Aliphatic hydrocarbon content of interstellar dust

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Abstract. The mid-IR spectrum of the interstellar medium contains both aromatic and aliphatic hydrocarbon features. These are generally attributed to carbonaceous dust. The aliphatic component is of particular interest because it produces a significant $3.4\,\mu$m absorption feature. The optical depth of this feature is related to the number and type of aliphatic carbon C−H bonds in the line of sight. It is possible to estimate the column density of aliphatic carbon from quantitative analysis of the $3.4\,\mu$m interstellar feature, providing that the absorption coefficient of interstellar aliphatic hydrocarbon is known. We produced interstellar dust analogues with spectra closely matching astronomical observations. Using a combination of FTIR and ^{13}C NMR spectroscopy, we determined an integrated absorption coefficient of the aliphatic component. The results thus obtained permit direct calibration of astronomical observations, providing rigorous estimates of the amount of aliphatic carbon in the ISM.

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1. Introduction

The element carbon plays an important role in the chemical richness of the ISM. Carbon has a special ability to form large variety of molecules via different types of covalent bonding. The bonding is described by the hybridization of valence orbitals as sp^3, sp^2, and sp, resulting respectively in aliphatic; olefinic and aromatic; and acetylenic compounds.

The total carbon abundance in the ISM includes carbon in both the gas and solid phase, and is given in terms of the C/H ratio in parts per million (ppm). There is a discrepancy between the total carbon abundance measured and the cosmic carbon abundance estimated based on models (Kim & Martin 1996; Dwek 1997). The total carbon abundance was estimated by Snow & Witt (1995) to be 225 ± 50 ppm. This has since been revised by estimates derived from Solar abundances (Grevesse & Sauval 1998; Asplund *et al.* 2006, 2009), and meteoritic/protosolar abundances (Lodders 2003) which gives up to 270 ppm carbon. Sofia & Meyer (2001) found the total ISM carbon abundance to be around 358 ± 82 ppm from the carbon abundance in young F, G type stars, which are considered to reflect the ISM abundances.

The gas phase carbon abundances are studied using atomic and molecular spectral lines (Cardelli *et al.* 1996; Parvathi *et al.* 2012). Models based on the extinction curves

(Mathis *et al.* 1977; Kim & Martin 1996) are used to indirectly estimate carbon abundances. From dust models, as much as 300 ppm carbon has been estimated to be found in the interstellar dust. Together with the average 140 ppm found in the gas phase one obtains a total abundance of ~ 440 ppm carbon, which is at the upper limit of the cosmic abundance estimations. However, instead of the abundance estimations based on indirect methods, a direct spectroscopic measurement is desired to yield more precise abundance estimates.

In the infrared, there are prominent spectral features of carbonaceous dust in spectra of the ISM. These absorption features are $3.28\,\mu$m, $3.4\,\mu$m, $5.87\,\mu$m, $6.2\,\mu$m, $6.85\,\mu$m and $7.25\,\mu$m (Dartois *et al.* 2004). The $3.4\,\mu$m absorption feature is of particular interest since it is the more prominent and prevalent feature towards IR background radiation sources.

The $3.4\,\mu$m absorption is attributed to the aliphatic $C-H$ stretch. Therefore, it is possible to measure the column density, N, of carbon incorporated in aliphatic hydrocarbon material of interstellar dust grains from quantitative analysis of the $3.4\,\mu$m absorption feature. Using the optical depth (τ) and the equivalent width ($\Delta\bar{\nu}$, cm^{-1}) of the $3.4\,\mu$m (2940 cm^{-1}) absorption measured by observations, one can determine the number of CH_x groups needed to produce this absorption by using the laboratory measurements of the integrated absorption coefficient (A, cm group^{-1}), $N = \tau\Delta\bar{\nu}/A$.

To date several forms of aliphatic hydrocarbons have been studied to determine the aliphatic integrated absorption coefficient, A, for astrophysical interest (e.g., d'Hendecourt & Allamandola 1986; Duley *et al.* 1998; Furton *et al.* 1999; Mennella *et al.* 2002; Dartois *et al.* 2004; Steglich *et al.* 2013; Gadallah 2015). All these measurements have been carried out with simple hydrocarbon molecules to ease the determination of the aliphatic amount of the sample. However, there is a discrepancy among the absorption coefficient for small molecules (d'Hendecourt & Allamandola 1986; Dartois *et al.* 2004) as it is strongly dependent on the structure of the molecule.

Carbonaceous interstellar dust is supposed to be a bulk material like kerogen, soot, HAC, MAON etc. (Kwok 2009, 2016; Chiar *et al.* 2013). It has been noted by Steglich *et al.* (2013) that aliphatic material in dust seems to have a lower CH_x extinction coefficient than small molecules. For dust analogues in a bulk form, the integrated absorption coefficient, per aliphatic group is found to be less than half that of the small molecules (Duley & Williams 1981; Furton *et al.* 1999; Mennella *et al.* 2002).

The problem with determining the integrated absorption coefficient based on an interstellar dust analogue (ISDA) is determining the fraction of carbon in aliphatic form. The most direct measurement of is ^{13}C NMR spectroscopy, where the chemical shift is determined by the bonding environment of the statistically incorporated ^{13}C nuclei (Robertson 2002). However, this technique requires a large sample. As such, ^{13}C NMR spectroscopy has not been applied to reliable interstellar dust analogues in order to determine the integrated absorption coefficient of the $3.4\,\mu$m feature until now.

