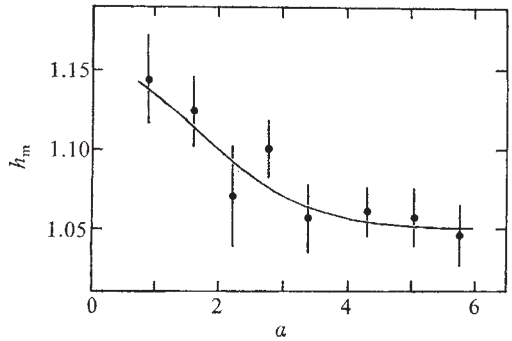

Fig. 2 Mean values of h_m against α in bins with errors bars and regression curve (see Table 1 and text). The last bin, containing only five points, is excluded.

could be present if clusters are actually greater than given by CGCG limits. So we have used another distance criterium, that is, galaxies are more distant than a cluster if $V > V_{cl} - 3\sigma(V)$. This change introduces no difference in our results, since only four galaxies are concerned by it, three slightly, and one ($h_m = 1.04$) having $\alpha = 5.1$ changed in $\alpha = 2.2$.

The second point is the possible relation with the Rubin *et al.* effect[7,8] which is now interpreted by them as a motion of the local group with respect to ScI galaxies ($3,500 < V < 6,500$). The simplest way to take it into account is to correct our data for this motion ($V_{GL} = 450$ km s^{-1} towards $\alpha = 4$ h 12 min, $\delta = 36°$). Our results are practically not affected by this correction. We obtain $\langle h_m \rangle_B{}^* - \langle h_m \rangle_A = 0.090 \pm 0.018$ ($t = 5.0$) and $\langle h_m \rangle_B - \langle h_m \rangle_A = 0.076 \pm 0.017$ ($t = 4.5$). It thus seems clear that if this solar motion exists, it is a small effect and independent of the Karoji–Nottale effect at the distances involved with our sample of Markarian galaxies ($V \sim 10,000$ km s^{-1}).

Remembering that this analysis was performed on a subsample not affected by a Malmquist bias, our conclusion is that these results strongly support the existence of a dependence of redshift on the position of galaxies relative to concentration of matter, that is, clusters of galaxies.

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Polysaccharides and infrared spectra of galactic sources

OBSERVATIONS over the infrared waveband 2–30 μm available for a number of astronomical objects are shown here to be reconcilable with the transmittance properties of polysaccharides. Using an experimentally determined transmittance spectrum for cellulose we can readily relate astronomical data in the 2–4-μm, 8–13-μm and 15–30-μm wavebands and we obtain close fits to astronomical spectra in these several bands. From this detailed spectral agreement we consider it reasonable to infer the detection of interstellar polysaccharides. The identification of this highly complex macromolecule, presumably formed by an abiogenic processing of interstellar formaldehyde, could have a profound bearing on interstellar chemistry including the evolution of prebiotic molecules.

Physical conditions within dense molecular clouds are known to favour the production of organic molecules, probably through electron-exchange reaction chains initiated by the cosmic-ray ionisation of hydrogen and helium atoms[1,2]. The majority of such molecules are fragile, however and are easily broken up by exposure to an appreciable intensity of starlight, which they will be if the parent clouds become dispersed to the normal density of the interstellar gas. Thus, since the interstellar gas undergoes alternating phases of compression and evaporation, there must be corresponding alternations of chemical complexity—molecular dissociations taking place during evaporation and association during compression. As Sagan has pointed out[3] such alternations provide a selective process for the emergence of those chemical forms that can best withstand the adverse conditions of the evaporative phases.

With the exception of H_2, H_2O and CO the most ubiquitous and very likely the most abundant molecule in the interstellar medium is H_2CO, probably formed by electron-exchange reactions[1,2]. Formaldehyde would seem an obvious example of a fragile molecule forming within dense clouds which dissociates as soon as the clouds evaporate. This will certainly be the case for individual molecules, but formaldehyde has the remarkable property of polymerising in many ways, the polymers being far more resistant to break-up than the individual molecules.

