Section V

Optical Propeties of Grains

ON THE INTERPRETATION OF THE λ2175Å FEATURE

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ABSTRACT. The interpretation of the interstellar λ2175Å feature is reviewed. Various proposed explanations for the feature are examined, and difficulties with each of the proposed interpretations are identified.

1. INTRODUCTION

The interstellar λ2175Å feature is a dramatic piece of spectroscopic evidence which should have much to tell us about, at least, part of the interstellar grain population. It is therefore frustrating that 23 years after its discovery by Stecher (1965), the physical origin of the feature remains controversial. Many papers have been written discussing the problems with proposed identifications of the λ2175Å feature; the reader is especially referred to the papers of Gilra (1972), Savage (1975), and Friedemann and Gürtler (1986).

In § 2 I summarize the principal observational constraints which apply to any proposed model for the origin of the λ2175Å feature. § 3 reviews some general theoretical considerations. In § 4 a number of proposed identifications are reviewed. Most attention will be given to those hypotheses which today appear (to the author) to be the most viable:

1. graphite grains;
2. non-graphitic carbonaceous material;
3. OH^- on small silicate grains; and
4. ultrasmall carbonaceous grains or large molecules.

It seems fair to say that at the present time every proposal must be considered to be to some degree unsatisfactory, either because we do not understand the physics well enough, or because the proposal seems to require excessive "fine-tuning" of the carrier population, or because the proposal does not satisfy known observational constraints. Conclusions are summarized in § 5, along with suggestions for further astronomical or laboratory studies.

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2. SALIENT OBSERVATIONAL CONSTRAINTS

Any discussion of the interpretation of the λ2175Å feature must begin with the observational constraints to which such an interpretation is subject.

Ubiquity: Extensive observational studies of the λ2175Å feature have been published (Savage, 1975; Dorschner, Friedemann, and Gürtler, 1977; Seaton, 1979; Meyer and Savage, 1981; Gürtler *et al.*, 1982; Witt, Bohlin, and Stecher, 1984; Carnochan, 1986; Massa and Fitzpatrick, 1986; Fitzpatrick and Massa, 1986, hereinafter FM86). A general conclusion of these studies is that the λ2175Å feature is quite well-correlated with visual extinction. Although the feature strength (relative to the underlying continuum extinction) can vary by as much as a factor of two away from the mean, both diffuse and "dense" clouds have the λ2175Å feature appearing with comparable strength. Therefore the λ2175Å carrier must not be strongly affected by aspects of the gas-phase chemistry which would exhibit major variations between diffuse and dense environments (i. e., it should not be a small molecule in the gas phase, and it must not be strongly affected by reactions with, or adsorption of, molecules which would be present in denser regions).

Strength: The λ2175Å feature is ***very strong.*** Let n_X/n_H be the number of absorbers per H atom, and let f_X be the oscillator strength (per absorber) associated with the λ2175Å feature. The observed strength of the feature can be used to determine the product $(n_X/n_H)f_X$:

$$\frac{n_X f_X}{n_H} = \frac{m_e c}{\pi e^2}\int \frac{\Delta\tau_\nu}{N_H} d\nu = 9.3 \times 10^{-6} \tag{1}$$

where the term: $\Delta\tau_\nu/N_H$ is the extinction cross section (per H atom) attributed to the feature. [1] Even very strong permitted transitions typically have oscillator strengths (per absorber atom) $f \lesssim 0.5\nu_e$, where ν_e is the number of electrons which can participate in the transition. Hence $n_X/n_H \gtrsim 2 \times 10^{-5}/\nu_e$: the carrier X of the λ2175Å feature must use elements with abundances $\gtrsim 1 \times 10^{-5}$ relative to H, and must therefore contain one or more elements from the set $\{C, N, O, Ne, Mg, Si, S, Fe\}$. Ne is nearly inert and can be ruled out as a carrier. Since S (solar abundance 1.9×10^{-5}) is believed to be at most weakly depleted in the diffuse ISM, and since N and O are electron acceptors [2] , we can conclude that the carrier ***must*** contain one or more elements from the 4 member set $\{C, Mg, Si, Fe\}$, with solar abundances relative to $H = \{4.2 \times 10^{-4}, 4.0 \times 10^{-5}, 3.8 \times 10^{-5}, 3.4 \times 10^{-5}\}$ (Cameron, 1982).

Profile: While a Lorentzian profile gives a good fit to the interstellar λ2175Å feature (Dorschner, 1973; Savage, 1975; Seaton, 1979; Massa and Fitzpatrick, 1986),

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[1] I have used the average Drude fit of FM86 for $\Delta\tau_\nu/E(B-V)$, and an average $N_H/E(B-V) = 5.8 \times 10^{21}\mathrm{cm}^{-2}$ (Bohlin, Savage, and Drake, 1978). For this case $\Delta\tau_{2175}/N_H = 5.27 \times 10^{-22}\mathrm{cm}^2$. It should be noted that for the Drude profile, approximately 76% of $n_X f_X/n_H$ is contributed by the portion of the profile lying in the region 3.35–5.9 $\mu\mathrm{m}^{-1}$ where FM86 have verified their fit; 20% of $n_X f_X/n_H$ is contributed by the assumed profile at $\lambda^{-1} > 5.9\ \mu\mathrm{m}^{-1}$.

