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ANHARMONICITY AND THE INTERSTELLAR POLYCYCLIC AROMATIC HYDROCARBON INFRARED EMISSION SPECTRUM

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ABSTRACT

The hypothesis that interstellar infrared emission originates from vibrationally excited polycyclic aromatic hydrocarbons (PAHs) requires that emission can arise from all vibrational levels that are energetically accessible. Due to anharmonicity, the emission from the upper vibrational levels is shifted to longer wavelengths from that of the $v = 1$–0 transition. We show that structure in the 3 μm region is readily and quantitatively explained by emission from upper vibrational levels of excited PAHs that contain a maximum of 20–30 carbon atoms. The asymmetrical broadening of the 11.3 μm emission band may also be due to anharmonicity.

Subject headings: infrared: spectra — interstellar: molecules — molecular processes

I. INTRODUCTION

It has recently been suggested that emission from free, highly vibrationally excited, polycyclic aromatic hydrocarbon molecules (PAHs) produces the infrared emission bands at 3.3, 6.2, 7.7, 8.6 and 11.3 μm (Leger and Puget 1984, hereafter LP; Allamandola, Tielens, and Barker 1985, hereafter ATB*a*). The intensity of the emission at 3050 cm^{-1} (3.3 μm) with respect to that at 885 cm^{-1} (11.3 μm) suggests the emission originates from individual species containing 20–50 atoms while some of the spectroscopic details (e.g., a broad pedestal under the 1300 cm^{-1} [7.7 μm] feature) suggest that emission from particles which contain hundreds of atoms is also present (Goebel 1986; Allamandola, Tielens, and Barker 1986 hereafter ATB*b*). Although the interstellar spectra associated with different objects are similar, they vary in detail from object to object (Cohen, Tielens, and Allamandola 1985; Cohen *et al.* 1986; ATB*b*). For example, the 885 cm^{-1} (11.3 μm) band is often asymmetric (Aitken and Roche 1982). Also there is structure associated with the 3050 cm^{-1} (3.3 μm) band and plateau, with a distinct feature at 2940 cm^{-1} (3.4 μm) and weaker bands at about 2900 cm^{-1} (3.45 μm) and 2850 cm^{-1} (3.51 μm) whose relative intensities are variable (Geballe *et al.* 1985; de Muizon *et al.* 1986). Although close, these frequencies do not coincide with those expected from functional groups (e.g., $-CH_3$ or $-CH_2$) (de Muizon *et al.* 1986).

In this *Letter* we show that these aspects of the spectra are a necessary consequence of the vibrationally excited molecule hypothesis. In most of the objects the molecules are excited by the absorption of UV photons. A large fraction of this energy is converted to vibrational energy which is statistically distributed among the vibrational modes in the molecule. In general, there is sufficient energy to populate several vibrational levels in each mode. Because the modes are anharmonic, emissions from these higher levels generally fall at slightly lower frequencies than that for the $v = 1 \rightarrow 0$ transition. Thus, emissions from the higher levels contribute to the spectrum and produce weak features to the red of the strong fundamentals. In addition to accounting for details in the interstellar IR emission band spectrum, anharmonicity could be important in producing some of the emission features from comet Halley in the 3050–2860 cm^{-1} (3.3–3.5 μm) region (Baas, Geballe, and Walther 1986). A detailed description of IR fluorescence from highly vibrationally excited molecules will be given by Allamandola, Tielens, and Barker (1987, hereafter ATB*c*). However, because the consequences of anharmonicity are so important, we describe them in this *Letter*. Anharmonicity accounts for previously unexplained details in the emission spectrum and provides a powerful diagnostic for molecular size and energy content.