The most refractory polymers are probably the polysaccharides, which have substructures built from H_2CO units, substructures with the empirical formula $(H_2CO)_n$, where $n \geqslant 3$. The commonest polysaccharides, cellulose and starch with $n = 6$, are particularly stable because each $(H_2CO)_6$ is able to form itself into a very stable ring, with the polysaccharide then becoming a chain of hexagonal ring substructures. Cellulose can maintain its structure (in a vacuum or in an inert atmosphere of low density) probably up to a temperature of around 625–900 K. (Laboratory data for wood cellulose indicate stability up to about 620 K (ref. 4), but in low-pressure interstellar conditions and in the absence of free oxygen there could exist polysaccharides similar to cellulose which can withstand temperatures up to about 900 K.)

In accordance with the selection occasioned by the alternating phases of compression and evaporation of the interstellar gas, can we expect fragile molecules of interstellar formaldehyde to have evolved into stable polysaccharides like cellulose and starch? Without supporting evidence, this would seem a bold conclusion, to say the least. Yet with the evidence presented here an affirmative answer does indeed seem warranted.

Interstellar solid material is strongly absorbing in two infrared bands, centred at 3 μm and at 10 μm. Because crystals of water-ice absorb at about 3 μm and magnesium silicate at 10 μm, it has seemed natural to attribute the infrared properties of interstellar 'dust' to a mixture of water–ice particles[5] and magnesium-silicate grains[6,7]. Indeed both these assignments are likely to be appropriate in certain types of localised region. But the detailed correspondence of a silicate–ice model to the observed infrared spectra of a wide range of galactic sources is not good, especially if one takes account of experimentally measured absorption spectra for silicate particles[8]. The failure to obtain detailed correspondences is the more disturbing because ice and silicate grains are rather simple materials, without much scope for their properties to be changed by other substances. For such simple materials the issue should be clear-cut, yet it is not. Rather it is frequently necessary to appeal to uncertainties in the astronomical models to explain away discrepancies between observation and theory.

This was the background which made it seem worthwhile to consider whether the infrared properties of interstellar 'dust'

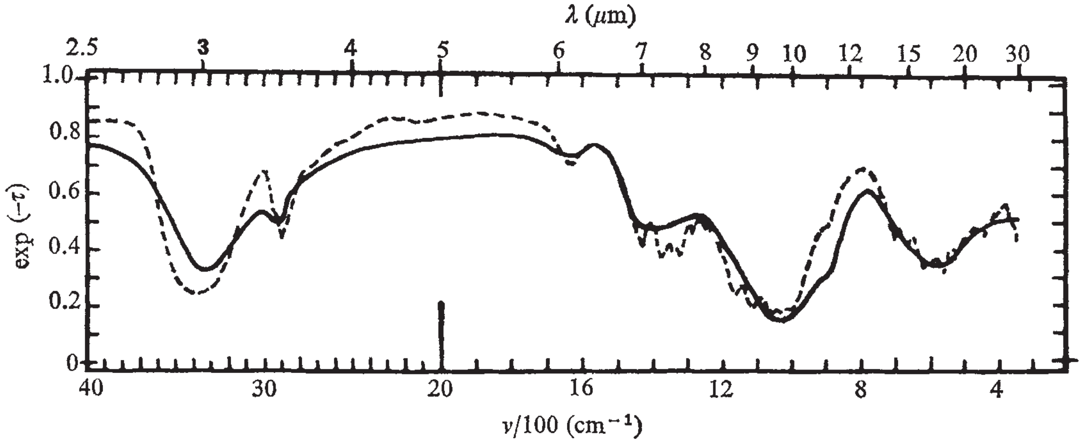


Fig. 1 Dashed curve is the transmittance data for cotton cellulose ('A cellulose 1') from ref. 9. Solid curve represents a smoother spectrum which we have estimated for an ensemble of related polysaccharides.