[2] Logically, N or O hydrides (NH_3, H_2O) could satisfy the abundance constraint, but lack suitable UV transitions.

FM86 have shown that a better fit is obtained using a Drude profile. FM86 have demonstrated that the central wavelength of the λ2175Å feature is nearly invariant from one line-of-sight to another: 2/3 of the cases have a central wavelength $\lambda_0 = 2175 \pm 10$Å, this represents a $\pm 2\sigma$ variation of only ±0.46%! [3] While only very slight variations in λ_0 are typical, Cardelli and Savage (1988) studied two unusual lines of sight and found $\lambda_0 = 2110$ and 2128Å. It is noteworthy that the FWHM shows appreciable variation: a 2σ variation of ±12% around the average FWHM $= 0.992 \mu\mathrm{m}^{-1}$ (FM86). Somewhat surprisingly, there is *no* evident correlation between the observed width of the feature and the observed central wavelength, although the two anomalous lines of sight with smallest values of λ_0 both have unusually large FWHM (Cardelli and Savage, 1988).

Lack of Associated Features: Searches have been made for other broad ultraviolet extinction features (York *et al.*, 1973; Seab and Snow, 1985; Fitzpatrick and Massa, 1988) with negative results, although Carnochan (1989) reports evidence for a weak feature near 1700Å. Therefore the carrier of the λ2175Å feature must not have associated strong extinction features.

Albedo: Determination of the ultraviolet scattering properties of interstellar grains has proven difficult, with conflicting results from different studies. Observations of the diffuse galactic light (Lillie and Witt, 1976), NGC 7023 (Witt *et al.*, 1982) and the Merope Nebula (Witt, 1985) appear to indicate a significant minimum in the λ2175Å feature, consistent with the feature being due to pure absorption. However, recent studies of two reflection nebulae (Witt, Bohlin, and Stecher, 1986) have reported evidence suggesting scattering on the long-wavelength shoulder of the feature. If confirmed, this scattering would appear to require that the carrier be located in grains with radii $\gtrsim 100$Å, since smaller particles or molecules are ineffective at scattering at $\lambda \approx 2300$Å. Alternatively, the "scattering" may actually be fluorescence, in which case large particle sizes are not required. Given the apparent contradictions between the various studies, however, additional observations are needed.

Correlation with Elemental Abundances: A clue as to the elements comprising the λ2175Å feature carrier is offered by observations of other galaxies with different ratios of C to other elements. Clayton and Martin (1985) noted that the sequence {SMC, LMC, Galaxy} appeared to have an increasing ratio of λ2175Å/E(B-V) and an increasing C/O ratio, suggesting that the carrier of the λ2175Å feature may be carbonaceous. Unfortunately, recent studies of the LMC seem to indicate that the λ2175Å feature outside the 30 Dor region has a strength relative to $E(B-V)$ which is fully 80% of the average Galactic value, and the "typical" extinction curve for the SMC is not yet known (Fitzpatrick, 1989).

Millar (1979) and Duley (1985) have considered the correlation of the strength of the λ2175Å feature with elemental depletions. They have argued that the feature is anticorrelated with the depletion of C. In view of the substantial uncertainties involved in determinations of C depletions, however, correlation studies involving

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[3] However, a number of carbon stars have a strong *circumstellar* extinction feature peaking at $\lambda \approx 2400$–2500Å (Hecht *et al.*, 1984), and the carbon-rich planetary nebula Abell 30 has a strong extinction feature peaking at ~ 2470Å (Greenstein, 1981).

C depletion are of questionable significance. Duley (1985) reported a slight positive correlation of the feature with depletion of Mg for a selected subsample.

Polarization: The only published data on possible polarization in the λ2175Å feature are the upper limits of Gehrels (1974) showing only that there is not a strong linear polarization associated with the feature. Since this could be due to lack of alignment of the carriers (and we do not yet understand the alignment process), the existing polarimetric data do not discriminate among different models for the carriers. WUPPE and the Hubble Space Telescope (HST) should be able to provide very sensitive observations of – or stringent upper limits on – linear (and circular) polarization associated with the λ2175Å extinction feature.