II. VIBRATIONAL ANHARMONICITY AND THE INTERSTELLAR 3 MICRON EMISSION FEATURES

Descriptions of molecular vibrations and derivations of vibrational frequencies are generally discussed in terms of the harmonic oscillations of two bodies connected with a spring and described by the expression

$$\nu = 1/2\pi\sqrt{k/\mu}\,, \qquad (1)$$

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where ν is the vibrational frequency, μ is the reduced mass $m_1 m_2/(m_1 + m_2)$, and k is the bond force constant (analogous to a spring force constant). The fundamental vibrational frequencies depend on the masses of the atoms involved in the vibration and the force constant which is determined by the molecular force field. The force field, which depends on the electron distribution and type of bonding in the molecule, describes the shapes and depths of the potential well which binds the atoms (Herzberg 1968). The analysis of vibrational spectra in terms of molecular force fields is a mature research area which has advanced steadily over the past several decades; force field calculations are now computed for extremely complex molecules such as PAHs (Cyvin *et al.* 1982, and references therein). While virtually all molecular force fields are anharmonic, the degree of anharmonicity can vary markedly. In general, one of the effects of anharmonicity is to continuously vary spacing between the adjacent vibrational states for higher values of v. (In a harmonic oscillator, the spacing between all adjacent levels is constant.) For CH stretching vibrations in most hydrocarbons, the $\Delta v = -1$ transitions between higher v levels occur at increasingly lower frequencies.

The extent of anharmonicity depends on the particular vibration involved. For example, the anharmonicity of the 3050 cm^{-1} (3.3 μm) aromatic CH stretch is much larger ($\Delta\nu \approx 100$ cm^{-1}) than that for the 1610 cm^{-1} (6.2 μm) C–C stretch and 885 cm^{-1} (11.3 μm) C–H out-of-plane bend ($\Delta\nu < 10$ cm^{-1}). Table 1 shows the measured anharmonicities for the C–H stretch of the aromatic molecule benzene, C_6H_6. The $6 \leftarrow 0$ C–H stretch overtone band in benzene falls at 16,550 cm^{-1}. In the small PAHs naphthalene ($C_{10}H_8$) and anthracene ($C_{14}H_{10}$) the corresponding frequencies are 16440 and 16,470 cm^{-1} respectively showing that anharmonicities are very similar to one another in the aromatic molecules studied to date (Swofford, Long, and Albrecht 1976; Reddy, Heller, and Berry 1982). This frequency spacing is very similar to that of the substructure observed in the interstellar 3050 cm^{-1} (3 μm) band complex.

If the interstellar IR emission bands originate from highly vibrationally excited molecules, emission from vibrational levels greater than $v = 1$ must contribute to the spectrum, and anharmonicity effects are expected.

TABLE 1

GROUND ELECTRONIC STATE VIBRATIONAL SPACINGS OF THE CH STRETCH IN THE AROMATIC MOLECULE BENZENE[a]

Transition	cm^{-1} [μm]
1–0	3047 [3.28]
2–1	2925 [3.42]
3–2	2814 [3.54]
4–3	2712 [3.69]
5–4	2574 [3.89]
6–5	2478 [4.0]

NOTE.—Overtone transitions for naphthalene and chrysene have very similar anharmonicities; Swofford, Long, and Albrecht 1976.

[a] Reddy, Heller, and Berry 1982.

At least three components appear to contribute to the 3000 cm^{-1} (3.3 μm) complex of interstellar emission features (Geballe *et al.* 1985). The prominent 3050 cm^{-1} (3.28 μm) band is due to the $v = 1 \rightarrow 0$ CH stretching transition. The 40–50 cm^{-1} breadth of this band may be contributed to by different PAHs, with each band slightly shifted. However, as this frequency is so characteristic for PAHs, a mixture will produce a band only slightly broader than the expected intrinsic line width which is determined by the intramolecular vibrational energy transfer time (Heisenberg uncertainty principle). We attribute the apparent pedestal which extends from about 3125 to 2700 cm^{-1} (3.2–3.7 μm) to the blending of lines originating from several types of transition. One consists of overtone and combination bands involving lower lying fundamentals (ATB*b*). Another important component is emission from $\Delta v = -1$ CH stretching transitions originating in higher v levels. With sufficient vibrational energy in the molecule these can produce resolvable structure on the pedestal. The variable 2940 cm^{-1} (3.4 μm) band discovered by Geballe *et al.* (1985), and many of the bands discovered by de Muizon *et al.* (1986) are attributable to transitions of this type (Figs. 1*b*, 1*c*, and 1*d*). We assign the emission feature at 2940 cm^{-1} (3.4 μm) to the $v = 2 \rightarrow 1$ transition from the species which predominantly contribute to the 3050 cm^{-1} (3.28 μm) band. Similarly, the peak at 2841 cm^{-1} (3.52 μm) is attributed to the $v = 3 \rightarrow 2$ transition. The weak structure at about 2925 cm^{-1} (3.42 μm) and 2801 cm^{-1} (3.57 μm) in the spectrum measured by de Muizon *et al.* (1986) could well originate from less abundant or less excited PAHs with slightly different anharmonicities. The fundamental ^{13}CH vibration in objects with a $^{12}C/^{13}C$ ratio on the order of 10 would also contribute to the emission near 3.4 μm. Finally, transitions between low-lying electronic states in a collection of PAHs might produce an underlying broad component which may extend into the red.