could be attributed to polysaccharides. Of all the polysaccharides, cellulose seems, because of its economic importance, to have been the most extensively studied, and the broken curve of Fig. 1 is reproduced from a calibrated study of the infrared spectra of cotton and its modifications[9]. Cellulose is immediately seen to have broad absorptions both at 3 μm and 10 μm, with the latter quite devoid of any unwanted spike of high transmittance, such as has been reported for silicates[8]. Transmittance values, $e^{-\tau}$, where τ is the opacity of the experimental sample, can be read off from the curve. Other polysaccharides possess similar transmittance properties, with slight wavelength displacements for the same general features (see ref. 12). The effect of such displacements for an ensemble of polysaccharides would therefore leave the general features unchanged, but must produce smoothing, as we have indicated by the solid curve of Fig. 1.

If the interstellar 'dust' has transmittance values corresponding to cotton cellulose, then the emission per unit wavelength band from an optically thin cloud of 'dust' at temperature T will be proportional to $\tau\ B_\lambda\ (T)$, where B_λ is the Planck function (This assumes the validity of the Rayleigh approximation for small particles with non-resonant absorptions. Technical issues relating to this assumption will be discussed elsewhere). Choosing the constant of proportionality to give a normalisation of 2.00 at $\lambda = 10$ μm, and taking $T = 175$ K, we obtain the dashed curve shown in Fig. 2. The solid curve is calculated from the estimated smoother spectrum for a polysaccharide ensemble (solid line in Fig. 1). Since these calculated curves give excellent fits to the observations for the Trapezium Nebula[10,11] (which are also given in Fig. 2) we consider that a *prima facie* case for the existence of interstellar polysaccharides has been established.

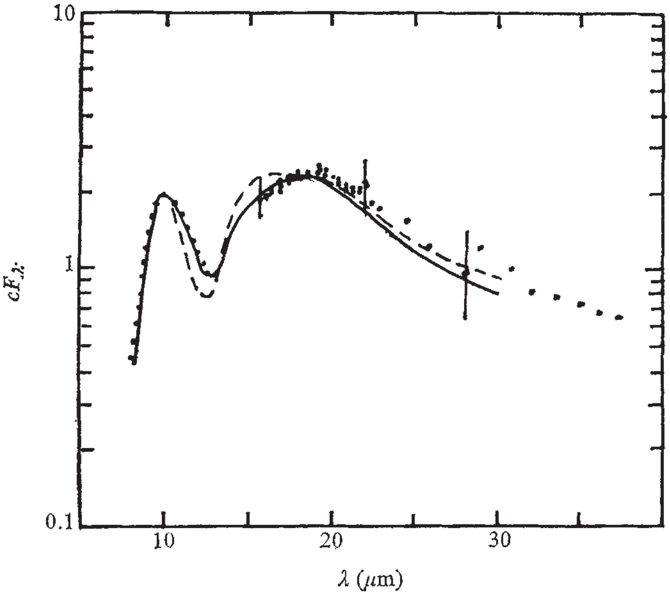


Fig. 2 Normalised flux from the Trapezium Nebula (refs 11, 12) (points) compared with emission from polysaccharide grains of temperature 175 K. Dashed curve is for cellulose (compare Fig. 1); solid curve corresponds to the polysaccharide ensemble spectrum as in Fig. 1.

