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OVERTONE EMISSION FROM INTERSTELLAR POLYCYCLIC AROMATIC HYDROCARBONS

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ABSTRACT

The origin of 3.40 μm, 3.51 μm, and other emission lines that accompany the 3.28 μm feature observed in many nebulae is discussed. The assignment of 3.40 and 3.51 μm emission to $2 \rightarrow 1$ and $3 \rightarrow 2$ transitions, respectively, of the fundamental CH stretch in relatively small polycyclic aromatic hydrocarbon (PAH) molecules is shown to be plausible even in the absence of $2 \rightarrow 0$ 1.67 μm overtone emission if the emitters (1) have a center of symmetry and (2) are in the gas phase. An analysis of electric-dipole–allowed transitions in such molecules shows that, while the 1.67 μm $2 \rightarrow 0$ overtone is forbidden, overtones of other fundamentals should occur in this spectral region, but not generally at 1.67 μm. The $3 \rightarrow 0$ overtone of the fundamental CH stretch is allowed and would occur at $\lambda = 1.1325$ μm (8830 cm^{-1}). An emission feature at this wavelength may be present in spectra of NGC 7027 and BD +30°3639.

Subject headings: infrared: ISM: lines and bands — ISM: molecules — molecular processes

1. INTRODUCTION

Infrared spectra of UV-excited nebulae are dominated by a family of emission features at 3.3, 6.2, 7.7, 8.6, 11.3, and 12.7 μm commonly attributed to aromatic hydrocarbons (Duley & Williams 1981; Léger & Puget 1984; Allamandola, Tielens, & Barker 1985). While the precise composition of these emitters is unknown, an origin in polycyclic aromatic hydrocarbon (PAH) molecules containing two or more rings is indicated (Allamandola, Tielens, & Barker 1989; Duley & Jones 1990). A series of weaker emission features appearing in the 3.2–3.6 μm region often (but not invariably) accompany the 3.3 μm band Geballe et al. 1985; de Muizon et al. 1986; Geballe et al. 1989; Tokunaga et al. 1991). In most spectra the strongest of these features occur at 3.40 and 3.51 μm. These wavelengths lie in the range expected for emission by CH_2 and CH_3 functional groups (Duley & Williams 1981; de Muizon et al. 1986) and $\Delta v = -1$ emission from excited ($v \geq 2$) states of the aromatic CH stretching vibration (Barker, Allamandola, & Tielens 1987). Both of these models have been criticized in the light of observational (Siebenmorgen & Peletier 1993; Magazzu & Strazzula 1992) and laboratory (Sandford 1991) data.

Spectroscopic evidence against the assignment of the 3.4 μm group of emission lines to CH_3 and CH_2 groups attached to PAH rings has been summarized by Sandford (1991) and relates primarily to (1) an inconsistency in the relative abundance of aliphatic and aromatic groups and (2) the failure to detect a characteristic additional spectral line from methylated PAH molecules at 3.65 μm (2740 cm^{-1}). Evidence against the harmonic emission or hot-band model of Barker et al. (1987) involves (1) the high intensity of 3.4 μm emission relative to 3.3 μm in some sources and (2) a failure to detect overtone emission at 1.67 μm in sources with strong 3.3 μm bands (Magazzu & Strazzula 1992; Siebenmorgen & Peletier 1993).

2. ABSENCE OF A 1.67 MICRON PAH EMISSION

An assignment of 3.40 and 3.51 μm emission lines as $v = 2 \rightarrow v = 1$ and $v = 3 \rightarrow v = 2$ transitions, respectively, involving the 3.28 μm aromatic CH stretching vibration in PAH, implies that the $v = 2$ and $v = 3$ vibrational levels are significantly populated under conditions where these lines are observed. This population would be consistent with a UV excitation model in which a significant portion of the UV photon energy is converted to vibrational excitation (Allamandola et al. 1989). Under these conditions, emission is nominally expected at the wavelength of the $v = 2 \rightarrow v = 0$ transition. This wavelength is 1.67 μm (5988 cm^{-1} = 3048 + 2940 cm^{-1}). The relative intensity of the 1.67 and 3.40 μm features, $I(1.67)/I(3.40)$, has been predicted to be in the range 1 to 0.16 (Jourdain de Muizon, d'Hendecourt, & Geballe 1990; Brenner & Barker 1992), while the observational detection limit now places this ratio at $\lesssim 0.02$ (Siebenmorgen & Peletier 1993).

