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The carriers of the unidentified infrared emission features: Clues from polycyclic aromatic hydrocarbons with aliphatic sidegroups

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ABSTRACT

The unidentified infrared emission (UIE) features at 3.3, 6.2, 7.7, 8.6, 11.3 and 12.7 μm are ubiquitously seen in a wide variety of astrophysical regions in the Milky Way and nearby galaxies as well as distant galaxies at redshifts $z \geq 4$. The UIE features are characteristic of the stretching and bending vibrations of aromatic hydrocarbon materials. The 3.3 μm feature which results from the C–H stretching vibration in aromatic species is often accompanied by a weaker feature at 3.4 μm . The 3.4 μm feature is often thought to result from the C–H stretch of aliphatic groups attached to the aromatic systems. The ratio of the observed intensity of the 3.3 μm aromatic C–H feature ($I_{3.3}$) to that of the 3.4 μm aliphatic C–H feature ($I_{3.4}$) allows one to estimate the aliphatic fraction (e.g., $N_{\text{C, aliph}}/N_{\text{C, arom}}$, the number of C atoms in aliphatic units to that in aromatic rings) of the carriers of the UIE features, provided that the intrinsic oscillator strengths (per chemical bond) of the 3.3 μm aromatic C–H stretch ($A_{3.3}$) and the 3.4 μm aliphatic C–H stretch ($A_{3.4}$) are known. In this review we summarize the computational results on $A_{3.3}$ and $A_{3.4}$ and their implications for the aromaticity and aliphaticity of the UIE carriers. We use density functional theory and second-order perturbation theory to derive $A_{3.3}$ and $A_{3.4}$ from the infrared vibrational spectra of seven polycyclic aromatic hydrocarbon (PAH) molecules with various aliphatic substituents (e.g., methyl-, dimethyl-, ethyl-, propyl-, butyl-PAHs, and PAHs with unsaturated alkyl chains). The mean band strengths of the aromatic ($A_{3.3}$) and aliphatic ($A_{3.4}$) C–H stretches are derived and then employed to estimate the aliphatic fraction of the carriers of the UIE features by comparing the ratio of the intrinsic band strength of the two stretches ($A_{3.4}/A_{3.3}$) with the ratio of the observed intensities ($I_{3.4}/I_{3.3}$). We conclude that the UIE emitters are predominantly aromatic, as revealed by the observationally-derived mean ratio of $\langle I_{3.4}/I_{3.3} \rangle \approx 0.12$ and the computationally-derived mean ratio of $\langle A_{3.4}/A_{3.3} \rangle \approx 1.76$ which suggest an upper limit of $N_{\text{C, aliph}}/N_{\text{C, arom}} \approx 0.02$ for the aliphatic fraction of the UIE carriers.

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Contents

1. Introduction	2
1.1. The UIE carriers: aromatic or aliphatic?	2
1.2. HAC	2
1.3. QCC	3
1.4. Soot	3
1.5. Coal and kerogen	4
1.6. Excitation mechanism: equilibrium temperatures or stochastic heating?	4
1.7. Are the UIE carriers aromatic or aliphatic? Constraints from the C–H stretching features	5
2. Computational methods and target molecules	6
3. Structures and stabilities of methylated PAHs	7

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4. Results	8
4.1. Frequencies and intensities of parent PAHs	9
4.1.1. Benzene	9
4.1.2. Important parent PAHs	9
4.2. Frequencies and intensities of toluene and methylated PAHs	10
4.2.1. Toluene	10
4.2.2. Important methylated PAHs	11
5. Theoretical level dependency of computed IR intensities	12
5.1. B3LYP vs. MP2 IR intensities of C–H stretching modes	12
5.2. Scaling approaches for the computed total intensities of C–H stretching modes	13
5.3. Theoretical level dependency of intensity scaling factors f_{aro} and f_{ali} : basis set effects at the B3LYP level	15
6. Recommended band intensities	16
7. Astrophysical implications	17
8. Summary	19
Acknowledgments	21
References	21

1. Introduction

A series of strong and relatively broad infrared (IR) emission features at 3.3, 6.2, 7.7, 8.6, 11.3, and 12.7 μm are ubiquitously seen in almost all astronomical objects with associated gas and dust, including protoplanetary nebulae (PPNe), planetary nebulae (PNe), young stellar objects, HII regions, reflection nebulae, the Galactic IR cirrus, and starburst galaxies (see Tielens, 2008). These features are a common characteristic of the interstellar medium (ISM) of the Milky Way and nearby galaxies as well as distant galaxies out to redshifts of $z \geq 4$ (e.g., see Riechers et al., 2014). Since their first detection four decades ago in two planetary nebulae (NGC 7027 and BD + 30°3639, Gillett et al., 1973), the carriers of these IR emission features have remained unidentified. Because of this, they are collectively known as the “unidentified infrared emission” (UIE or IIR) bands. Nevertheless, it is now generally accepted that these features are characteristic of the stretching and bending vibrations of some sorts of aromatic hydrocarbon materials and therefore, the UIE features are sometimes also referred to as the “aromatic infrared bands” (AIB).

