THE SPECTROSCOPIC IDENTIFICATION OF INTERSTELLAR GRAINS *

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Abstract. It is shown that the condition of matching the 3.3–3.9 μm spectrum of the galactic infrared source GC-IRS 7 leads to a remarkably tight convergence on the transmittance curve measured in the laboratory for the dessicated bacterium *E. coli*. Other materials, including certain biochemicals and postulated prebiologic compounds, are shown to be deficient with regard to meeting this condition.

1. Introduction

The source of the radiation from the infrared source GC-IRS 7 is thought to be a late-type supergiant. After experiencing interstellar reddening according to a $1/\lambda^n$ law (with n between 1 to 2) the radiation over a limited wavelength range centred around 3.4 μm can be represented as approximating a black-body distribution corresponding to a lower temperature than the supergiant itself. The actual observations of Allen and Wickramasinghe (1981) over the range from $\lambda = 2$ μm to $\lambda = 4$ μm have an envelope that is well-represented by a black-body distribution for a temperature of 1100 K.

Over and above the smooth $1/\lambda^n$ reddening, which includes scattering effects, there are wavelength-dependent absorptions produced by gas and dust lying between the Earth and the centre of the Galaxy. For example, there is an absorption band at $\lambda \cong 2.4$ μm due to CO, and another broad absorption at $\lambda \cong 3.4$ μm that is very likely due to CH stretching. Whereas the 2.4 μm absorption can be explained by the presence of CO in gaseous phase, the 3.4 μm absorption is much larger than can be attributed to gaseous CH, or to CH bonds in other gaseous organic molecules, the deficiency being by several orders of magnitude. Hence the 3.4 μm absorption must be attributed to linkages present in solid particles, presumably of an organic nature.

No solid organic material of which we are aware has a mass absorption coefficient at 3.4 μm that is appreciably in excess of 1000 cm^2 g^{-1}. It follows therefore that, since the amount of the 3.4 μm absorption obtained by Allen and Wickramasinghe is about 0.42 mag corresponding to an optical depth of $\sim$ 0.4, the required amount of organic grain material must be $\sim$ 0.4 mg at least. This mass is to be distributed over the $\sim$ 10 kpc distance from the Earth to the galactic centre,

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requiring a lower limit of $\sim 10^{-26}$ g cm^{-3} for the average density of the organic dust, a value comparable with the total grain density. Thus an appreciable fraction of all the grains appears to be organic.

Suppose one had a typical sample of the interstellar grain material available for examination in the laboratory, and that a measurement of the infrared spectrum of the sample yielded an opacity function $\tau(\lambda)$ due to absorption. Then the measured flux $F(\lambda)$ near 3.4 μm from GC-IRS 7 would be given by

$$F(\lambda) = AB(\lambda, T = 1\,100) \exp[-\alpha\tau(\lambda)], \tag{1}$$

where α is the factor by which the column density from the Earth to the galactic centre exceeds the laboratory sample, $B(\lambda, T{=}1\,100)$ is the Planck function for a temperature of 1100 K, and A is a constant dependent on the distance and the intrinsic emission of the source.

If we had such a sample, the application of (1) would be only a consistency check. Actually of course we do not have such a sample, and so the application of (1) becomes elevated into a condition that a theory of the nature of the interstellar grains must satisfy. The procedure is to measure $\tau(\lambda)$ for a finely-dividend sample of the material which one seeks to test, and then to calculate the right-hand side of (1) using choices for α, A, that do not violate broad constraints such as the available abundance of grains. For consistency, the outcome of this calculation must match the observed values of $F(\lambda)$ to within the accuracies of the observations and measurements, and this agreement must hold, not just at a few selected wavelengths, but *over the whole waveband centred at* 3.4 μm.

It is worth noticing a fortunate circumstance concerning laboratory measurements of $\tau(\lambda)$. It is usual to seal the samples under investigation inside KBr disks at a pressure sufficiently high ($\sim$ 6 ton cm^{-2}) to cause crystals of KBr to form a clear glassy material. The refractive index of KBr is 1.56, which is close to the real part of the refractive indices of many biogenic materials. This means that transmission through disks containing such materials is not appreciably affected by scattering due to inhomogenicities of chemical composition, which is a necessary requirement for measured transmittance values to be equated to $\exp[-\tau(\lambda)]$. Absence of scattering can also be explicitly demonstrated for all those materials with which we ourselves have been concerned, because it happens for them that $\tau(\lambda) \cong 0$ in several widely-separated ranges of λ. Absence of scattering is then proved by the transmission values in these ranges of λ being essentially the same as for a blank KBr disk.