Two additional points should be made regarding the 3000 cm^{-1} complex of bands. The first is that in a molecule which is vibrationally excited, modes and combinations with frequencies similar to those of the emitting transitions are expected to become more intense due to coupling (Fermi resonance). Thus transitions which would normally be weak (or inactive) could contribute to the emission. The second is that many of the emitting species are likely to be singly ionized and thus in doublet states. The extent to which band splitting into doublets will affect the frequencies and relative intensities of the bands is not clear as there are neither theoretical nor experimental data available on this type of system. This may affect the overall appearance of the spectrum, particularly in this region because of the contribution of emission from higher vibrational states.

III. INFRARED FLUORESCENCE FROM HIGHLY VIBRATIONALLY EXCITED, ANHARMONIC MOLECULES

The infrared emission intensity due to a $v \rightarrow (v - 1)$ vibrational transition in a molecule with total vibrational energy E can be calculated from the following fundamental equation (Herzberg 1968; Durana and McDonald 1976; Rossi, Pladziewicz, and Barker 1983):

$$I(E, i, v) = h\nu_i A_i^{v, v-1} N_v(E), \qquad (2)$$

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where ν_i is the frequency, $A_i^{v,v-1}$ is the Einstein coefficient for the $v \rightarrow (v-1)$ transition, and $N_v(E)$ is the population of molecules with energy E and v quanta in the ith vibrational mode. From the harmonic oscillator approximation, which is thought to be accurate to 5%–10%, $A_i^{v,v-1} \approx vA_i^{1,0}$. According to the ergodic assumption, the energy is distributed statistically among the accessible vibrational states and the fractional number of molecules with total vibrational energy E that have v quanta in the ith mode is a ratio equal to the number of ways of distributing the energy while the ith mode has v quanta, divided by the total number of ways of distributing the energy, subject only to conservation of total energy. Thus, $N_v(E)$ is approximated by

$$N_v(E) = N(E)\rho_r(E - vh\nu_i)/\rho(E), \quad (3)$$

where $N(E)$ is the total number of molecules with energy E, $\rho(E)$ is the total density of vibrational states, and $\rho_r(E - vh\nu_i)$ is the density of vibrational states for all modes, except the emitting mode, which contain v quanta. The integrated IRF band intensity for a particular $\Delta v = 1$ transition is then given by

$$I(E, i, v) = N(E)h\nu_i vA_i^{1,0}\rho_r(E - vh\nu_i)/\rho(E). \quad (4)$$

It should be noted that the most important assumption in equation (3) is the ergodic approximation, which assumes statistical distribution of energy. For energies in excess of a few thousand wavenumbers, the statistical redistribution of energy is completed on a microsecond time scale which is much faster than the IR emission time scale of a few tenths of a second (Oref and Rabinovitch 1979; Bondybey 1984). Thus, as long as the densities of states are properly estimated, equation (4) is expected to be reliable, as confirmed in experimental tests (Durana and McDonald 1976; Rossi, Pladziewicz, and Barker 1983). The density of states, ρ, has been calculated both by exact counts, and the Whitten and Rabinovitch (1963) approximation as described in ATB*c*. In the earlier study (ATB*a*) spectral resolution and anharmonicity were neglected and only the total emission in specific spectral regions was considered. In benzene, naphthalene, and anthracene, the anharmonicities of the C–H stretching vibrations near 3050 cm^{-1} are quite large (100–120 cm^{-1}), and since the observed band widths are only about 30 cm^{-1}, the lines are easily resolved.

