

The infrared spectrum of interstellar dust: Surface functional groups on carbon

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Summary. A variety of chemical functional groups will be bound at reactive surface sites on small carbon grains in the diffuse interstellar medium. These groups give rise to infrared spectral features characteristic of aromatic molecules. In diffuse clouds the dominant group appears to be $-\text{CH}_3$. When carbon grains are heated in emission objects aromatic CH groups are produced. It is shown that both the absorption and emission spectra of dust can be understood in terms of the existence of these and other simple functional groups combined with carbon at grain surfaces. Specific identifications are proposed for several absorption and emission features including the $3.4\ \mu\text{m}$ absorption band and the $3.3\ \mu\text{m}$ emission feature.

1 Introduction

Infrared spectroscopy has always been an important diagnostic technique for the identification of chemical species in laboratory systems. Until recently it was not possible to apply this technique to the characterization of chemical compounds in the interstellar medium because of limited observational data. Now, with a series of higher quality spectra of various astronomical sources available, such characterization is possible. Infrared spectra showing features of likely molecular origin are obtained in absorption along the line of sight to the Galactic Centre (Willner *et al.* 1979; Wickramasinghe & Allen 1980) and emission in a variety of objects (for a survey see Dwek *et al.* 1980). Spectra of infrared sources associated with molecular clouds (Willner *et al.* 1980) also show absorption features due to molecular species. All objects show spectral features at 3.3 and/or $3.4\ \mu\text{m}$ in either absorption or emission. Such features are characteristic of the resonances within CH bonds in organic material (Duley & Williams 1979).

A variety of proposals have been made concerning the origin of these features (Dwek *et al.* 1980), however, no model proposed to date satisfies all observational and physical/chemical constraints. It now appears, however, that the emission features observed in objects such as NGC 7027 (Merrill, Soifer & Russell 1975), HD 44179 (Russell, Soifer & Willner

1978) and the Orion Ridge (Aitken *et al.* 1979) are consistent with thermal emission by small grains heated to ≈ 300 K in these objects. The relationship between these grains and those responsible for absorption at $3.4\ \mu\text{m}$ in diffuse clouds is unclear at present.

In this article we show that these observations are compatible with emission/absorption by surface functional groups on small carbon particles. In Section 2 we review some data concerning the properties of graphitic and amorphous carbon and the nature of surface functional groups on these materials. Section 3 outlines a model for such grains in the interstellar medium (ISM) and relates observed spectral features to specific surface groups on these solids. We conclude from this analysis that both aromatic and aliphatic CH functional groups are present on carbon particles in diffuse clouds and that these species are responsible for many of the observed infrared features. The existence of other surface functional groups and their properties are also discussed.

2 Carbon particles

It is generally accepted at present that a solid containing carbon must be a component of interstellar dust. The assumed form for this carbon is in graphite with this assumption gaining strength from the observation of a strong extinction feature at $2200\ \text{\AA}$ in interstellar spectra. Apart from this requirement, however, there is no *a priori* reason for the preference of graphite over the more general amorphous, form of carbon. We will consider, therefore, that interstellar carbon is amorphous although little difference in surface properties would occur with graphitic carbon.

There are a variety of forms for amorphous carbon (Boehm 1966) but all are characterized by microcrystallinity. The structure is of graphitic platelets randomly oriented in a larger particle. The C—C distance within these platelets is the same as in graphite; however, the interlayer distance is larger. In addition, some carbon is tetrahedrally bonded. The randomness of this structure and its lack of long-range order results in a higher proportion of chemically active sites where C atoms on the periphery of crystallites are in chemically unsaturated states. As a result amorphous carbon is highly reactive with respect to sorption of atoms and molecules at these sites. This high reactivity leads to combination with a wide variety of