The usual practice of organic chemists appears to be to look for characteristic 'thumbprints' in the function $\tau(\lambda)$ over small ranges of λ, and to ignore the behaviour of $\tau(\lambda)$ over the full range of λ. As best we can tell, this practice has arisen because chemists working with non-biogenic materials often run into a scattering problem, because the real parts of the refractive indices do not match that of KBr. Since the effect of scattering is hard to estimate, the measured transmittance values tell one little in such a case, unless in small wavelength ranges the

absorption function $\tau(\lambda)$ happens to be rapidly varying with respect to λ – i.e. for 'thumbprints'.

To bring this point home even more forcefully, it may be noted that the constant A disappears when (1) is applied both at a variable wavelength λ and at some fixed wavelength, λ_0, say. It is then easy to obtain

$$\tau(\lambda_0) - \tau(\lambda) = \frac{1}{\alpha} \ln \left[\frac{F(\lambda)}{B(\lambda, 1\,100)} \frac{B(\lambda_0, 1\,100)}{F(\lambda_0)} \right]. \tag{2}$$

Since the Planck function is known, astronomical measurements of $F(\lambda)$ determine what $\tau(\lambda_0) - \tau(\lambda)$ must be to within a multiplying constant depending on the quantity of the absorbing grains.

Consider a hypothetical situation in which $F(\lambda)$ turned out to be proportional to $B(\lambda, 1\,100)$. The right-hand side of (2) would then be zero and we would have $\tau(\lambda) = \tau(\lambda_0)$. Suppose further that $\tau(\lambda_0)$ were significantly different from zero. According to the thumbprint procedure one could deduce nothing in such a situation, whereas in fact the need to find a material with a significant non-zero opacity that was maintained strictly constant over a considerable wavelength range would set extremely severe constraints on the nature of the material.

2. The Absorption Spectra of Microorganisms

In the early months of 1980 we found to our surprise that specimens of prokaryotic cells had essentially identical spectra over the waveband from $\lambda \cong 3.3$ μm to $\lambda \cong 3.5$ μm as had a typical eukaryotic cell such as yeast. Exposure of *E. coli* to varying temperatures ranging from liquid nitrogen to 350 °C also produced no appreciable difference for this waveband. Since 1980 methanogens (as representatives of the archaebacteria) have been found also to have the same behaviour, as have diatoms. Thus we have samples of archaebacteria, eubacteria, eukaryotes and algae all with sensibly the same spectra for the wavelength range $3.3 \leq \lambda \leq 3.5$ μm. Since we have frequently suggested this invariance to be general for all such microorganisms and have received no discrepant reports over a three-year period, the broader conjecture appears likely to be true.

The curve of Figure 1 shows the right-hand side of (1), calculated for $\tau(\lambda)$ obtained from *E. coli* while the points of Figure 1 are the measured values of $F(\lambda)$ for GC-IRS 7 given by Allen and Wickramasinghe (1981). Varying the constant A on the right-hand side of (1) moves the calculated curve up or down in the figure, while varying the constant a can make the minimum near 3.4 μm appear either deeper or more shallow. But varying these constants has no important effect on the general shape of the curve from one wavelength to another. For example, the fact that the curve has its minimum at just the value of λ where the astronomical measurements of $F(\lambda)$ have their minimum depends on $\tau(\lambda)$, not on the choices made for α, A.

The scales of Figure 1 are linear for both ordinate and abscissa, and both are large, so that deviations that would scarcely be seen if logarithmic plots had been used show up in Figure 1 as effects amounting to a percent or two, corresponding to the accuracy of the observations, which accuracy is represented by the size with which the points have been plotted.

The fit of the points to the curve of Figure 1 is so good as to raise the question of whether the fit can be interpreted as a demonstration of the presence of microorganisms in space. The answer to this question evidently turns on whether other materials of a non-biogenic nature compounded largely out of the common elements H, C, N, O, can be found with absorption functions $\tau(\lambda)$ that provide a fit to the observations as good as Figure 1.

When the astronomical observations became available (shortly *after* the laboratory measurements had been made) and the agreement of Figure 1 had emerged, we made a search of the chemical literature in order to test the question of whether non-biogenic materials could or could not match the fit of Figure 1. The outcome of our search was that matching for anything other than an obviously contrived complex mix of materials seemed unlikely. Interstellar grains have optical properties that are remarkably similar from one region of the Galaxy to another, which precludes mixtures with many arbitrarily-chosen components.

