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Singlet and doublet states UV–vis spectrum and electronic properties of 3-methylchrysene and 4-methylchrysene in glass matrix

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Abstract

The ultraviolet–visual spectrum of 3-methylchrysene, 4-methylchrysene and their radical cations formed by ultraviolet radiations, were measured in glass matrix at the room temperature. In the measured singlet state spectrum we were able to identify the α, p, β, β′ (Clar's) or ^1L_b, ^1L_a ^1B_b, ^1B_a (Platt's notation) bands. The presence of α, β or ^1L_b, ^1B_b was confirmed by calculating their wavelength ratio $\lambda_\alpha/\lambda_\beta$. Since matrix induces perturbation in the measured spectrum; it becomes necessary to take into account the perturbation while computing the spectrum. An effort has been made in this work to simulate the electronic spectrum in the same environment as is measured. This study presents the first calculated spectrum of these systems and their cations in glass matrix by semi empirical methods. To observe the magnitude of perturbation and hence to see the spectral shift in glass matrix, the spectrum was calculated in the free state as well. Spectral properties such as frontier orbitals gap, dipole moment, mean polarizabilities and its tensors were also computed both in glass matrix and free state using semiemperical method. The measured bands of 3-methylchrysene cation at wavelength 416.50 and 473.85 nm closely match with the available diffuse intersteallar bands (DIBs) at 417.55 and 472.64 nm, respectively. Also the observed 474.85 nm band of 4-methylchrysene cation matches the DIB at 476.00 nm.

Keywords: UV–vis spectra; 3-Methylchrysene; 4-Methylchrysene; Diffuse interstellar bands; Semi empirical calculations

1. Introduction

Discovered about 80 years ago [1] the Diffuse interstellar bands (DIBs) are a series of absorption features that occur in visible and near infrared region [2,3]. Currently over 300 DIBs are known [4] and a variety of molecules have been suggested, as their source but not yet conclusively identified. There are strong indications that polycyclic aromatic hydrocarbons (PAHs) and their derivatives exist both in neutral and ionic form are present in interstellar medium (ISM) [5–10] and they have been suggested to be the possible carriers of DIBs [11,12]. Salama et al. [13] reported a detail study of UV-to-near-IR absorption spectrum of neutral and ionized PAHs and pointed out that small neutral PAHs (less than 25 carbon atom) absorbs UV and cannot contribute to any known DIBs, which lies in visible or near IR. However ions of the smaller PAHs absorb in visible and near IR region, close to the position of well known diffuse interstellar bands. Recently PAHs including derivatives such as methyl have been proposed to be very good DIBs candidates [7,12–15]. In order to identify the methyl substituted molecules of PAHs which may be responsible for DIBs Husain et al. [16] studied the electronic spectrum of 1-methyl and 2-methyl phenanthrenes and their radical cations and showed that the electronic band at 448 nm of 1-methylphenanthrene and that at 486 nm of 2-methylphenanthrene cations shows matching with 450 and 488 nm known DIBs, respectively. The 442 nm electronic band of 2-methylanthracene and 638, 698 nm of 9-methylanthracene cations reported [17] in boric acid glass shows a good match with the DIBs positioned at 442.8, 637.920 and 699.307 nm [18]. It therefore becomes highly interesting to further explore the spectrum and spectral properties of other

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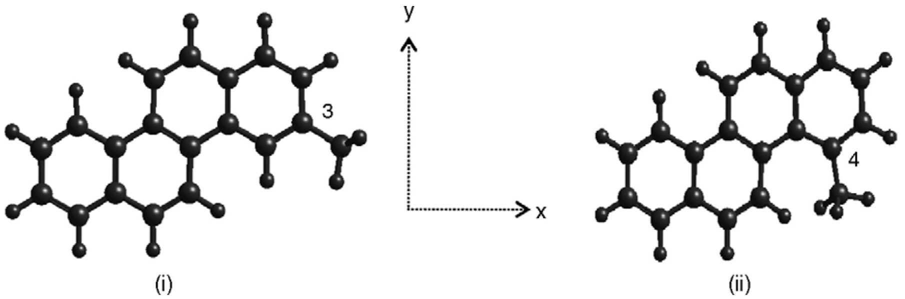
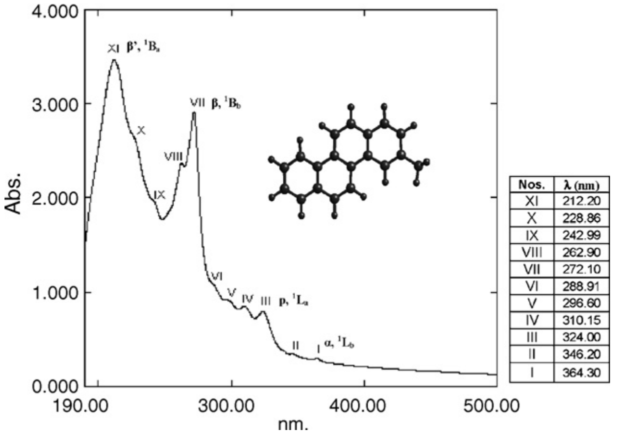