Since both transitions arise from the same initial state ($v = 2$),

$$\frac{I(1.67)}{I(3.40)} \propto \frac{A_{20}}{A_{21}} \frac{\nu_{20}}{\nu_{21}} = 2.04 \frac{A_{20}}{A_{21}} ,$$

where A_{20}, A_{21} are Einstein coefficients for spontaneous emission in the $2 \rightarrow 0$ and $2 \rightarrow 1$ transitions, respectively. Overtone transitions such as $2 \rightarrow 0$ are strongly forbidden in a molecule with a center of symmetry in the harmonic approximation. However, when anharmonicity is present, these transitions can become weakly allowed (Herzberg 1945). For low anharmonicity and low-amplitude vibrations (v small), selection rules based on symmetry still provide the best indication of whether or not a particular transition will be electric-dipole–allowed. In molecules with high symmetry, the 2–0 transition of allowed fundamentals will be forbidden.

This can be illustrated by referring to vibrational states in the simple PAH anthracene, $C_{14}H_{10}$, which has the point-group symmetry D_{2h}. The CH stretch fundamental occurs at 3058 cm^{-1} (3.27 μm) and corresponds to an electric-dipole–

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allowed transition from the A_{1g} ground state to an upper ($v = 1$) level with B_{2u} symmetry. The first overtone of this fundamental ($v = 0 \rightarrow v = 2$) is of symmetry $B_{2u} \times B_{2u}$ and is an electric-dipole–forbidden transition. The second overtone ($v = 0 \rightarrow v = 3$) is, however, symmetry-allowed. A similar result is obtained for all unsubstituted acenes (benzene, naphthalene, tetracene, etc.) as well as for certain acene derivatives (e.g., *p*-xylene) which have high symmetry. The 0–2 overtone of the fundamental CH stretch is also forbidden in symmetric compact PAHs such as pyrene and coronene.

While the 0–2 overtone of the CH stretch fundamental with B_{2u} symmetry is forbidden in such symmetry groups as D_{2h}, D_{6h}, and C_{2h}, CH stretch modes with other symmetries may combine to yield combination states with energies near that of the B_{2u} (0–2) overtone. In anthracene, intercombinations involving $A_{1g} \times B_{2u}$, $A_{1g} \times B_{3u}$, and $B_{1g} \times B_{3u}$ modes are connected via electric-dipole radiation to the A_{1g} ground state. Energies for these intercombination states (in the harmonic approximation) have been calculated for anthracene using the data of Sverdlov, Kovner, & Krainov (1974) and are summarized in Table 1. Actual energies are expected to be slightly increased or decreased due to anharmonicity (Talbi, Pauzat, & Ellinger 1993). These states should be populated under conditions where the $v = 2$ level of the CH IR-active mode (B_{2u}) is excited. An important conclusion to be reached at this point is that *while the* $2 \rightarrow 1$ *and* $1 \rightarrow 0$ *transitions of the IR-active* CH *fundamental appear as spectral features, the* $2 \rightarrow 0$ *transition will not be observed at an energy* (~ 5988 cm^{-1}) *equal to the sum of the* $2 \rightarrow 1$ *and* $1 \rightarrow 0$ *transitions.* Instead, emission will occur near energies of the intercombination bands of the type summarized in Table 1.

The $3 \rightarrow 0$ overtone ($B_{2u} \times B_{2u} \times B_{2u} \rightarrow A_{1g}$) of the IR-active CH stretch is electric-dipole–allowed in D_{2h} symmetry, suggesting that a search for this overtone in the spectra of nebulae with strong 3.4 and 3.5 μm emission would be appropriate even in the absence of $2 \rightarrow 0$ emission at 1.67 μm. The energy of this transition would be 8830 cm^{-1} (3040 + 2940 + 2850 cm^{-1}) which corresponds to $\lambda = 1.1325$ μm. A weak emission line near 1.31 μm does appear to be present in spectra of BD +30°3639 (Rudy et al. 1991) and NGC 7027 (Rudy et al. 1992). If this is indeed the $3 \rightarrow 0$ overtone of the CH transition, then $I(3 \rightarrow 0)/I(3 \rightarrow 2) \sim 0.18$ in BD +30°3639. This yields $A_{32}/A_{30} \sim 17$.