We felt our search of the literature to be sufficiently thorough for us to risk the opinion that no common organic material of non-biologic origin, satisfying the obvious constraints of the problem, can match the agreement of Figure 1. A typical organic molecule that might at first sight be thought to have a satisfactory spectrum, when properly compared with the *E. coli* shows the discrepancy indicated in Figure 2.

Even highly esoteric materials produced under abnormal conditions failed to do so. To be satisfactory, the spectrum of a material must be the same as *E. coli* to within a few percent at all wavelengths from 3.3 μm to $\sim$ 4 μm, since we know from Figure 1 that the transmittance values for *E. coli* match the astronomical flux values over the whole of this wavelength range. The gross misfit of esoteric materials to the *E. coli* spectrum is shown by the examples given in Figure 3. Both these materials were obtained by a Urey-Miller type of experiment in which a high-grade form of energy was used to disrupt a mix of reduced inorganic molecules. Although the energy input was quite different in the two cases, ultraviolet light for Khare and Sagan (1977) and particle collisions for Moore and Donn (1982), the two spectra are much more similar to each other than they are to *E. coli*, suggesting that esoteric materials produced in any kind of Urey-Miller experiment are likely to have the characteristics shown by the examples of Figure 3, and therefore cannot be serious contenders for the interstellar grain material. Other claims for synthetic materials have appeared in the literature, as for instance in papers by Greenberg (1982), but since the claims have not been supported by appropriately calibrated spectra, they cannot be regarded as valid.

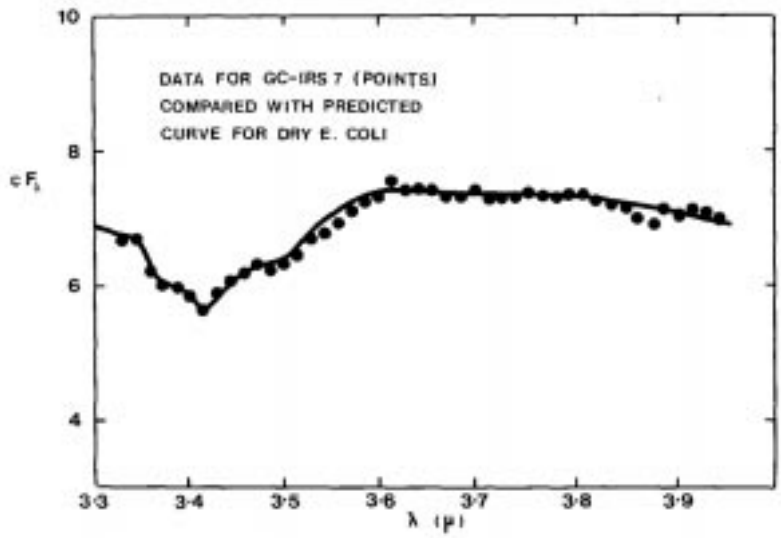

Figure 1. The waveband 3.3–3.9 μm showing the detailed agreement between bacterial data and the flux curve for GC-IRS7.

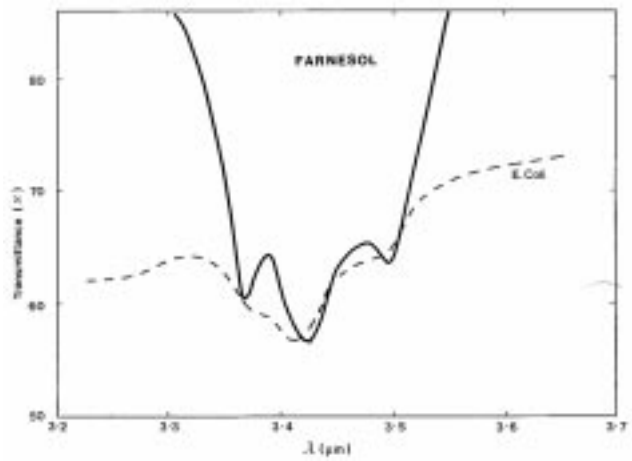

Figure 2. The laboratory absorption spectrum of Farnesol compared with that of *E. coli*. Normalisation is to $100e^{-a\tau(\lambda)}$, with a chosen so as to equalise transmittances at the minimum of the 3.4 μm band.