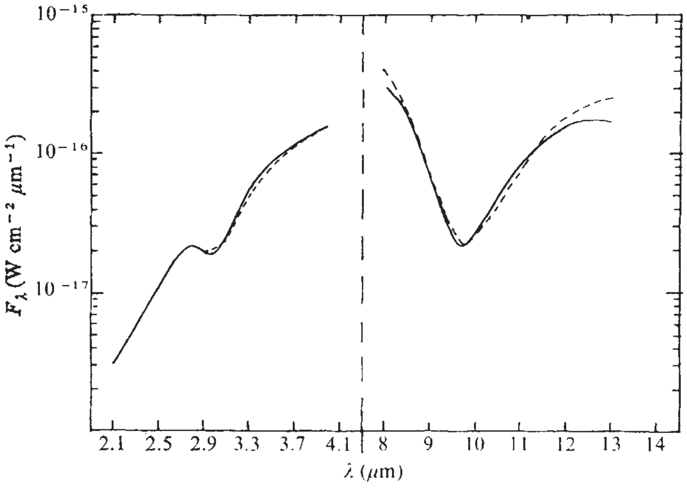


Fig. 3 Solid curve is a plot of the normalised flux against wavelength for an optically thin polysaccharide model with $T = 43$ K, $\alpha = 2.6$. Dashed curve is the observational data for the astronomical source H_2O 610+18.

It has become well known among astronomers that material with the same emissivity as that which gives rise to the Trapezium spectrum also provides a thoroughly satisfactory explanation of the observed characteristics longwards of 8 μm for a wide range of other sources (see refs 13, 14). Hence the agreement of the cellulose data (and of the smooth curve of Fig. 1 in particular) with the Trapezium Nebula already ensures that the polysaccharide data must fit the observed characteristics longwards of 8 μm for the same wide range of sources. Our concern here will therefore be directed to the shorter-wave band 2–4 μm, since it is here that a more interesting situation arises.

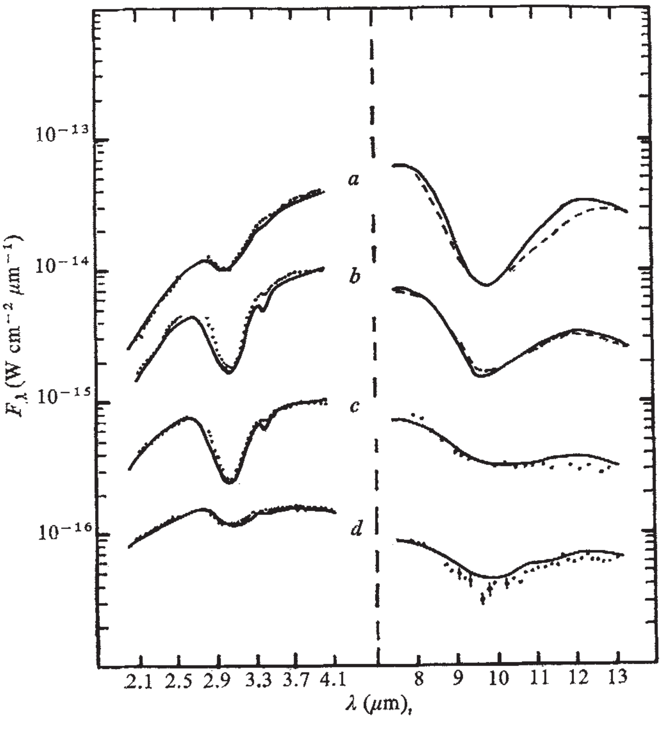
We ask two questions. First, is there a satisfactory agreement of the polysaccharide data to observation for the shorter wavelength band, 2–4 μm? And second, can the shorter wavelength band be related in its intensity to the intensity of the longer wave band?

Taking the latter question first, Fig. 3 shows the relation of observations (broken curve) for the source H_2O 610+18 to the calculated curve (solid) given by the following model:

An optically-thin emitting cloud of temperature T lies behind a foreground cloud that is cool enough for its emission to be not relevant over the wavelength range under consideration here. The relative intensity is determined in the same way as for the Trapezium Nebula, except that an extra factor $\exp(-\alpha\tau)$ must be included to take account of absorption by the cool cloud. Thus the intensity is determined by $\tau B_\lambda(T)\ \exp(-\alpha\tau)$. The particular values chosen to represent the source H_2O 610+18 were $T = 430$ K, $\alpha = 2.6$. The answer to the first of the above questions is therefore affirmative, since the two wavebands are properly related (see also ref. 15, which gives a similar calculation for the source OH 26.5+0.6 taken over the very wide wavelength range of 2–30 μm).

