THE IR EMISSION FEATURES AND HYDROGENATED AMORPHOUS CARBON (HAC) PARTICLES

W. W. DULEY
York University

ABSTRACT. Various sources of non-equilibrium radiation from interstellar dust are discussed. It is shown that the existence of cirrus emission at 12 and 25 μm is consistent with the presence of amorphous carbon dust and arises from thermal spikes within $\simeq$ 10Å subvolumes of normal (0.01-0.1 μm radius) dust grains. The 3.28 μm unidentified infrared (UIR) feature also arises in this way, as the radiative relaxation of high energy vibrational modes accompanying a thermal spike in hydrogenated amorphous carbon. Extended red emission (ERE) and near-infrared (NIR) emission are also discussed and are postulated to originate as edge and defect luminescence from HAC solids with bandgaps $E_g \lesssim$ 2.5eV.

1. INTRODUCTION

Recent observational data suggests that excess emission of various kinds is a fairly common phenomenon under interstellar conditions. The detection of the infrared cirrus at 12 and 25 μm (Weiland *et al.*, 1986) is one example of this type of emission. Other examples include the observation of intense discrete emission at 3.28 μm in a variety of objects (Allamandola *et al.*, 1987) and the detection of broad R and I band (extended red emission) excesses in a number of nebulae (Sellgren, 1984; Witt *et al.*, 1984; Witt and Schild, 1985). There is also some evidence that a broad emission feature centered at about 1.7 μm^{-1} is present in the diffuse galactic radiation field (van Breda and Whittet, 1981).

It is obvious that the observations of diffuse galactic luminescence and extended red emission excesses are incompatible with thermal emission by interstellar dust or molecules since the temperatures required to excite this emission would exceed 2000 K and this would lead to rapid destruction of the emitter involved. On the other hand, emission excesses at 12 and 25 μm can be understood if a mechanism exists whereby dust grains can be transiently excited to temperatures in the 100 – 300 K range. One possibility is temperature spiking (Duley, 1973; Purcell, 1976). Draine and Anderson (1985) have shown that an enhancement in the fraction of graphite grains with sizes < 0.01 μm could explain the IRAS data when temperature spiking is taken into account.

L. J. Allamandola and A. G. G. M. Tielens (eds.), Interstellar Dust, 141–146.

https://doi.org/10.1017/S0074180900125173 Published online by Cambridge University Press

The discrete emission features at 3.28 and 3.4 μm represent an important intermediate case. Thermal emission at this wavelength would require grain temperatures approaching 1000 K (Léger and Puget, 1984). An alternative view assigns the 3.28 and 3.4 μm emissions to ultraviolet pumped infrared fluorescence in PAH-like molecules (Allamandola *et al.*, 1985). It is likely that both these interpretations are to a certain extent correct.

2. STRUCTURE OF CARBON DUST

As discussed elsewhere (Duley and Williams, 1981, 1983; Duley, 1987) a primary component of interstellar dust is likely to be hydrogenated amorphous carbon (HAC). This material exists as a layer on silicate cores and is sensitive to ambient interstellar conditions (Jones *et al.*, 1987) in the sense that it can be removed in weak shocks and graphitized by exposure to the interstellar radiation field.

What is apparent from structural studies (Robertson and O'Reilly, 1987) is that HAC dust can be considered to be a collection of molecular clusters loosely aggregated to form an extended solid. The size of these molecular clusters depends on the H content of the carbon and is typically 1-8 rings in HAC and 20-40 rings in unhydrogenated amorphous carbon (Robertson, 1986). It is these clusters that give HAC the properties of a collection of PAH-like molecules. The relative isolation of these ring clusters from each other has a profound effect on the thermal and electronic properties of HAC. Indeed, as I will show, the apparent excess emission from dust observed in the infrared and visible regions of the spectrum can be directly attributed to the presence of these clusters. In diffuse clouds, photo-oxidation reactions (Duley and Williams, 1986) result in the elimination of clusters with fewer than 6 rings from the surface of HAC, leaving the surface of this material rich in 6-8 ring clusters.