Furthermore, such spectra of esoteric materials as have been published have had only a poor scale, requiring extensive enlargement before they could be compared with the *E. coli* spectrum, which we ourselves published on the clear-cut scale of Figure 4. Spectra published on a poor scale probably suggest that they were obtained from traces of material, not from bulk samples, and that the amounts obtained in the experiments were vestigial, perhaps being materials in low concentrations among much greater quantities of waste product, unlike the astronom-

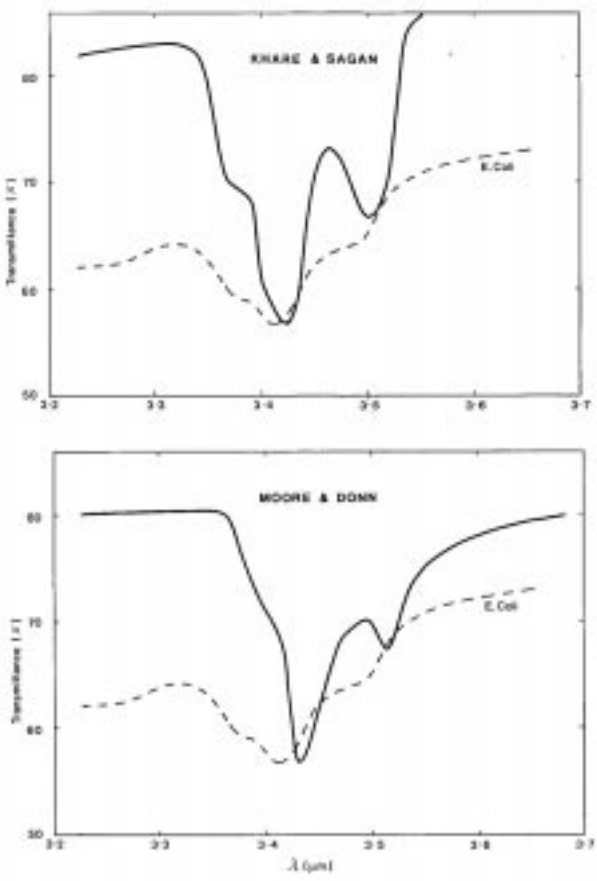

Figure 3. The comparison with *E. coli* of the $\tau(\lambda)$ functions (plotted as $100e^{-\tau(\lambda)}$) for the synthetic polymers obtained in Urey-Miller type experiments by Khare and Sagan (1973) and Moore and Donn (1982). Normalisation is to $100e^{-a\tau(\lambda)}$, with a chosen so as to equalise transmittances at the minimum of the 3.4 μm band.

ical situation in which the material responsible for the 3.4 μm absorption must constitute an appreciable fraction of all the grain material.

3. The Carbonaceous Component of the Murchison Meteorite

Figure 5 compares the spectra of *E. coli* and the carbonaceous component of the Murchison meteorite. The latter contains both organic materials and free carbon in essentially bulk form. If one takes the view that the carbon is a product of a coalification process applied to an orginally wholly organic material, it is possible to estimate what the spectrum of the original material would have been like. This can be done by the following procedure. Define $\exp[-\tau(\lambda)]$ to be the Murchison

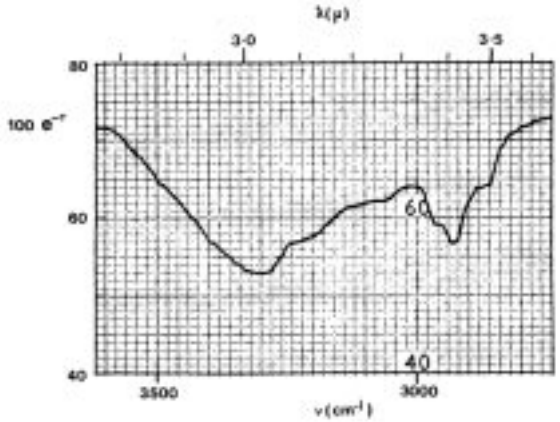

Figure 4. Calibrated laboratory spectrum over the 2.6–3.6 μm waveband for *E. coli* heated to 350 °C in KBr discs (Hoyle *et al.*, 1982).