3. SOME THEORETICAL CONSIDERATIONS

The optics of "surface plasmon" absorption have been thoroughly treated elsewhere (e. g., Gilra, 1972; Bohren and Huffman, 1986), but it is appropriate to remind the reader of a few general points. For small spheroidal particles and an electric field either parallel or perpendicular to the symmetry axis, the absorption cross section is:

$$C_{abs} = \frac{2\pi V}{\lambda L^2} \frac{\mathrm{Im}(\epsilon)}{[\mathrm{Re}(\epsilon) + L^{-1} - 1]^2 + [\mathrm{Im}(\epsilon)]^2} \tag{2}$$

where L is the shape-dependent "depolarization factor" along the direction of the electric field ($L = 1/3$ for spheres), ϵ the dielectric function, and V the volume. Thus for small spheroids C_{abs} has a peak near $\mathrm{Re}(\epsilon) = 1 - L^{-1}$ (assuming that $\mathrm{Re}(\epsilon)$ actually passes through this value); this is sometimes referred to as "surface plasmon" absorption, although in the small-particle limit the energy is in fact absorbed uniformly over the volume of the particle. The term "surface plasmon" is nevertheless appropriate, since the position of the resonance depends upon the particle shape; for spheroidal shapes the appropriate value of the depolarization factor L depends upon whether the electric field is parallel or perpendicular to the symmetry axis of the spheroid; with $L < 1/3$ along a "long" axis, and $L > 1/3$ along a "short" axis. While the detailed wavelength dependence of the absorption depends upon the precise shape, nonspheroidal particles are qualitatively similar to spheroids of similar aspect ratio. As the particle size increases, the extinction profile tends to shift toward longer wavelengths as a result of scattering which contributes predominantly on the long-wavelength side of the absorption peak.

Because of the dependence of the extinction profile (position and width) on the particle shape and size, attribution of the λ2175Å feature to grains tends to be somewhat difficult to reconcile with the observed stability of the central wavelength of the λ2175Å feature: possible variations of the shape and size distributions for the absorbing particles from one line-of-sight to another are strongly constrained.

Even without knowing the grain material, one can show that the observed strength of the λ2175Å feature is such that $\mathrm{Re}(\epsilon)$ of the absorber must exhibit large variations in the neighborhood of λ2175Å, and probably takes on negative values (Draine, 1989). If the volume of the carrier is less than $\sim 20\%$ of the total silicate grain volume, $\mathrm{Re}(\epsilon)$ is likely to take on sufficiently negative values that it can satisfy the surface plasmon condition for spheres, $\mathrm{Re}(\epsilon) = -2$ (Draine, 1989). Because of the pronounced wavelength-dependence of $\mathrm{Re}(\epsilon)$, the extinction cross section must show significant dependence on (1) particle size; (2) particle shape; and (3) possible coatings or substrates. The observed near-constancy of the central wavelength therefore suggests that (Draine, 1989) (1) the absorbing grains are small enough to be in the Rayleigh limit ($a \lesssim 50$Å); (2) the shape distribution of the absorbers probably varies little from one line-of-sight to another; (3) the absorbing material is probably free of significant substrates or coatings.

4. PROPOSED IDENTIFICATIONS

4.1. GRAPHITE

Graphite was the first proposed carrier of the λ2175Å feature (Stecher and Donn, 1965), and remains one of the favored candidates. The dielectric function of graphite is not known precisely; here we will use the dielectric function adopted by Draine and Lee (1984), and tabulated by Draine (1985, 1987). The "surface plasmon" condition for spheres ($\mathrm{Re}(\epsilon_\perp) = -2$) is satisfied at $\lambda = 2700$Å and 2200Å, and a strong absorption feature near 2200Å is obtained. For graphite spheres with radii $a < 50$Å, the λ2175Å feature is almost purely due to absorption; however, for $a > 100$Å, scattering is significant. For example, $a = 150$Å graphite spheres have an albedo of 0.09 at $\lambda = 2200$Å.

It is important to acknowledge limitations in our ability to theoretically compute the optical properties of small graphite particles. The computed graphite profile is sensitive to the detailed behavior of the dielectric component $\epsilon_\perp$, which remains somewhat uncertain even for macroscopic graphite crystals studied in the laboratory (see the discussion by Draine and Lee, 1984). Furthermore, the applicability of the "bulk" dielectric function when calculating optical properties of $a \lesssim 100$Å graphite particles is somewhat uncertain [the fraction of the atoms in which lie in the surface monolayer of a graphite sphere is $\simeq 0.06\,(100\text{Å}/a)$]. In the ultraviolet the dielectric function should not be strongly affected by small particle effects, but modest shifts would not be surprising. Unfortunately, there appears to be only very limited experimental evidence regarding small particle effects in the ultraviolet. Day and Huffman (1973) measured the ultraviolet optical properties of arc-produced graphite particles with $< a > \approx 150$Å and found an extinction peak at $\lambda^{-1} = 4.5$ $\mu\mathrm{m}^{-1}$; the measured profile was significantly broader than the observed interstellar feature. There are several possible explanations for the discrepancy between the measured profile and the theoretical cross sections for spheres: (1) a broad range of shapes and sizes among the smoke particles, as noted by Day and Huffman; (2) incomplete graphitization of the particles; and (3) small graphite particles may not be accurately described by the bulk dielectric function.