3. ELECTRONIC PROPERTIES OF AMORPHOUS SOLIDS

Duley and Williams (1988*a*) have recently discussed the infrared response of a HAC solid exposed to the interstellar ultraviolet radiation field. The model utilized was one of a collection of graphitic islands loosely bonded to each other and acting as partially independent entities. Energy deposited in one of these islands, for example by the absorption of an ultraviolet photon of energy E, is taken to be redistributed over the $3N$- 6 internal modes of the N-atom cluster over a timescale of some 10^{-12} seconds. The average energy per mode under these conditions is then $e = E/(3N\text{-}6)$. Clusters therefore become electronically hot and may radiate one or more vibrational quanta before this excess energy can leak away into the surrounding solid. Using a simplified energy transfer model, Duley and Williams (1988*a*) showed that excess thermal emission can occur from these islands at temperatures $\lesssim 200$ K. Under these conditions large grains would exhibit excess thermal emission at $\lesssim 20$ μm when exposed to the interstellar radiation field.

The thermal spike model has been previously utilized to describe the radiation response of many amorphous solids (see, for example, Malinovsky, 1987). It has been shown in this work that the energy of an absorbed light quantum tends to localize on a $10^{-21} - 10^{-22}$ cm^3 volume in such amorphous materials. This localization leads to a strongly non-thermal excitation of high frequency phonons (Baumgartner *et*

https://doi.org/10.1017/S0074180900125173 Published online by Cambridge University Press

al., 1983). Phillips (1982) has shown that the effective temperature to be assigned to these thermal spikes can exceed 800 K and that these excitations can persist for up to 10^{-2} seconds. Under these conditions, there is a high probability that the excited microvolume will emit infrared photons (Duley and Williams, 1988*a*).

The analogy between this behaviour and the observed properties of excess interstellar emission is clear. If HAC and amorphous carbon dust are excited with ultraviolet photons, energy will be localized on the graphitic islands that constitute this material. These islands will undergo thermal spiking while still attached to large dust particles. In the case of amorphous carbon, where islands have 20-40 rings, the temperature excursion produced by absorption of an 8 eV photon will be $\Delta T \simeq$ 400-500 K. This thermal spiking is likely the source of the excess emission observed by IRAS in the 12 and 25 μm bands and previously (Puget *et al.*, 1985) ascribed to free-flying PAH molecules. The observation of infrared cirrus emission then confirms the amorphous nature of interstellar carbon dust.

4. EXCESS EMISSION AT 3.28 μm

Generally, emission at this wavelength consists of two components with a sharp feature superimposed on a somewhat broader background (see Allamandola *et al.*, 1987). This emission is customarily observed in regions of higher excitation (e.g. NGC 7027, HD 44179) and can therefore be ascribed in part to the dissolution of HAC grains (Duley and Williams, 1986). The dissolution of HAC dust will lead to the liberation of PAH-like fragments as clusters separate from the parent HAC material. These PAH fragments have a transient existence but will emit at 3.28 μm (the aromatic CH stretch frequency) when excited with ultraviolet radiation. This emission will be narrower in spectral extent than that obtained from PAH fragments on dust. However, emission linewidths of $\gtrsim 25$ cm^{-1} are compatible with cluster emission from dust particles.

The size of molecules emitting under these conditions will be given by the cluster size in the parent solid. Clusters in HAC will therefore consist of up to 6-8 rings while those in amorphous carbon will contain 20-40 rings. It is significant in this regard that Barker *et al.* (1987) conclude from an analysis of the satellite structure associated with the 3.28 μm feature that the emitter contains about 30 carbon atoms. This would imply that the 3.28 μm emitter contained 6-7 aromatic rings. ΔT for a 6-8 ring cluster in HAC excited with 8 eV photons is about 1200 K.

Therefore it appears that the observation of discrete and continuum 3.3 μm emission can be understood in terms of the spontaneous decay of high energy vibrational excitations in superheated 6-8 ring islands in HAC. Because of the thermal-spike nature of this emission, the emitter can be attached to larger grains.