We produced ISDAs in the laboratory under simulated circumstellar/interstellar-like conditions. We ensured that their spectra closely matched interstellar absorption profiles. The aliphatic carbon ratio of the ISDAs is determined by ^{13}C NMR spectroscopy. This information was used with FTIR spectra to determine the integrated absorption coefficient, A, for aliphatic carbon in ISDAs (Günay *et al.* 2018).

2. Experimental methods

The interstellar dust analogues were produced from acetylene (HC≡CH) and isoprene ($H_2C=C(CH_3)$-CH=CH$_2$). The acetylene precursor was expected to generate a largely unsaturated ISDA, while the isoprene was used to favour a branched aliphatic structure. The apparatus used for interstellar dust analogue production which providing the relevant circumstellar dust formation conditions (Contreras & Salama 2013) was described in
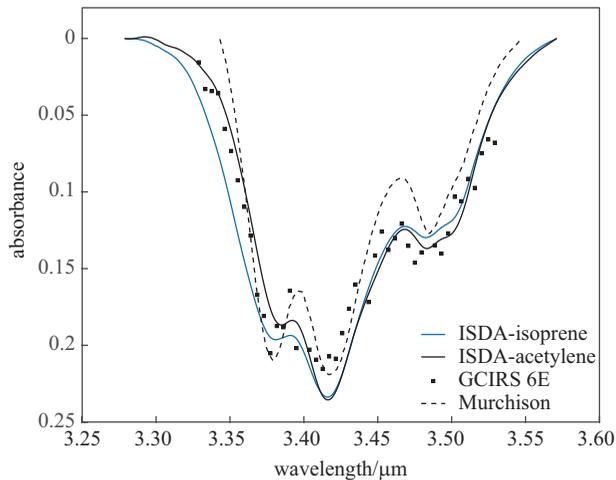
Figure 1. A comparison of the ISM absorption spectrum through the line of sight of GCIRS 6E (Pendleton *et al.* 1994) and the aliphatic absorption feature of ISDA-isoprene and ISDA-acetylene. A normalising factor has been applied to facilitate comparison of the absorption profiles.

Günay *et al.* (2018). The absorption spectra of ISDAs were recorded with an FTIR spectrometer and compared with observational spectra through the line of sight of the Galactic Centre source; GCIRS 6E and Murchison meteorite spectra from Pendleton *et al.* (1994) in Fig. 1. The profile and sub-peak positions of the $3.4\,\mu$m aliphatic C−H stretch absorption were in remarkably good agreement with the profile of the interstellar and Murchison meteorite spectra. This comparison indicates that ISDAs reproduce the average aliphatic environment of the interstellar dust.

In our holistic approach, we aim to obtain the total integrated absorption coefficient for the $3.4\,\mu$m aliphatic feature of the ISDAs, without distinguishing the CH, CH_2 or CH_3 groups. That the infrared spectra in Fig. 1 are so similar to the absorption towards the galactic centre shows that the CH_2/CH_3 ratio in the ISDAs is close to astronomical.

FTIR spectral measurements were recorded for different column densities (cm^{-2}) of aliphatic carbon, as determined by sample mass and the proportion of aliphatic carbon as determined by quantitative ^{13}C NMR spectroscopy. Total integrated areas of the resultant $3.4\,\mu$m aliphatic absorption features were calculated to obtain the integrated absorbance $(\mathcal{A},\ cm^{-1})$ as a function of the column density of aliphatic groups. The integrated absorbance was plotted against aliphatic carbon column density $(N,\ group\,cm^{-2})$. The integrated absorption coefficients $(A,\ cm\,group^{-1})$ were obtained from the slope. The absorption coefficients obtained were $4.76(8) \times 10^{-18}\,cm\,group^{-1}$ for ISDA-isoprene and $4.69(14) \times 10^{-18}\,cm\,group^{-1}$ for ISDA-acetylene.

The results obtained in this study are less than half those obtained by Sandford *et al.* (1991) and Dartois *et al.* (2004) using small hydrocarbons. However, they are consistent with the work of Duley *et al.* (1998), who analysed a dust analogue. In converting our values into mass extinction coefficients, accounting for only the aliphatic carbon mass, we obtain values consistent with the previous studies of Furton *et al.* (1999); Mennella *et al.* (2002) and Gadallah (2015).

3. Astrophysical implications

Using the absorption coefficients determined above, the column density of aliphatic carbon was calculated for lines of sight toward Galactic Centre source GCIRS 6E. Since the results for both ISDAs are so similar, only the ISDA-acetylene results are presented.

Pendleton *et al.* (1994) studied the 3.4 μm feature towards a range of sources including the galactic centre and local diffuse ISM. Towards GCIRS 6E at $A_V = 31$, they estimated a total carbon column density of 2.2×10^{19} cm^{-2} from $N(H) = 1.9 \times 10^{21} A_V$ and $N(C)/N(H) = 370$ ppm. A total aliphatic column density of 9.3×10^{17} was reported, comprising 4.2 % of the available carbon. In this study, we treat the aliphatic absorption as a single feature and have determined its integrated absorption coefficient to be 4.7×10^{-18} cm group^{-1}. Moreover, the equivalent width of our feature is 111 cm^{-1} (integral of the feature with unit peak absorbance), which compares favourably with the integral of the feature towards GC IRS 6E (~ 108 cm^{-1}). Reappraising the observations of Pendleton *et al.* (1994), we determine an aliphatic carbon column density of 4.87×10^{18} cm^{-2}. This is a factor of five higher than previously reported, corresponding to about 22 % of the available carbon.

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