Since the first two of these explanations may well account for the observations, we do not yet have any direct evidence indicating that the bulk dielectric function (in the ultraviolet) cannot be used for small graphite particles. Nevertheless, any theoretical calculations for small graphite grains must regarded as tentative because the dielectric function remains uncertain.

Hecht (1986) has recently proposed a variant of the graphite hypothesis, where he proposes that the λ2175Å feature is produced by small $a \lesssim 50$Å spherical graphite grains with the variations in FWHM being due to variations in the temperature and size distribution, which, he argues, will affect the dielectric function in such a way as to affect the width of the absorption profile with minimal effect on the central wavelength. Larger carbon grains are assumed to be hydrogenated and non-graphitic, and therefore would not contribute to the $\lambda 2175$Å feature.

How does the graphite hypothesis fare with the observational constraints?

Ubiquity: Graphite grains, if they exist, should be reasonably robust, and the ubiquity of the feature is probably not a problem. The weakness of the feature toward some HII regions could perhaps be due to chemisputtering of the grains (Draine, 1978).

Strength: The graphite hypothesis has no problem with abundances: in the limit $a \rightarrow 0$, the absorption feature in graphite spheres has an oscillator strength per C atom $f = (3m_e m_C c^2)(4\pi^2 \rho a^3 e^2)^{-1} \int \Delta C_{ext} \lambda^{-2} d\lambda = 0.16$ so that only $\sim$ 14% of the solar carbon abundance in small particles is required.

Central Wavelength: For $a \lesssim$ 100Å particles, the peak wavelength is nearly independent of particle size, but shifts toward longer wavelengths as the particle size is increased to $\sim$ 200Å; this result is true both for spheroids (Gilra, 1972) and non-spheroidal shapes (Draine, 1988). Using a recent estimate of the dielectric tensor for bulk graphite (Draine and Lee, 1984; Draine, 1985) and assuming spherical particles, then a particle size $a \approx$ 150Å is required to match the central wavelength of the observed feature. In this case, however, the position of the peak is sensitive to changes in the particle size distribution. Changing the particle shape, however, allows one to obtain a peak at $\lambda 2175$Å in the small particle limit; for the adopted dielectric function this can be achieved with oblate spheroids with an axial ratio of $\sim$ 1.6. Figure 1 shows the extinction cross section for randomly-oriented oblate graphite spheroids; also plotted is a "fit" to the computed cross section, consisting of a linear function of frequency plus a Drude profile with a central frequency $\lambda_0^{-1} = 4.60\ \mu\text{m}^{-1}$, and FWHM $\gamma = 0.99\ \mu\text{m}^{-1}$ (the parameters of the Drude term are those obtained by FM86 for the average extinction curve). It is clear that the fit is excellent! It is notable that with just one adjustable parameter (the axial ratio) the graphite hypothesis is able to reproduce two observed quantities: λ_0 and γ.

It is worth noting that graphite particles minimize their free energy when they are flattened, since the surface free energy associated with the boundaries of the graphite sheets are greater than the surface free energy of the basal plane.

Coatings will cause a shift in the central wavelength (Gilra, 1972), although for thin coatings the shift is only slight (Hecht, 1981). For radii $a \gtrsim$ 50Å the computed graphite profile is sensitive to the particle size: with increasing particle size the feature shifts to longer wavelengths (Gilra, 1972; Draine, 1988). The lack of variation in the central wavelength of the observed $\lambda 2175$Å feature therefore appears to force graphite proponents to postulate that the graphite size distribution is either (1) concentrated at $a \lesssim$ 50Å, or (2) relatively constant from one line-of-sight to another (constant in the sense that the relative amounts (by mass) of small ($a \lesssim$ 100Å) and intermediate ($a \approx$ 200Å) size graphite particles remain constant. If the size distribution over this size region is a power-law (as in some grain models), then the power-law index presumably reflects the physical processes (shattering?