5. RELATION TO OTHER TYPES OF DUST

Recent laboratory data on the IR/UV absorption of HAC films (Ogmen and Duley, 1988) points to a possible connection between the carbon dust present in interstellar clouds and that observed in energetic environments through the UIR emissions. HAC formed by condensation at low temperatures in a hydrogen atmosphere shows 3.4 μm but not 3.28 μm absorption. In addition, the 6.2 μm absorption characteristic of aromatic rings is suppressed. This dust has a 2.9–3.6 μm absorption spectrum that is quite similar to that observed by Butchart *et al.* (1986) in the galactic source IRS-7. Ogmen and Duley (1988) found that exposure of this material to UV (λ >160 nm) light in vacuum resulted in the enhancement of the 6.2 μm "aromatic" feature. This shows that HAC can be partially graphitized by exposure to UV radiation and suggests a possible connection between dark cloud dust and that observed via the UIR features. It may also be significant that the IR spectrum of partially graphitized HAC produced in our laboratory is virtually identical to that obtained from insoluble Orgueil residue by Wdowiak *et al.* (1988). Further laboratory data is required to elaborate on possible connection between UIR, meteoritic, cometary and diffuse cloud dust.

6. EXCESS VISIBLE AND NEAR-INFRARED EMISSION

The question of the excitation of the extended red emission (ERE) and near- infrared (NIR) emissions has been discussed by Duley and Williams (1988*b*) and by Duley (1984, 1987). Widespread emission in the R and I bands has been detected recently by Witt and Schild (1987) and identified with the presence of HAC dust.

HAC is known to be an efficient luminescent solid when excited at energies exceeding 2.5 eV (e.g. Watanabe *et al.*, 1982). This emission can be attributed to edge emission, i.e. to the radiative recombination of electron-hole pairs. The bandgap energy E_g determines the wavelength of this emission, and E_g is, in turn, controlled by the hydrogen content – large E_g is obtained with a high H density in HAC. This implies that the wavelength of peak extended red emission can be used to estimate the hydrogen content of dust within a particular emitting region.

It is significant that a bandgap for interstellar HAC of 2–2.5 eV, as inferred from the interstellar extinction curve (Duley, 1987), is compatible with an average cluster size of 5-7 rings (Robertson and O'Reilly, 1987). As we have seen, this is also in the range of cluster sizes inferred from the unidentified infrared (UIR) emission data. Thus, the unidentified infrared and extended red emissions are likely related and should be spatially correlated.

It appears that newly-formed HAC dust or rehydrogenated amorphous carbon dust has large E_g and therefore will emit strongly in the R band. HAC appears to lose hydrogen after extended exposure to the interstellar radiation field and the emission then shifts to the I band. Still older dust will emit at longer wavelengths as E_g decreases further. The equilibrium cluster size on HAC will also depend on the ambient radiation conditions. When the radiative intensity is small, clusters with fewer than 6 rings will exist on dust. Emission from these clusters would exhibit a higher 3.4/3.3 μm ratio.

The origin of the near-infrared (1-3 μm) continuum observed in many objects (Witt *et al.*, 1984) can be identified with edge emission from carbon dust with smaller E_g. Alternatively, by analogy with emission from other amorphous solids (Street, 1980), this emission could be attributed to defect luminescence within the bandgap of HAC.

TABLE 1

Feature	Wavelength Range	Assignment
Cirrus	$\lambda \geq 12\ \mu m$	T-spike in αC/HAC islands
UIR bands	6.2, 7.7, 8.6, 11.3 μm	T-spike in HAC islands
UIR bands	3.3 μm	T-spike in HAC (high frequency modes)
NIR	R, I band	Luminescence from HAC (defect states)
ERE	R, I band	Luminescence from HAC ($E_g \simeq$ 2–2.5 eV)

7. SUMMARY

Table 1 summarizes the conclusions of this paper with respect to the origin of the various types of non-equilibrium emission observed from interstellar dust. The origin of this emission is consistent with widespread presence of amorphous carbon and HAC dust in the interstellar medium.

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