The expected emission spectrum has been computed for chrysene ($C_{18}H_{12}$) assuming anharmonicity is 120 cm^{-1} and a Lorentzian line profile (30 cm^{-1} width). Rotational structure contributes very little to the line widths and is incorporated into the Lorentzian profile. The calculated emission spectrum in the C–H stretching region from this PAH is shown in Figure 1*a*, as a function of vibrational energy content. Other PAHs will exhibit similar spectra, with 100–120 cm^{-1} separation between the peaks, but the exact location of the peaks depends on the particular molecule. More realistic simulations would include the other C–H vibrational stretch modes, which may have slightly different frequencies, and the effects of the energy-cascade, which we have neglected in preparing Figure 1*a*. Figure 1 shows there is a remarkable resemblance to the spectrum observed from NGC 7027, IRAS 21282+5050, and (possibly) from HD 44179. Comparison with the observed spectra shows distinct satellite peaks at the position expected. Thus, the peak observed near 2940 cm^{-1} in the various objects provides additional strong support for the hypothesis that the emission originates from highly vibrationally excited molecules.

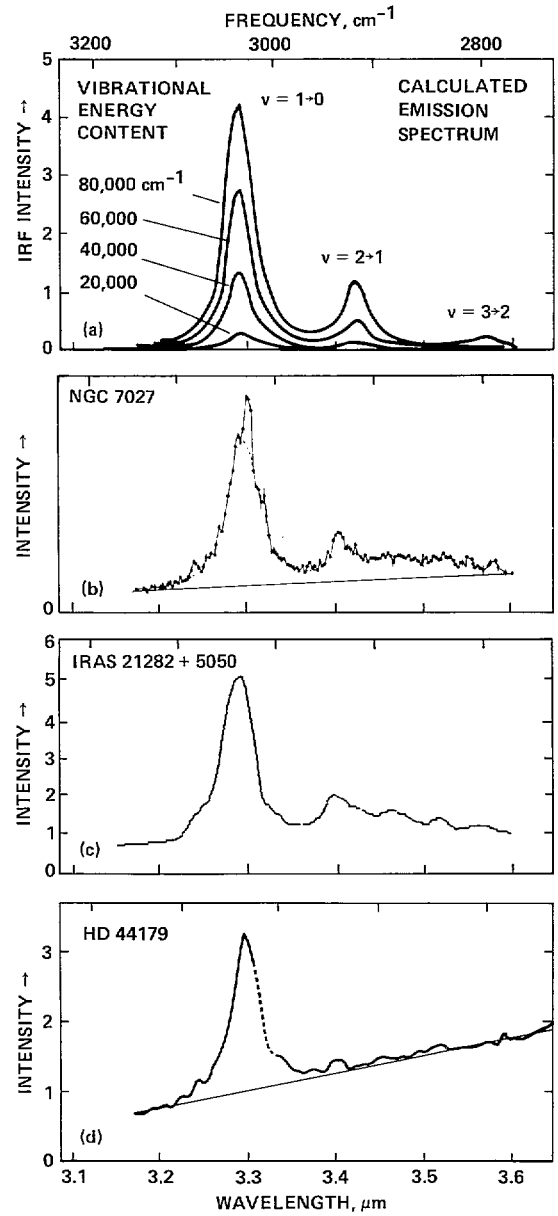

FIG. 1.—(*a*) The calculated emission spectrum for chrysene in the CH stretching region as a function of vibrational energy content. Anharmonicity is assumed to be 120 cm^{-1}. (*b*)–(*d*) The observed emission spectra of NGC 7027 (Geballe 1983), HD 44179 (Geballe *et al.* 1985); and IRAS 21282+5050 (de Muizon *et al.* 1980) showing how emission from higher vibrational levels depends on the availability of energetic photons. In NGC 7027, where the most energetic photons are available, emission from higher levels is important and produces a prominent $v = 2 \rightarrow v = 1$ band, whereas in the relatively benign HD 44179, emission from $v = 2$ is barely discernible.