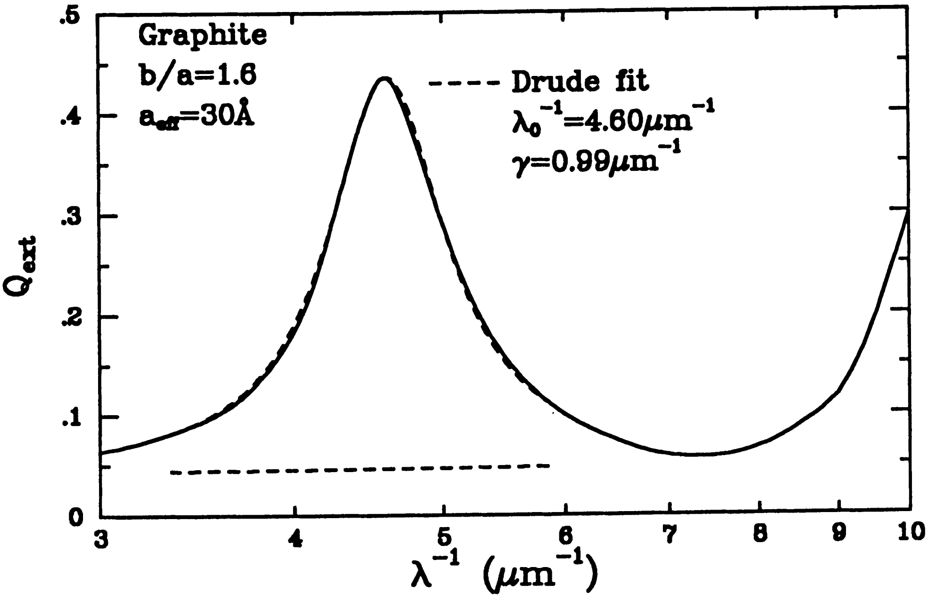

Fig. 1. Q_{ext} for randomly-oriented $a = 30$Å oblate graphite spheroids with axial ratio $b/a = 1.6$. A fit to the computed Q_{ext} is shown for 3.35–5.9 μm^{-1} (see text).

coagulation?) responsible for producing the size distribution, and it would perhaps not be surprising if this index was relatively constant from one line-of-sight to another.

Width: It is somewhat difficult to see how the graphite hypothesis can account for the observed variations in the width of the λ2175Å feature when constrained not to appreciably vary the central wavelength. Perhaps variations in the shape distribution may be responsible: for example, if the λ2175Å feature is due to very small grains, then the shape distribution might remain "peaked" around axial ratio ∼ 1.6, but with a varying width. This could explain λ2175Å features which are broader than that resulting from a single particle shape. If the "central" axial ratio ∼ 1.6 is favored because it minimizes the free energy, then such shape distributions might not be unreasonable. A serious problem, however, is presented by the narrowest observed λ2175Å features, since such a distribution of shapes cannot give a profile narrower than the profile of the preferred axial ratio which, as seen above, has $\gamma = 0.99$ μm^{-1}. Several stars are reported to have λ2175Å features which are significantly narrower: the most extreme example, HD93028, has $\gamma = 0.77$ μm^{-1} (FM86). It does not appear possible to produce such a narrow feature with graphite spheres using the best estimate for the dielectric function; however, it is possible that modest changes in $\epsilon_\perp$ (within the uncertainties) might allow a suitably narrow feature to be produced by small particles with a narrow distribution of shapes.

Associated Features: Graphite has no other conspicuous extinction features at $\lambda >$ 912Å, so that the lack of associated features is consistent with the graphite hypothesis. Small graphite particles should exhibit a strong extinction peak at $\lambda \approx 750$Å (Draine and Lee, 1984), but only the extreme shoulder of this feature would have been present in the $\lambda > 1000$Å *Copernicus* observations of York *et al.* (1973). A weak infrared resonance is predicted at 11.52 μm (Draine, 1984), but this feature is too weak to be observed in interstellar extinction. Even very small graphite particles (too small to scatter appreciably) can contribute substantial absorption at $\lambda^{-1} = 10\ \mu\mathrm{m}^{-1}$; the grains of Fig. 1 have $Q_{ext}(10\ \mu\mathrm{m}^{-1}) = 0.77\ \Delta Q_{ext}$, where ΔQ_{ext} is the portion of $Q_{ext}(4.6\ \mu\mathrm{m}^{-1})$ associated with the feature. The average λ2175Å feature of FM86 has a central optical depth $\Delta\tau/N_H = 5.72 \times 10^{-22}\mathrm{cm}^2$; if due to small graphite grains then those grains must contribute $\tau\ (10\ \mu\mathrm{m}^{-1})/N_H = 4.4 \times 10^{-22}\mathrm{cm}^2$ – approximately 19% of the total extinction at 10 $\mu\mathrm{m}^{-1}$.

Albedo: The claim by Witt *et al.* (1986) to have observed scattering on the long-wavelength shoulder of the λ2175Å feature is approximately what one would have expected for a MRN size distribution of graphite particles, for which the albedo peaks at about 2500Å (Draine and Lee, 1984). It is *not* expected if the λ2175Å feature is produced by very small particles; for this case the feature should be almost purely absorptive in character.

4.2. NONGRAPHITIC CARBONACEOUS SOLIDS

Given the large abundance of carbon, carbonaceous materials are a very attractive means of explaining the λ2175Å feature. The previous section has considered one specific carbonaceous material – graphite. Here we review a number of other proposed carbon-based materials, some of them quasi-graphitic.

Kroto and McKay (1988) have suggested that a quasi-icosahedral shape may be favored for small carbon particles, with nearly-spherical "graphitic" sheets. Wright (1988) has used the discrete dipole approximation to calculate the expected ultraviolet absorption by such a particle, but found that the UV absorption by these particles does not fit the observed λ2175Å feature – the absorption peak is too broad and at too short a wavelength.

Using a plasma discharge in methane, Sakata *et al.* (1983) have produced a material which they refer to as "quenched carbonaceous composite" (QCC). X-ray diffraction studies of QCC indicate the presence of fine graphitic microcrystals containing some hydrogen. Absorption spectra of some samples of QCC show a peak near 2200Å; however, the peak appears to be considerably broader than the observed interstellar λ2175Å feature.