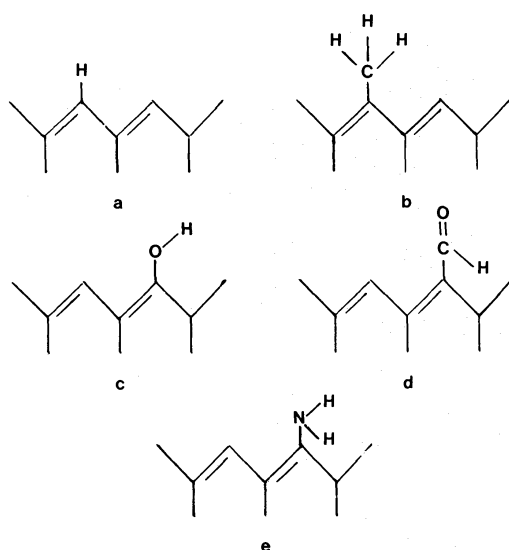


Figure 1. Surface functional groups on carbon: (a) aromatic CH; (b) example of aliphatic CH; (c) phenolic OH; (d) aldehyde group; (e) aromatic amine. The surface is represented by an array of hexagonal C_6 rings. C atoms in rings are not shown explicitly.

chemical species under laboratory conditions. As stated by Snoeyink & Weber (1972) 'nearly every type of functional group known in organic chemistry has been suggested as being present on the surface of microcrystalline carbon'.

Under interstellar conditions, one expects that many of these reactive sites will be occupied by H atoms or groups containing H atoms. Puri (1970) has shown that amorphous carbons typically contain 1–10 per cent H by number and that these H atoms are bound at surface C sites as either CH, CH₂ or CH₃ groups. These surface functional groups together with other likely groups are shown schematically in Fig. 1. The aromatic CH bond is essentially covalent and therefore has the strength typically found in such aromatic molecules as C₆H₆. Snoeyink & Weber (1972) report that H atoms bonded in this way to surface C atoms are extremely stable and are eliminated from the surface only after prolonged heating to 1200°C in vacuum.

Other surface functional groups likely under interstellar conditions include phenolic OH (Fig. 1c), aldehyde (Fig. 1d) and amine (Fig. 1e). These groups may also influence the chemical and optical properties of carbon dust in the ISM.

3 IR features from surface groups

There is little data available on the IR spectra of surface functional groups on carbons or graphite. That which is available has been obtained on laboratory samples exposed to the ambient atmosphere and hence may contain a variety of surface species not expected on grain material (Friedel & Carlson 1972; Hallam & Drushel 1958). In many ways, groups on the surface of a carbon crystallite with a graphitic structure resemble substituents on large fused-ring aromatics (coronene, etc.). As the IR functional group frequencies for these molecules are well known, we have adopted these frequencies as typical of those that would be found for similar groups on the surface of interstellar carbon particles. In a sense, this approach follows that suggested by Donn (1968) who pointed out the similarity between large fused-ring aromatic molecules and graphite particles.

A summary of expected surface group frequencies derived in this way is given in Table 1.

Table 1. Infrared spectral features due to simple functional groups in benzenoid-aromatics (Colthup *et al.* 1964).

Surface group	Frequency	Mode
Aromatic –CH	3030 cm ⁻¹ (3.3 μm)	Stretch
	870–900 (11.3)	Lone H wag
	2925 (3.4)	Asymmetric stretch
	2865 (3.5) Weak	Symmetric stretch
	1465 (6.8)	Asymmetric deformation
	1375 (7.3)	Symmetric deformation
	1040 (9.6)	Rocking
	3640 (2.75)	OH stretch
	1350 (7.4)	OH deformation
	1265 (7.9)	CO stretch
–CHO	2860 (3.5)	CH stretch
	2740 (3.65)	
	1700 (5.9)	CO stretch
–NH ₂	1390 (7.2)	CH rock
	3450 (2.9)	NH stretch
	3330 (3.0)	NH stretch
	1610 (6.2)	NH ₂ deformation
	1300 (7.7)	CN stretch
	800 (12.5)	