The identification of the exact carriers of the UIE bands is crucial for modern astrophysics: (1) the UIE bands account for > 10–20% of the total IR power of the Milky Way and star-forming galaxies (Tielens, 2008; Smith et al., 2007), and therefore by implication, their carriers must be an important absorber of starlight in the ultraviolet (UV) wavelength region (e.g., see Joblin et al., 1992; Cecchi-Pestellini et al., 2008; Mulas et al., 2013); (2) their carriers dominate the heating of the gas in the diffuse ISM by providing photoelectrons (Lepp and Dalgarno, 1988; Verstraete et al., 1990; Bakes and Tielens, 1994; Weingartner and Draine, 2001); (3) as an important sink for electrons, their carriers dominate the ionization balance in molecular clouds and hence they influence the ion-molecule chemistry and the ambipolar diffusion process that sets the stage for star formation (see Verstraete, 2011); and (4) because of their ubiquitous presence in the ISM of the local and distant universe, the UIE bands are often taken as a reliable indicator of the star-formation rates across cosmic time up to high redshifts (see Calzetti, 2011, but also see Peeters et al., 2004a).

1.1. The UIE carriers: aromatic or aliphatic?

A large number of candidate materials have been proposed as carriers of the UIE bands. All of these materials contain aromatic structures of fused benzene rings. The major debate lies in the exact structure of the UIE carriers: are they free-flying, predominantly aromatic gas-phase molecules, or amorphous solids with a mixed aromatic/aliphatic composition? In this context, the proposed carriers can be divided into two broad categories:

- Gas-phase, free-flying polycyclic aromatic hydrocarbon (PAH) molecules (see Fig. 1a). The PAH model attributes the UIE bands to the vibrational modes of PAHs (Léger and Puget, 1984; Allamandola et al., 1985, 1989), with the 3.3 μm feature assigned to C–H stretching modes, the 6.2 μm and 7.7 μm features to C–C stretching modes, the 8.6 μm feature to C–H in-plane bending modes, and the 11.3 μm feature to C–H out-of-plane bending modes. The relative strengths of these bands depend on the chemical nature of the PAH molecule (i.e., size, structure, and charge) and their physical environments (e.g., the intensity and hardness of the starlight illuminating the PAHs, the electron density, and the gas temperature; see Bakes and Tielens, 1994; Weingartner and Draine, 2001). Ionized PAHs emit strongly at 6.2, 7.7, and 8.6 μm while neutral PAHs emit strongly at 3.3 and 11.3 μm . The PAH model readily explains the UIE band patterns observed in various regions in terms of a mixture of neutral and charged PAHs of different sizes (e.g., see Allamandola et al., 1999; Li and Draine, 2001). PAHs have also been proposed as a possible carrier of several other unidentified interstellar spectral features, including the diffuse interstellar bands (DIBs; see Salama, 2011), and the 2175 Å extinction bump (Joblin et al., 1992; Li and Draine, 2001; Cecchi-Pestellini et al., 2008; Steglich et al., 2010).
- Amorphous solids with a mixed aromatic/aliphatic composition (see Fig. 1 for illustration). This category includes hydrogenated amorphous carbon (HAC; Jones et al., 1990), quenched carbonaceous composites (QCC; Sakata et al., 1990), and coal or kerogen (Papoular et al., 1989). As originally suggested by Duley and Williams (1981), all of these materials share the basic molecular structure of PAHs by containing arenes.¹ They also contain aliphatic C–H bonds as well as other molecular structures often with other elements besides C and H.

1.2. HAC

HAC can be considered to be a collection of molecular clusters loosely aggregated to form an extended, three-dimensional bulk solid, with discrete aromatic “islands” embedded in a three-dimensional matrix held together unsaturated (sp and sp^2) and saturated (sp^3) spacers (see Fig. 1b). The aromatic units typically contain ~ 1 –8 benzene rings.² Bulk HAC dust was proposed as a

¹ A benzene ring is C_6H_6 . If the H atoms are gone, then it is not really “benzene” anymore. It is an aromatic ring system which can be called “arene”. Arene is a hydrocarbon with alternating double and single bonds between carbon atoms forming rings.

² Compared to HAC, amorphous carbon (AC) has a smaller H content and a larger aromatic cluster size of typically ~ 20 –40 rings and even up to several hundred rings (see Robertson, 1986).

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