Fig. 1. Molecular structures (optimized geometry by AM1 method) of (i) 3-methylchrysene and (ii) 4-methylchrysene.

methyl substituted aromatic systems in order to identify the source of DIBs. In this regard, the vibrational spectra of neutral and ionized chrysene and 1-methylchrysene in gas phase have been computed [19] as a number of DIBs lies in this region. Theoretical spectroscopic properties of a number of methyl substituted chrysenes (methyl substitution from positions 1–6) calculated using semiemperical methods AM1 and PM3 have been studied earlier [20]. The electronic spectral shift of chrysene and 1-methyl chrysene in aqueous media has also been reported [21]. In the present work, we have extended the idea methyl substitution to chrysene and measured (and calculated) the UV–vis spectrum of neutral and ionized 3-methylchrysene and 4-methylchrysene in glass matrix. The visible and near UV spectrum of aromatic hydrocarbons and their derivatives are of considerable theoretical interest for several reasons. First, the main bands in these spectrum are due to $\pi \rightarrow \pi^*$ electronic transitions. Secondly, their spectrum show some remarkable regularities given by Clar [22] and Platt [23] which represented a challenge to theoretical analysis. In the present work, we have extended the of methy substitution to chrysene and measured the UV–vis spectrum of neutral and ionized 3-methylchrysene and 4-methylchrsene in glass matrix.

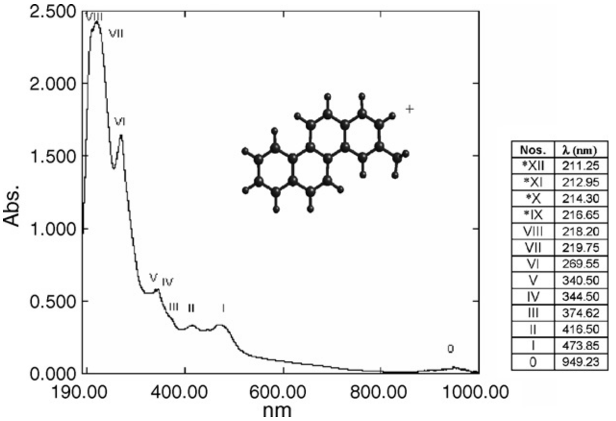
2. Experimental section

Boric acid (H_3BO_3) glass is the most suitable matrix for the measurement of electronic absorption spectrum in 200–1400 nm range [24] at room temperature, at which it forms a rigid solution. Boric acid from Qualigens Fine Chemical (A division of GlaxoSmithKline Pharmaceuticals Ltd., Mumbai) is used for making glass and the methyl substituted chrysenes (purity 99.9%) are procured from Sigma–Aldrich for doping in the “boric acid melt”. The substituted chrysenes are used without further purification. The glass preparation technique [25] requires that the fine boric acid grains kept in a silica crucible and heated it to about 240 °C in a hot air furnace. Methyl substituted chrysenes are then mixed (separately) with the boric acid melt and stirred properly; the melt is then sandwiched between two glass plates slightly heated and smeared with mustard oil so as to protect the boric acid glass from cracking and sticking the glass plates. High-pressure mercury lamp (Philips, 125 W/250 V) was used for irradiating the sample and producing cations. The UV-light is focused on the sample through a quartz plano convex lens (Melles Griot make). The samples, on UV irradiation acquire color, indicating the formation of cation [24]. The formation of cation on irradiation has earlier been reported by several research groups [26–28] on the basis of optical and ESR studies of certain aromatic hydrocarbons. The electronic absorption spectra were recorded by a Shimadzu Spectrophotometer (Model UV–VIS 2450) in the wavelength range of 190–1100 nm. The singlet state spectra of chrysene was recorded upto 500 nm and of doublet state upto 1000 nm depending upon the region of presence electronic bands. While measuring absorption, the spectrophotometer was kept at medium scan speed and 0.01 nm sampling interval.



Nos.	λ (nm)
XI	212.20
X	228.86
IX	242.99
VIII	262.90
VII	272.10
VI	288.91
V	296.60
IV	310.15
III	324.00
II	346.20
I	364.30

Fig. 2. Electronic absorption spectrum of 3-methylchrysene.



Nos.	λ (nm)
*XII	211.25
*XI	212.95
*X	214.30
*IX	216.65
VIII	218.20
VII	219.75
VI	269.55
V	340.50
IV	344.50
III	374.62
II	416.50
I	473.85
0	949.23

Fig. 3. Electronic absorption spectrum of 3-methylchrysene cation. *These bands are very close to each other and are not shown in spectrum.