Since one does not have free molecules in the carbon-surface group system, only certain of the aromatic vibrations will produce discrete spectral lines. For example, we assume that no C–C ring vibrations will be observed as discrete features since these resonances will be broadened into a band in the solid. It is for this reason that bulk graphite shows only continuous absorption in the middle infrared. We also neglect cooperative vibrational modes between adjacent ring substituents since the density of surface functional groups is expected to be small. For example, the coupling between adjacent H atoms in a molecule such as benzene (C_6H_6) gives rise to several features between 670 and 890 cm^{-1} corresponding to the excitation of various hydrogen wagging modes (Colthup, Daly & Wiberly 1964). Under interstellar conditions it is likely that only the lone H wagging mode will be important since adjacent C sites will not, in general, contain H atoms or other functional groups (see Fig. 1).

In compiling the data in Table 1 no attempt has been made to order the vibrational resonances in terms of strength. Considerable variation in strength between features corresponding to a given group is expected. In addition, as we will show, the population of different groups on carbon particles is likely to depend on ambient conditions in the ISM.

4 The model

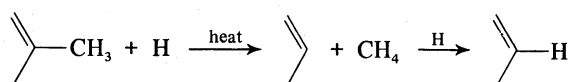
We propose here that infrared features seen in absorption in diffuse clouds and in emission in bright infrared sources arise from small quantities of surface groups bound to chemically active sites on the surfaces of carbon particles. This also assumes that carbon particles in diffuse clouds are not coated by mantles and are essentially free of other chemical species (ices, etc.) except for these groups.

It is a simple matter to show that such a relatively small number of chemical groups is compatible with the observed absorption strength at 3.4 μm in diffuse clouds. Assuming $\sigma = 10^{-19} cm^2$ as typical of the cross-section for absorption due to CH bonds at 3.4 μm (Duley & Williams 1979), $\tau(3.4 \mu m) = 1.086 \sigma NL(CH)$. Taking $NL(CH) = NL(C) = 3.7 \times 10^{-4} N(H)$ and $N(H) = 1.9 \times 10^{21} A_V cm^{-2}$ we obtain $(\tau/A_V)_{max} = 0.075$. This is the ratio of $\tau(3.4 \mu m)/A_V$ that would be obtained if all C atoms were combined with H to form CH bearing compounds. The observed value of this ratio in diffuse clouds is $(\tau/A_V)_{obs} = 3-6 \times 10^{-3}$ (Willner *et al.* 1979; Wickramasinghe & Allen 1980). Using an average value $(\tau/A_V)_{obs}/(\tau/A_V)_{max} = 0.06$, it is evident, therefore, that only about 6 per cent of available carbon is in CH bonds in the diffuse ISM. Since 1–10 per cent of C atoms in amorphous carbons are bound in CH bonds (Section 2) it appears that sufficient CH would be present in this form on interstellar carbon particles to account for the observed strength of the 3.4 μm absorption feature in diffuse clouds.

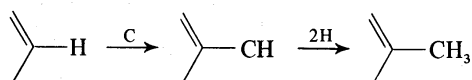
This and other infrared features seen in emission in bright objects have been shown (Dwek *et al.* 1980) to be compatible with thermal emission by a minor constituent of interstellar dust present in the form of small grains (size 0.005–0.01 μm). Since surface effects are largest in small particles this result is in agreement with the present model. Furthermore a carbon composition for these particles is suggested by the observation of strong emission in C-rich objects (Aitken *et al.* 1979).

Most emission objects show bands at 3.3, 3.4, 6.2, 7.7, 8.7 and 11.3 μm while the absorption spectrum obtained by Willner *et al.* (1979) shows only a single absorption feature at 3.4 μm although further weak absorption may be present between 6 and 8 μm while the region between 8 and 12 μm is obscured by Si–O absorption. Any model proposed for the origin of these features must account for the limited overlap between these two sets of data. In the present model, the 3.3 and 11.3 μm emission features are to be identified with resonances in aromatic CH groups (Table 1 and Fig. 1a). Emission and absorption features at 3.4 μm

are associated with aromatic methyl (CH_3) groups. The observation of a $3.3\ \mu\text{m}$ feature only in emission while that at $3.4\ \mu\text{m}$ occurs in both emission and absorption is understandable if CH_3 is the dominant surface group in low temperature carbon dust while CH groups are formed at higher temperatures. A possible reaction converting CH_3 to CH would be



The reverse reaction could occur in low temperature regions via C atom insertion.



