et al. 1990), the intensity of the 1.68 μm feature is approximately 270 times less than that the 3.3 μm feature, after correcting for reddening ($A_V = 5.8$; Cohen & Jones 1987). We have calculated the value of this ratio for different molecular sizes (Fig. 2). The intensity ratio is given by

$$\frac{I(3.3\ \mu\mathrm{m})}{I(1.68\ \mu\mathrm{m})} = \frac{A_{10}}{A_{20}} \frac{\rho_r(E_{\mathrm{UV}} - h\nu_{10})}{\rho_r(E_{\mathrm{UV}} - h\nu_{20})} \frac{h\nu_{10}}{h\nu_{20}}$$

(Allamandola, Tielens, & Barker 1989), where $\rho(E)$ is the density of states of energy E, A_{10}, and A_{20} are the Einstein coefficients, and E_{UV} is the internal energy of the system. The density of states is calculated for all modes except the emitting mode, i, which contains an energy $h\nu_{i0}$. The density of states as a function of the PAH size is given by Tielens (1993). Laboratory absorption studies show that the Einstein coefficient A_{20} is one-sixth of A_{10} for several small PAHs (JHL94), in agreement with the value for benzene (Reddy et al. 1982). This is also consistent with the intensity ratio of the 2–0 and 1–0 bands in the IR fluorescent cascade of UV-excited naphthalene (Brenner & Barker 1992). In the calculation, we assumed an internal energy of 10 eV appropriate for an exciting star of $T_{\mathrm{eff}} =$ 30,000 K, and for PAH molecules which strongly absorb in the UV (Joblin, Martin, & Léger 1992). As expected for increasing PAH size, the average excitation level decreases and hence $I(3.3)/I(1.68)$ increases (Fig. 2). The observed ratio of 270 implies a size of 60 carbon atoms for the emitting PAH. Excitation energies of 7.5 and 12.5 eV yield sizes of 50 and 70 C atoms, respectively. Similar results are obtained when using the thermal mode approximation (Léger, d'Hendecourt, & Défourneau (1990). Thus the PAHs responsible for the 1.68 μm band in IRAS 21282+5050 contain about 60 carbon atoms per molecule. The anharmonicity of the CH stretching mode in these molecules is about 120 cm $^{-1}$, which in principle can be used to identify the emitting molecules. The anharmonicity does not appear to depend on the ionization state of the molecules (Talbi, Pauzat, & Ellinger 1993).

The wavelengths of the 1–0 and 2–0 bands imply that the $v = 2$–1 hot band occurs at about 3.43 μm. The intensity of the hot band can be determined from the flux of the $v = 2$–0 feature and the previously mentioned ratio of the A coefficients for $v = 1$–0 and 2–0 transitions. We estimate that the flux of the hot band in IRAS 21282+5050 is 4.8×10^{-16} W m^{-2} in a 5″ beam which is about 0.11 of the total flux of the 3.40 μm feature (Jourdain de Muizon et al. 1990). Hence, both the wavelength of the peak and the intensity of the 3.40 μm band in IRAS 21282+5050 argue against its identification with the $v = 2$–1 transition. However, the 3.40 μm band does have a shoulder at about 3.43 μm in IRAS 21282+5050 (Fig. 3).The estimated intensity of the 2–1 band indicates that it contributes significantly to the shoulder. It is not plausible to attribute the shoulder to the CH stretching mode of ^{13}C isotopically substituted PAHs, which also occurs at 3.43 μm, because the ^{12}C/^{13}C ratio of 200 or greater derived from CO observations (Likkel et al. 1988) suggests that the UIR band-emitting region has a high ^{12}C/^{13}C ratio as well. The flux of the ^{13}CH stretch in IRAS 21282+5050 is expected to be $\lesssim 1 \times 10^{-16}$ W m^{-2}, much less than that of the 2–1 band.

5. SUMMARY

A broad emission feature centered at about 1.68 μm has been detected in IRAS 21282+5050. The new feature corresponds well in both position and shape with laboratory spectra of the overtone of the CH vibrational stretch in PAHs. This suggests that the 1.68 μm band in IRAS 21282+5050 is the 2–0 CH stretching mode of molecules responsible for the strong 3.3 μm UIR band. Both the detected strength and the off-source location of the new emission feature argue that UIR bands are due to free molecules rather than dust particles. The 2–1 hot band is expected to be centered approximately at 3.43 μm. This and its inferred strength imply that most of the flux in the 3.40 μm sàtellite of the 3.3 μm feature is not due to the hot band. We suggest that the 3.40 μm band is due largely to sidegroups on PAHs, but that the hot band contributes to its long wavelength shoulder. A mean size of about 60 carbon atoms is derived for the emitting PAHs.

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