matters arising

Formaldehyde polymers in interstellar space

THE suggestion[1] that polyoxymethylene (POM) crystals exist in interstellar space must be reviewed in terms of the thermodynamics of polymer–monomer equilibria[2]. The formaldehyde–POM equilibrium is notoriously mobile[3], unless the polymer is end-capped[4]. This treatment is applied to commercial samples such as those whose infrared spectra were reported by Tadokoro *et al.*[5], which provided data for the argument[1] for POM in space.

The partial pressure of formaldehyde in equilibrium with POM has been determined over a small temperature range[6], and, by extrapolation, the partial pressure at 20 K (the temperature at which the polymer is supposed to form[1]) is equivalent to 2×10^{-143} molecules cm^{-3}. Chemical thermodynamics thus supports the hypothesis that the polymer exists in some regions of space: a mechanism for initiating the polymerisation process on the surface of mineral particles may be provided by ionising radiation, though the rate of propagation must be extremely small at such a temperature.

At 445 K, the temperature assumed for the dust in the Trapezium nebula[1], the equilibrium partial pressure of formaldehyde above POM, is more than 1 atmosphere, which is greatly in excess of any likely nebulous condition. Only if there were a means for end-capping interstellar POM would it exist at 445 K, and the survival time of such material in the ionising radiation of an H II region would be short. It is, therefore, doubtful that the infrared emission from the Trapezium nebula is from a POM source at that temperature.

It is interesting to note that the concentration of formaldehyde molecules in the Trapezium nebula seems to be greater where ionised atomic material is most dense[7], and it is possible to postulate a role for the formaldehyde–POM equilibrium in the globular model[8] of the core of the nebula, assuming that the temperature and formaldehyde molecule concentrations were suitable.

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WICKRAMASINGHE AND SANTHANAN REPLY—Preliminary remarks on the end-capping of formaldehyde polymers have already been made in the context of the formation of interstellar POM[1]. The vapour pressure data for such stabilised polymers (for example, resins consisting mainly of $(H_2CO)_n$) do not seem to be readily available. The extrapolations of vapour pressure[2,3] data discussed by Fawcett[4] relate to unstabilised POM. For a gas kinetic temperature of 100 K, as may be appropriate to an H I region, the number density of gaseous H_2CO molecules in equilibrium with unstabilised POM reaches the observed value $\sim10^{-8}$ cm^{-3} at a particle temperature, T, $\sim$ 115 K. As that temperature is less than the temperature of most grains, there can be no doubt about the stability of POM even if it were not suitably end-capped in normal interstellar conditions.

We consider it unlikely, however, that interstellar polyformaldehyde will not be end-capped. The formation of POM mantles or whiskers is expected to occur mainly in molecular clouds in the presence of considerable abundances of OH, H_2O and other molecules including CH_3OH. The H_2CO polymerisation could be initiated by the well established process of anionic polymerisation[5]. For example, HO^- from interstellar water molecules may have a crucial role:

$$HO^- + CH_2O \rightarrow HOCH_2O^- + CH_2O \rightarrow HOCH_2OCH_2O^- + (n-2)CH_2O \rightarrow HOCH_2O(CH_2O)_{n-2}CH_2O^- + H^+ \rightarrow HO(CH_2O)_nH$$

End-capping which would ensure maximum stability may be achieved by a similar interaction with interstellar methanol (CH_3OH) molecules.

The polymerisation of interstellar formaldehyde could be initiated and end-capped by this or any other process involving anionic attack. Suitably end-capped formaldehyde polymers (for example, CH_2O resins) are highly stable at room temperature. Such crystalline polymers are expected to have sufficiently low vapour pressures to ensure their stability in H II regions up to temperatures, T, of about 400–500 K, or even higher. Particles heated to temperatures T, of more than 300 K could account for the observed 8–12 band in the Trapezium nebula[5,6].

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Longitudinal photons in the fireball

BYRNE AND BURMAN have discussed the significance of astrophysical data for the problem of the photon mass[1]. A question might arise concerning the possible presence of longitudinal photons in the microwave background were the photon mass not zero. In true thermal equilibrium, the longitudinal modes of the field would have to be populated to the same extent as the transverse modes. Bass and Schrödinger concluded some time ago that millions of years would be required for an appreciable fraction of longitudinal photons to build up in any terrestrial situation[2]. Such time intervals, however, are available when dealing with cosmology.

The probabilities for the emission of longitudinal and transverse vector mesons with wave number k in a given process are in the ratio $m^2c^2/(\hbar^2k^2+m^2c^2)$, where m is the meson rest mass[3]. When $\hbar k \gg mc$, this is approximately $(\lambda/\lambda_c)^2$, where λ is the wavelength and $\lambda_c = h/mc$. If the mean free path of the photon is L, the number of collisions per second is c/L, and the fraction of transverse photons converted