The relative importance of the emission from $v = 2$ depends on the internal energy of the excited molecule and on

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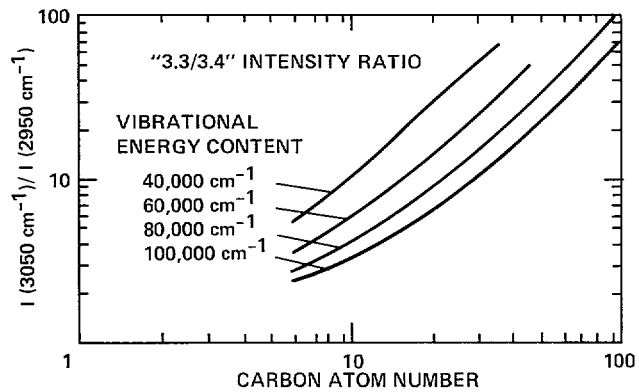

FIG. 2.—The 3.3 μm/3.4 μm intensity ratio as a function of carbon atom number and vibrational energy content. The relative fluorescence intensities include integration over the vibrational cascade.

the relative Einstein coefficients which *can* be accurately calculated by the harmonic oscillator approximation. Thus, the ratio of intensities from $v = 1$ and $v = 2$ provides a firmer measure of excitation energy and molecular size than is possible by comparing the intensity of the 3050 cm^{-1} (3.3 μm) band with the intensity of the 885 cm^{-1} (11.3 μm) band, for which the relative values of the Einstein coefficients are somewhat uncertain (ATB*b*). Furthermore, in the observations, the intensity of the 885 cm^{-1} (11.3 μm) band may be augmented by emission from large PAHs which contribute little to the 3050 cm^{-1} (3.3 μm) band.

Predictions for the intensity of the $v = 1$ line compared to that for the $v = 2$ line are presented in Figure 2 as functions of molecular size and excitation energy. As an initially excited molecule relaxes by infrared emission, it must emit many infrared photons before it reaches equilibrium with the low temperatures of the ISM. Thus, the observed UIR bands are due to emission from molecules in all stages of energy relaxation following excitation to some initial energy. The effects of the energy-cascade are included in this figure. The satellite band observed in NGC 7027 is about 10 times less intense than the main band (cf. Fig. 1). In Figure 2, a ratio of 10 and a maximum excitation energy of 80,000–100,000 cm^{-1} are consistent with molecules of about 20–30 carbon atoms, a conclusion consistent with the broader molecular size range deduced from the relative intensities of the 885 and 3050 cm^{-1} (11.3 and 3.3 μm) bands (ATB*a*, *b*). Thus two independent measures indicate the same relatively small, molecular size.

Experimental data are not available concerning the anharmonicities of the other PAH vibrational modes. However, anharmonicity on the order of a few wavenumbers is expected for the out-of-plane C–H vibrations and C–C stretching modes (R. Eggars, J. Pliva, and S. Cyvin, private communication). We have calculated the effects of anharmonicity on the 885 cm^{-1} (11.3 μm) feature by arbitrarily assuming an anharmonicity of 5 cm^{-1} and a Lorentzian line width of 10 cm^{-1} (other choices could give better agreement with the observations). The vibrational frequency is much lower than that for the CH stretch (885 compared to 3050 cm^{-1}) and emission from considerably higher vibrational states (v levels) contributes to the band. Although the