3. DISCUSSION

The absence of an electric-dipole–allowed $2 \rightarrow 0$ transition involving the IR active B_{2u} CH stretch can be understood if the emitter has a center of symmetry. This requirement can be met by cata-condensed PAH molecules such as the acenes and triphenylene, but not by the phenes such as phenanthrene (C_{2v} symmetry). This requirement is also met by compact symmetric pericondensed PAHs such as perylene, coronene, ovalene, and pyrene. Substitution of other functional groups at hydrogen sites will, in general, eliminate the center of symmetry, allowing the 2–0 transition to become IR-active. Certain exceptions exist, however, such as in *p*-xylene (C_{2h} symmetry). Substitution with identical groups or dehydrogenation at para-sites also maintains the center of symmetry. A failure to detect a 2–0 transition of the IR-active CH fundamental then confirms that 3.28 μm emitters are relatively small, symmetric molecules.

The 2–0 forbidden overtone can also be induced by an external perturbing electric field. This occurs, for example, in condensed media or by collision in the gas phase and is likely an important factor in the measurements of the overtone-band intensities for coronene, etc., reported by Jourdain de Muizon et al. (1990). They found that the intensity of overtones in the sequence $0 \rightarrow v$ exhibited only a modest decrease with v for molecules such as coronene sampled in the solid state. The decline in intensity with v was much more dramatic in gaseous benzene. This suggests that the absence of a 2–0 transition at 1.67 μm is indicative of emission by gas-phase molecules.

While these arguments provide support for the hot-band hypothesis for the origin of 3.40 and 3.51 μm emission, they cannot be used to exclude the possibility of additional emission by $-CH_2$ and $-CH_3$ species in this spectral region. If these groups are present, it seems reasonable that they should be attached to the PAH molecules that yield 3.28 μm emission. Sandford (1991) has concluded that such methylated PAH molecules are of low abundance in IR emission sources because of the absence of a characteristic weak feature at 2740 cm^{-1} (3.65 μm). The predicted intensity of this feature was inferred from laboratory spectra of solids and liquids and may therefore be enhanced by crystal field interaction. IR emission spectra of several gas-phase methylated PAH molecules show both 3.3 and 3.4 μm emission without an accompanying emission feature at 3.65 μm (Shan, Suto, & Lee 1991). Indeed, the spectrum of 9-methylanthracene was shown by Shan et al. (1991) to provide a good fit to both the 3.28 and 3.40 μm emission features. Duley & Jones (1990) have suggested that methylated anthracenes may be formed in photodissociation regions by the decomposition of hydrogenated amorphous carbon solids.

Finally, to illustrate the role that combination bands may

TABLE 1

ESTIMATED ENERGIES FOR ALLOWED-INTERCOMBINATION BANDS OF ANTHRACENE IN THE CH STRETCH (2–0) OVERTONE REGION

Upper State	Energy (cm^{-1})
$A_{1g} \times B_{2u}$	6070, 6102, 6114, 6146, 6162, 6206
$A_{1g} \times B_{3u}$	6084, 6128, 6133, 6177
$B_{1g} \times B_{3u}$	6084, 6128, 6133, 6177
$B_{2u} \times B_{2u}$	Forbidden

TABLE 2

POSSIBLE ALLOWED COMBINATION BANDS OF 1398–1634 cm^{-1} FUNDAMENTALS OF ANTHRACENE IN THE 3.3–3.6 MICRON (3030–2780 cm^{-1}) RANGE

Energy (cm^{-1})	Interstellar Feature (cm^{-1})	Energy (cm^{-1})	Interstellar Feature (cm^{-1})
3132.........	...	2959.........	...
3103.........	...	2950.........	...
3097.........	...	2942.........	2940
3096.........	3085	2939.........	...
3058.........	...	2927.........	...
3043.........	3040	2878.........	2890
3032.........	...	2876.........	...
3026.........	...	2865.........	...
3023.........	...	2850.........	2850
3016.........	...	2812.........	...
2994.........	2995	2801.........	2810

play in generating additional weak features in the 3.3–3.6 μm region, energy levels for symmetry-allowed combinations of fundamental of anthracene are listed in Table 2. These combinations utilize the mode and symmetry designations identified by Sverdlov et al. (1974). Only fundamentals in the 1398–1634 cm^{-1} range have been included. Although a detailed comparison with interstellar features is not justified at the point, it is evident that combination bands of this kind are capable of providing a multitude of spectral features in this region.

4. CONCLUSION

The assignment of 3.40 and 3.51 μm emission to hot bands associated with the CH IR-active stretch in PAH is shown to be consistent with the absence of emission of the $2 \rightarrow 0$ overtone if the emitting molecules have high symmetry and are not perturbed by a crystal field. Emission at *other* wavelengths in the 1.67 μm range is, however, predicted to occur, but this will involve intercombinations of other CH stretching modes. An emission at 1.1325 μm, the $3 \rightarrow 0$ overtone of the IR-allowed CH fundamental, is predicted.

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