Amorphous carbon particles exhibit an absorption peak at approximately 2500Å (Stephens, 1980; Borghesi *et al.*, 1985; Maggipinto *et al.*, 1985; Bussoletti *et al.*, 1987); such particles may account for the *circumstellar* extinction around various carbon stars (Hecht *et al.*, 1984) and Abell 30 (Greenstein, 1981). Bussoletti, Colangeli, and Orofino (1987) have recently claimed that the peak shifts to shorter wavelengths when the particle size is reduced; they suggest that in very small ($a \approx 10$Å) amorphous carbon grains the peak may be shifted to match the λ2175Å feature. More experimental work is required to test this conjecture.

Starting with various organic molecules in an argon matrix, UV photolysis generates products with strong ultraviolet absorption bands (van der Zwet *et al.*, 1987; de Groot *et al.*, 1988). Unfortunately, the experiments have thus far not produced a material giving a good fit to the λ2175Å feature; in many cases the photolysis products also show unacceptably strong absorptions at other wavelengths.

Sakata *et al.* (1977) reported evidence for an absorption feature at 2200Å in organic extract from the Murchison carbonaceous chondrite; however, Yabushita *et al.* (1987) recently examined organic extracts from two Yamato carbonaceous chondrites and found an absorption peak at 1950Å, but no evidence of a feature at 2200Å.

In summary, there is as yet no evidence indicating a suitable λ2175Å band in any non-graphitic carbonaceous material. Given the attractiveness of carbonaceous materials as the band carrier, however, continuing experimental efforts on such materials are called for.

4.3. OH^- ON SMALL SILICATE GRAINS

Steel and Duley (1987) have suggested that OH^- ions in low-coordination sites on or within Mg_2SiO_4, Fe_2SiO_4, and $MgSiO_3$ particles may be responsible for the interstellar λ2175Å feature. These hydrogenated silicates fluoresce at ~ 4400Å under ultraviolet irradiation; the "absorption spectra" of Steel and Duley – with a peak near 2200Å which strongly resembles the observed λ2175Å profile – are actually inferred from the measured yield (luminescence photons per incident photon) as a function of the energy of the irradiating photons, *assuming* the efficiency (emitted photons per absorbed photon) to be independent of the incident photon energy. Direct laboratory measurements of the absorption profile would be valuable. Whether there are additional absorption features at $6 < \lambda^{-1} < 10\ \mu m^{-1}$ is not known.

If we assume a chemical composition $(Mg, Fe)_2SiO_4$, and assume that a fraction δ of the solar abundance of Mg, Fe, and Si are utilized, then these silicate grains contain approximately $1.5 \times 10^{-4}\delta$ O atoms per H atom. These grains would produce significant continuous ultraviolet extinction. In the small particle limit, silicate grains have an extinction efficiency at $\lambda = 1000Å$ (Draine and Lee, 1984) $Q_{ext}(\lambda = 1000Å) = 1.1(a/100Å)$ which would entail an extinction cross section per H atom $\tau_{ext}/N_H = 2.9 \times 10^{-21}\delta \mathrm{cm}^2$. Since the total observed extinction at 1000Å is $\tau_{ext}/N_H = 2.3 \times 10^{-21}\mathrm{cm}^2$ (Savage and Mathis, 1979) these small hydrogenated silicate particles *must* have $\delta < 0.8$. If we now suppose that p_O is the fraction of the O atoms which are in low-coordination OH^- ions and if f is the oscillator strength of the transition, then $p_O f\delta = 9.3 \times 10^{-6}/1.5 \times 10^{-4} = 0.062$. Since $f \lesssim 1$ and $\delta < 0.8$, this implies $p_O \gtrsim 0.08$. The grains must be either very small or extremely porous to have such a large fraction of the O atoms both hydrogenated *and* in low-coordination sites.

The OH^- hypothesis makes two predictions which may be testable. Steel and Duley (1987) have pointed out that the OH^- hypothesis predicts an absorption feature near 2.9 μm associated with the OH^- stretch mode. The central optical depth of the feature would be $\Delta\tau_{2.9} = (f_{2.9}/f_{2175})(\gamma_{2175}/\gamma_{2.9})\Delta\tau_{2175}$, where $f_{2.9}$ and $\gamma_{2.9}$ are the oscillator strength and FWHM of the 2.9 μm^{-1} feature. For the average λ2175Å profile, this gives $\Delta\tau_{2.9} = 9 \times 10^{-3}E(B-V)(f_{2.9}/3 \times 10^{-4})f_{2175}^{-1}(1000\mathrm{cm}^{-1}/\gamma_{2.9})$.

While weak, this may permit a test of the OH^- hypothesis. In addition, Steel and Duley have pointed out that these grains would be expected to luminesce at ~ 4400Å.