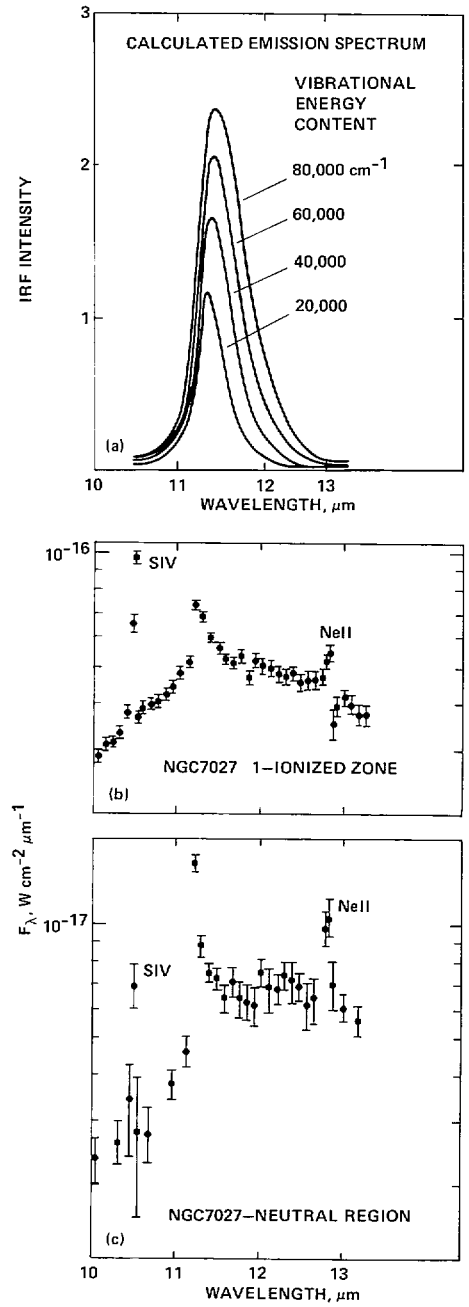

FIG. 3.—(*a*) The calculated emission spectrum in the CH out-of-plane bending region for chrysene as a function of vibrational energy content. Anharmonicity is assumed to be 5 cm^{-1}, natural line width, 10 cm^{-1}, and $v = 1 \rightarrow v = 0$ at 880 cm^{-1}. (*b*) and (*c*) The 10–13 μm spectrum of NGC 7027 emitted from the ionized and neutral regions, respectively (Aitken and Roche 1983). As expected, the 885 cm^{-1} (11.3 μm) band is markedly more asymmetric in the ionized region than in the neutral zone (see text). Note that the Ne II and S IV line profiles are independent of position, showing that changes in the 11.3 μm band profile are not an instrumental effect.

anharmonicity is only a few wavenumbers, it effectively broadens the band by skewing it to lower frequencies. Thus, as shown in Figure 3*a*, the band will be rather asymmetric for highly vibrationally excited molecules, and it will also be

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considerably broader and peaked at slightly lower frequencies than that from molecules containing less vibrational energy. This variation is observed in interstellar objects.

Figure 3 shows the interstellar 11.3 μm band at two of the positions in NGC 7027 (Aitken and Roche 1983). In the central ionized region, where the most energetic photons are available, the band is substantially broader and markedly more asymmetric than the band originating in the outer neutral zone, where far less energetic photons are available. Until a more quantitative measure of the anharmonicity for these lower frequency modes is available, one cannot determine the size of the emitting species responsible as precisely as the analysis of the 3050 cm^{-1}/2930 cm^{-1} (3.3 μm/3.4 μm) band intensity ratio allows. Within the framework of the assumptions made here (anharmonicity = 5 cm^{-1}, Lorentzian width = 10 cm^{-1}), the size of the emitting species, assuming 100,000 cm^{-1} of vibrational energy, is again in the 20–30 C atom range.

Although this analysis of the 885 cm^{-1} (11.3 μm) band is based on the out-of-plane bend of isolated, peripheral H atoms, it can be extended to doubly and triply adjacent peripheral H atoms as well: each band will broaden just as shown here. Blending of these broadened bands, which fall in the 860–800 cm^{-1} (11.6–12.7 μm) and 810–750 cm^{-1} (12.3–13.3 μm) regions, respectively, will contribute to and should produce weak structure on the 885–770 cm^{-1} (11.3–13 μm) plateau observed in *IRAS* spectra (Cohen, Tielens, and Allamandola 1985).

In ATB*b* and ATB*c*, a thermal treatment of the fluorescence process is considered, and it is concluded that for long wavelength emission and for highly excited small molecules, the approximation gives reasonable results. However, for large molecules at low energy per mode and high-frequency modes, it fails. Thus the thermal approximation must be used with great caution. This is particularly true in describing the emission from upper vibrational levels such as $v = 2 \rightarrow 1$ transitions. The approach presented here avoids those problems and shows that the most intensely emitting molecules contain 20–30 carbon atoms.

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