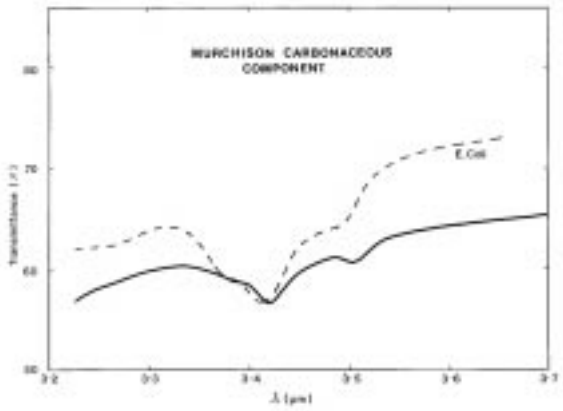

Figure 5. The absorption spectrum of organic material in the carbonaceous component of the Murchison meteorite after removing a flat graphite spectrum contributing 50% to the measured absorption at 3.289 μm. Normalisation as in Figure 2.

transmittance values given in Figure 5, and then determine original opacity values, $\tau_{\text{orig}}(\lambda)$, from

$$\tau_{\text{orig}}(\lambda) = B[\tau(\lambda) - b]. \tag{3}$$

The second term in the brackets on the right-hand side of (3) is the contribution of the free carbon to $\tau(\lambda)$, the free bulk carbon being taken to have a flat absorption over the 3.2–3.7 μm waveband, with the value of b depending on the fraction of the material that is graphite. The multiplying constant B permits $\tau_{\text{orig}}(\lambda)$ to be normalised so that $\tau_{\text{orig}}(\lambda)$ is equal to $\tau(\lambda)$ for *E. coli* at the minimum near $\lambda = 3.4$ μm.

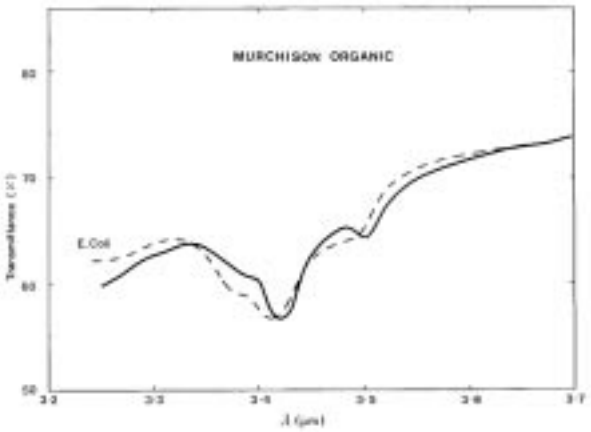

Figure 6. The laboratory absorption spectrum of the carbonaceous component of the Murchison meteorite compared with that of *E. coli*. Normalisation as in Figure 2.

TABLE I

Murchison meteorite amino-acid D/L values

Extract	Glu	Asp	Pro	Leu	Ala
H_2O^1	0.322 (±0.044)	0.202 (±0.005)	0.342 (±0.065)	0.166 (±0.021)	0.682 (±0.062)
H_2O^2	0.30 (±0.02)	0.30 (±0.04)	0.30 (±0.02)	N.D.	0.60 (±0.03)
Hcl^1	0.176 (±0.013)	0.126 (±0.004)	0.105 (±0.017)	0.029 (±0.002)	0.307 (±0.010)

By choosing B, b appropriately we obtained the values of $\exp[-\tau_{\text{orig}}(\lambda)]$ plotted in Figure 6. Here for the first time is a reasonable approximation to a match with the *E. coli* spectrum, a result that can be interpreted in two quite different ways. Undoubtedly the antibiological squad will claim *a priori* knowledge that the Murchison organic material was abiologic in origin, and so will roar until its collective voice is hoarse that an abiologic possibility for the interstellar grain material (responsible for the 3.4 μm absorption in GC-IRS 7) is thereby demonstrated. Others who value their vocal chords will note, however, that Engels and Nagy (1982) obtained the following values for the D/L ratios of amino acids in the Murchison meteorite (see Table I).

These values fit very well to a picture in which the stereochemistry of the original amino acids was of the biological L-forms, with the D-forms being produced

gradually and partially during the coalification process, a situation that is known to occur in the terrestrial fossilisation of biological material.

One can also note that Pflug (1982, 1984) has found very many objects in the carbonaceous material of the Murchison meteorite that are morphologically of distinctive biological forms, as for instance the distinctive bacterium *Pedomicrobium*. Hence one can argue that the spectrum of the original material of the meteorite was like biological material for the good reason that it was biological. Even more boldly, one can see Figure 6 as yet another confirmation that life exists outside the Earth.

Acknowledgement

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