4.4. *POLYCYCLIC AROMATIC HYDROCARBONS*

As discussed elsewhere in this Symposium, free polycyclic aromatic hydrocarbons (PAHs) have been proposed as an explanation for the infrared emission bands observed from a number of reflection nebulae, HII regions, and planetary nebulae (Léger and Puget, 1984). In order to account for the strength of the IR emission features, these molecules would contain $\simeq$ 6% of the total carbon abundance (Léger and Puget, 1984; Puget *et al.*, 1985; Léger and d'Hendecourt, 1986), entailing significant ultraviolet absorption, possibly accounting for the observed λ2175Å feature. Coronene ($C_{24}H_{12}$), for example has a strong absorption feature centered on $\lambda =$ 2000Å (UV Atlas, 1967). Integrating under the measured profile from 1820Å to 2220Å, the oscillator strength of this feature is found to be $f = 2.9$, for an oscillator strength per C atom of 0.12, very similar to the oscillator strength per C atom (=0.16) associated with the λ2175Å feature in small graphite grains. It is therefore clear that if PAHs contain, say, $\simeq$ 6% of the total carbon abundance, they will contribute UV absorption features with an oscillator strength per H atom $\simeq 3 \times 10^{-6}$, $\simeq$ 1/3 of the strength of the observed λ2175Å feature. The principal difficulties with this interpretation are:

1. Thus far, no absorption profile for a PAH or mixture of PAHs provides an acceptable match to the observed λ2175Å profile. Léger *et al.* (1989) has measured absorption for mixtures of PAHs, in all cases obtaining profiles which are significantly broader than the observed feature.
2. Coronene (and other similar PAHs) shows strong optical absorption features (for coronene, peaking near 3000Å; for ovalene $C_{32}H_{14}$ peaking near 3400Å). These optical features are very strong: coronene has an oscillator strength per C atom = 0.06 between 2700Å and 3450Å – fully 40% of the strength of the 2000Å feature. Given our limited understanding of these molecules, however, it is possible that ionization and/or partial dehydrogenation in the ISM may significantly alter their optical properties, *perhaps* in such a way as to permit some mixture of PAHs to account for the observed λ2175Å feature without producing unacceptable absorption features in the 3000–3500Å region.
3. It would be remarkable if Nature conspired to alter the PAH mixture from one line-of-sight to another in just such a way as to vary the width of the profile with minimal effect on the central wavelength!

While further studies of PAHs may discover a class of molecules with properties compatible with the λ2175Å feature, it seems fair to conclude that those PAHs for which UV absorption has been measured *cannot* contribute significantly to the λ2175Å feature. Indeed, as originally noted by Donn (1968) the abundance of interstellar PAHs may be severely constrained by the absence of PAH-related structure in the optical and ultraviolet extinction.

4.5. OTHER HYPOTHESES

Small MgO, CaO particles: It has been proposed that the λ2175Å feature is due to electronic transitions associated with O^{2-} ions in low-coordination sites on the surface of very small MgO and CaO particles. (Duley, 1976; MacLean and Duley, 1982; MacLean, Duley and Millar, 1982). The absorption process involves excitation of O^{2-} $(2p^6)$ to an electronically excited state $(2p^5 3s)$ by photon absorption. If the O^{2-} is located in a surface site of four-fold Mg^{2+} coordination, this absorption occurs at λ2175Å (MacLean, Duley and Millar, 1982). The MgO hypothesis is therefore seen to require that a fraction $0.23/f_X$ of the interstellar Mg atoms be located in *four-fold coordination surface sites*. With $\nu_e = 6$ electrons available, f_X could conceivably be as large as $\simeq 3$. The most obvious difficulty with this hypothesis is that it implies strong associated features: if in a three-fold coordination site, the O^{2-} absorption is at $\simeq$ 2700Å (MacLean, Duley, and Millar, 1982); if the O^{2-} is located within the solid in a site of six-fold Mg^{2+} coordination, the absorption occurs at $\simeq$ 1610Å (MacLean and Duley, 1982). However, observations (Massa, Savage and Fitzpatrick, 1983; Seab and Snow, 1985) show that no strong extinction feature is present near 1600Å or 2700Å. Massa *et al.* have concluded from the upper limit on the 1600Å feature that no more than 3% of the interstellar Mg can be in the form of MgO (in six-fold coordination "bulk" substance). Since it seems difficult to envision MgO particles in which O^{2-} in six-fold coordination sites did not outnumber O^{2-} in four-fold coordination sites, the MgO hypothesis appears to be ruled out.

Dessicated Microorganisms: Hoyle, Wickramasinghe, and Al-Mufti (1985) reported measurements of UV absorption properties of *E. coli* bacteria and diatoms, claiming to find a strong absorption feature near 2200Å. However, Yabushita and Wada (1985) and Yabushita *et al.* (1986) found no 2200Å feature in *E. coli*, yeast, or spores of *Bacillus subtilis*.