C atom insertion reactions have been observed to occur at cryogenic temperatures (Lemmon 1973). The H atom addition reaction to generate CH_3 surface groups probably occurs at temperatures as low as 7 K (Bar-Nun, Litman & Rappaport 1980).

The possible role played by other surface groups in absorption and emission spectra is uncertain at present. The aromatic amine group (NH_2) could provide emission features at 6.2 and $7.7\ \mu\text{m}$. However, this group should be held less strongly than aromatic CH and so might not be expected to be present at elevated temperatures. Furthermore, emission should also occur at $2.9\text{--}3.0\ \mu\text{m}$ in disagreement with observation. The phenolic OH group would emit in the $7.7\ \mu\text{m}$ region due to OH and CO modes and might be stable at high temperatures (Boehm 1966).

Other surface functional groups exhibiting *double* bonds to surface carbons are possible. The frequencies of these groups are expected to be similar to those of substituents on cyclohexane. The simplest example would be >CH_2 which is typical of cyclohexane itself. This group would absorb at 3.4 , 3.5 (weak), 6.8 , 7.7 (weak) and $13\ \mu\text{m}$.

5 Discussion

The surface chemistry of carbon (Boehm 1966; Snoeyink & Weber 1972; Puri 1970) indicates that under a wide range of physical conditions various chemical species can be bound to reactive C atom sites. Since the proportion of unsatisfied valences must increase in small particles, the surface of interstellar carbon particles will be highly chemically active. This implies that many surface sites will combine with atoms and molecules from the gas to form stable surface functional groups such as those shown in Fig. 1 (see also Stecher & Williams 1966). Because of this reactivity it is expected that the dominant surface species in diffuse clouds may be different from those on grains in emission regions. This is another manifestation of the role of surface reactions in determining the optical properties of interstellar particles (Duley 1980). It appears from the infrared data available that methyl groups may be abundant on C grains in diffuse clouds. Reactions with H atoms on the periphery of emission objects converts these groups to methane leaving CH groups to emit in the infrared. As the grain temperature rises and the level of ionization increases even these groups will be lost and no discrete infrared emission will occur. Thus emission at 3.3 and $11.3\ \mu\text{m}$ would tend to be limited to the boundary between cold cloud material and the H II region. Such an effect is of course observed in the Orion Ridge (Aitken *et al.* 1979). The frequent occurrence of weak emission at $3.4\ \mu\text{m}$ then reflects the chemical balance between CH and CH_3 groups on grain surfaces. As a result of this balance, which shifts in favour of CH at high temperatures, the strength of the $3.4\ \mu\text{m}$ emission feature should decrease relative to that at $3.3\ \mu\text{m}$.

as the temperature of the emitting dust increases. Furthermore emission at $3.3\ \mu\text{m}$ and $11.3\ \mu\text{m}$ should be correlated. Such a relationship has been observed (Russell, Soifer & Merrill 1977).

While we have limited this discussion to carbon particles, surface groups will also be present on other types of grain in the interstellar medium. A likely group on oxide or silicate particles will be OH. It has been suggested that surface OH on oxides may influence chemical reaction routes on such particles (Duley & Williams 1979).

6 Conclusions

Surface functional groups bound to small carbon particles are shown to be a likely source of infrared absorption at $3.4\ \mu\text{m}$ in diffuse clouds together with emission at a variety of wavelengths in emission objects. Aromatic CH groups dominate on grains at elevated temperature while aromatic CH_3 groups are important in diffuse clouds. The balance between these two species is controlled by chemical reactions involving C and H. A variety of other chemical groups are likely including $-\text{OH}$, $-\text{CHO}$ and $-\text{NH}_2$. These will contribute additional spectral features and may influence chemical reaction routes on carbon grain surfaces.

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