The answer to the second question is also affirmative, as can be seen from the excellent fit of observation and calculation for the four sources given in Fig. 4. The model used here for the 2–4-μm waveband was the same as that described above, except that the hot emitting cloud was taken to be optically-thick. This has the effect of simplifying the formula used in the calculation, through the omission of the factor τ, to $B_\lambda(T)\ \exp(-\alpha\tau)$. The values chosen for T and α are shown in the legend to Fig. 4. The details of these calculations, together with a discussion of several other sources, will be given elsewhere. In particular, the matching of the shorter and longer wavebands for these sources which involves a new feature in the model, will be discussed separately.

Fig. 4 Cases *a–d* represent observational data (points) and normalised theoretical fluxes (solid curves). *a*, Observational points for CRL2591 × 20; theoretical curve on short wave side corresponds to an optically thick polysaccharide model with $T = 650$ K, $\alpha = 0.6$. *b*, Observational points for BN × 4; theoretical curve on short wave side is for an optically thick model with $T = 650$ K, $\alpha = 1.75$. *c*, Observational points for NGC2264IR; theoretical curve on short wave side is for optically thick model with $T = 800$ K, $\alpha = 1.7$. *d*, Observational points for CRL490 ÷ 3; theoretical curve on short wave side is for optically thick model with $T = 850$ K, $\alpha = 0.25$. All the observational data are from ref. 12 and the theoretical curves are normalised to match the observations at one wavelength. The longwave calculations involve model refinements to be discussed elsewhere.



We conclude by noting that near 3 μm the sources of Fig. 4 show dips of very different depths one to another. Yet the same transmittance data was used in all cases—the difference arises from the choices of T and α. In the past, the dips at 3 μm have been attributed to water–ice, with *ad hoc* assumptions of different degrees of condensation of the ice necessary in order to explain the variability of the dips. There are no such *ad hoc* assumptions here. Nor is water–ice required at all.

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Mechanism for formaldehyde polymer formation in interstellar space

CONSIDERING the properties of galactic dust clouds in the wavelength region 8–12 μm Wickramasinghe[1] concluded that formaldehyde undergoes polymerisation in interstellar space to polyformaldehyde. Applying more stringent constraints for matching infrared spectra of galactic sources over the waveband 2.5–30 μm Hoyle and Wickramasinghe[2,3] recently argued for the identification of interstellar polysaccharides—which could be regarded as a further chemical evolution of formaldehyde polymers. A considerable fraction of all interstellar O and C may be locked up as some form of polymerised formaldehyde, making up the main component of interstellar dust. I argue here that molecular tunnelling in condensed formaldehyde is the only viable mechanism for the formation of formaldehyde polymers in interstellar conditions. Such a polymerisation process may be initiated by the action of ionising radiation.

The concentration of gaseous formaldehyde in dense molecular clouds with density $n_{\mathrm{H,H_2}} \sim 10^4\ \mathrm{cm}^{-3}$ is $n_{\mathrm{H_2CO}} \sim 10^{-5}\ 10^{-6}\ \mathrm{cm}^{-3}$. Using appropriate values for the heat of polymerisation of gaseous formaldehyde with the formation of crystalline polyoxymethylene (POM) ($\Delta H = 16{,}700$ cal mol^{-1} at 1 atm) and of the corresponding decrease in the entropy ($\Delta S = 42.6$ cal mol^{-1} deg^{-1}) (ref. 4) one can easily see that at the above-mentioned $n_{\mathrm{H_2CO}}$ values interstellar POM would be thermodynamically stable below ~ 100 K. Furthermore, silicate grains of dimension $\lesssim 0.1$ μm (ejected from cool stars) which many serve as the sites of condensation and polymerisation of formaldehyde have temperatures below ~ 20 K. Thus thermodynamical considerations confirm the possibility of the formation of stable polyformaldehyde