Radiation-Damaged SiO_2: Wickramasinghe (1971) suggested that the λ2175Å feature could be due to "color centers" in SiO_2 created by radiation damage. However, this hypothesis appears to be ruled out by the absence of strong features at 6.0μm^{-1} (Gilra, 1972) and 8.4 μm^{-1} (Savage, 1975).

Charge Transfer: Carnochan (1988) has proposed that the λ2175Å feature is due to a hypothetical charge transfer process

$$H + X^+ + h\nu \rightarrow H^+ + X \qquad (3)$$

where $X = Si, Fe, Mg$. The H atom and the X^+ ion are presumed to be in close proximity on or within the grain. The photon absorption cross section is presumed to peak at $h\nu = I_H - I_X$; for X=(Si, Fe, Mg) this is at $h\nu$ = (5.45, 5.73, 5.95), close to the observed central energy = 5.70 eV of the feature. There are a number of difficulties with this proposal:

1. This process has apparently not been observed in the laboratory;
2. If the process occurs at all, there seems to be no reason to expect it to be strong – on the contrary, the limited spatial overlap between the $H(1s)$ wavefunction

and the wavefunction of the outermost electron shell in the metal atom would suggest that the oscillator strength of the transition is unlikely to be large.

3. Carnochan has underestimated the required number of absorbers by a factor of 5. If f is the absorption oscillator strength, then a fraction $0.15(f/0.5)^{-1}$ of all of the Mg, Si, and Fe atoms must be in ionic form and adjacent to an H atom.
4. As noted by Carnochan, the coincidence of the difference in *in vacuo* ionization potentials with the observed energy must be coincidental, since the atom-ion interaction potential, as well as the polarization of the surrounding grain, has been ignored.
5. If the process occurred at all, one would expect it to be accompanied by absorptions resulting in the transfer of the electron to an excited state of the metal atom; e. g., in the case of Mg (using *in vacuo* energies), there should be an absorption band at ~ 10.3 eV, corresponding to transfer of the electron to an Mg $3p$ orbital.

Absorption Edge in Silicate Grains: Huffman and Stapp (1971) suggested that for olivine particles with radii $a \simeq 600$Å, the variation of the dielectric function across the absorption edge could result in an absorption feature at ~ 2200Å. However, the resulting feature is extremely sensitive to the particle size distribution (Gilra, 1972; Savage, 1975) and therefore this hypothesis appears to be ruled out by the observed near-invariance of the feature.

5. CONCLUSIONS

Two of the above proposals stand out as being well-defined, based on at least some laboratory data, and not obviously ruled out by the known observational constraints:

1. graphite grains; and
2. OH^- absorption on the surface of small silicate grains (Steel and Duley, 1987).

In the case of graphite, we have a reasonably good (laboratory-based) knowledge of the dielectric function, and can therefore actually calculate the optical properties of graphite grains (though with the lingering uncertainty that surface effects may modify the dielectric function). The graphite hypothesis has been subjected to quite stringent comparison with the observational constraints, and appears thus far not to have encountered a fatal objection. If scattering turns out to be associated with the λ2175Å feature, then it would appear to be necessary to include graphite grains with radii as large as $a \simeq 150$Å, in which case the observed near-invariance of the central wavelength (FM86) would preclude significant variation of the size and shape distribution from one line-of-sight to another. If, however, the λ2175Å feature is actually purely absorptive in character, then the particles responsible would have to be small: $a \lesssim 50$Å. In this size range the position of the absorption is independent of the particle size (though it does still depend upon the particle shape). As seen above, for one particular estimate of the graphite dielectric function, the λ2175Å feature could be reproduced using small oblate particles with an axial ratio of ~ 1.6, using ~ 14% of the cosmic carbon abundance. It is not clear how the graphite hypothesis can account for the narrowest observed features unless the effective dielectric function actually differs significantly from bulk graphite.

The hypothesis that the feature is produced by OH^- absorption on small silicate grains appears not to be ruled out by known constraints, but this hypothesis is not as well-developed as the graphite proposal. As more laboratory data for this absorber becomes available (oscillator strengths, absorption profiles), detailed calculations (and confrontation with observational constraints) will become possible.

Of the currently viable hypotheses, at present the above two appear to be the best-defined, but some other identification may, of course, turn out to be correct. It would appear to be feasible to obtain laboratory evidence bearing upon the charge-transfer hypothesis of Carnochan (1988), given the fact that the transitions must have large oscillator strengths if they are to account for the λ2175Å feature. Given the cosmic abundance constraints, nongraphitic carbonaceous materials, including PAHs, remain attractive; while published absorption profiles do not appear to satisfactorily match the interstellar profile, it seems worthwhile to pursue laboratory investigations in this area.

In addition to laboratory studies of the properties of proposed absorbers, additional astronomical data would be valuable:

1. To clarify the confusion regarding the albedo of the λ2175Å feature;
2. Further studies of the profiles of "extreme" λ2175Å features, especially the narrowest profiles;
3. Spectropolarimetry of the λ2175Å feature.

The λ2175Å feature remains a puzzle awaiting a convincing solution.

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