Chemical routes to dust formation in the ejecta of novae

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Summary. The feasibility of the chemical formation of dust-grain nucleation sites in the ejecta of novae has been investigated. Following previous work it is found to be essential for the region of ejecta out of which dust will condense to be carbon neutral. The physics of such a region are not those of a gas in LTE. In particular there is an intense UV radiation field which strongly limits the chemistry. It is found that the only satisfactory route to the formation of nucleation sites is via a limited hydrocarbon chemistry. The depletion of oxygen into CO (and hence the appearance of the 5-μm excess) is thus an essential prerequisite to the formation of hydrocarbon-based nucleation sites. A time-dependent model of the hydrocarbon chemistry indicates that, for the formation of nucleation sites to occur, the ionization must be within certain limits and the H2 abundance must be high in the region of the ejecta where dust formation occurs. This implies that the ejecta configuration and ionization are extremely important factors in determining whether or not a nova will produce dust, and may explain, for example, why certain slow novae such as HR Del failed to produce any dust.

1 Introduction

Of all the cosmic dust-forming objects that have been observed, novae must surely be the most dramatic in that a light-obscuring dust shell is seen to form and evolve as a result of a single eruptive event. Observations of novae can thus be used as a test of our understanding of the processes leading up to the following grain nucleation. There have been numerous papers on the subject of grain formation and growth following nucleation (e.g. Clayton & Wickramasinghe 1976, hereafter referred to as CW). These papers tend to assume that the formation of nucleation sites is rapid and uninhibited by the conditions within the ejecta; occurring when the ejecta temperature falls below some condensation temperature which is determined by the condition that the partial pressure of the carbon gas is greater than the vapour pressure of graphite (CW). Extra constraints such as the state of ionization of the ejecta are important (e.g. Gallagher 1977), particularly during the period of grain growth where coulombic effects are significant. However, the assumption made by many authors, that the ejecta are essentially in
LTE, is clearly not valid; the region of dust nucleation may have a kinetic temperature of 1 or 2 \times 10^3 \text{ K}, but the radiation field is extremely strong and harsh, being characterized by a diluted blackbody at a temperature of some tens of thousand kelvin. In the region of interest, the photodissociation radiation field (\( \lambda \sim 1000 \) to 2000 Å) is several orders of magnitude greater than the ambient interstellar flux, so that the typical lifetime of a small, unshielded molecule may be as short as a few seconds. This is an important point, as it implies that the formation of nucleation sites in an unshielded environment must occur on a comparable timescale and not on the time-scale of several days as we might be led to infer from the observations alone. For simple associative reactions e.g. \( \text{X} + \text{H} \rightarrow \text{XH} \), where \( \text{X} \) is say a metal, complete conversion requires the somewhat large rate coefficient of about \( 10^{-9} \text{ cm}^3 \text{ s}^{-1} \) (for an ejecta density of \( 10^9 \text{ cm}^{-3} \)).

The main hypothesis of this paper is that large hydrocarbon molecules act as the nucleation sites. If and when these nucleation sites have formed, the formation of grains is likely to be fast and efficient (subject to the conditions outlined above), e.g. Gail & Sedlmayr 1987b. The viability of the formation of these nucleation sites is then the most important factor which determines whether or not dust can form in the ejecta.

2 Physical conditions

Before going any further it is necessary to consider the physical conditions in the dust-formation region. Previous work (Rawlings 1986, 1988) has shown that if the region is carbon ionized then molecular formation is inhibited so that the fractional abundances of even the most basic of molecules will be very small, i.e. \( n(\text{CO})/n(\text{H}) \leq 10^{-10} \), \( n(\text{H}_2)/n(\text{H}) \leq 10^{-8} \). This is mainly because all molecules including the \( \text{H}_2 \) and CO are unshielded from the UV radiation field at wavelengths down to 912 Å (the Lyman limit). In a neutral carbon region the carbon continuum and the \( \text{H}_2 \) and CO self/mutual shielding continua can result in a limited chemistry provided the gas temperature is below about 4000 K, above which collisional dissociation destroys the \( \text{H}_2/\text{CO} \) shielding envelope. In any case it is highly unlikely that a neutral carbon region could exist at temperatures greater than this, especially bearing in mind the close coupling between the carbon continuum and the \( \text{H}_2/\text{CO} \) shielding (cf. Rawlings 1988). At temperatures below 4000 K the \( \text{H}_2 \) fractional abundance can rise to about \( 10^{-3} \) or \( 10^{-2} \) and the CO abundance rapidly rises to saturation, i.e. \( X(\text{CO}) \) is the smaller of \( X(\text{C}_{\text{TOTAL}}) \) or \( X(\text{O}_{\text{TOTAL}}) \). However, most other molecules which are unshielded from the radiation field (\( \lambda \geq 1102 \text{ Å} \)) have negligible fractional abundances \( [X(\text{mol}) < 10^{-9}] \).

3 Nucleation mechanisms

If we consider the situation where the carbon is ionized, then the only possible way of forming molecular nucleation sites is by simple atomic bimolecular radiative associations of the sort

\[
\text{C}^+ + \text{H} \rightarrow \text{CH}^+ + h\nu \quad k = 1.7 \times 10^{-17} \text{ cm}^3 \text{ s}^{-1}
\]

(since direct homogenous nucleation of carbon grains is prohibited by coulombic effects and in any case is very slow). These reactions are very slow indeed (as are the equivalent for \( \text{Fe}^+, \text{Si}^+, \text{S}^+, \text{etc.} \)) and yield products which are unstable to the intense radiation field.

However, if the carbon is neutral then the conditions are likely to be more hospitable. The temperature will be lower, the radiation field at least partly blocked and important molecular species such as \( \text{H}_2 \) may be present. An important point, however, is that if the ejecta is carbon rich and – as suggested above – the chemically inert CO saturates, the main components of the
ejecta will be CO, H, H₂ and C (+ N, He, etc....), while if it is oxygen rich (i.e. O > C) then its composition will be CO, H, H₂ and O. Observations tend to indicate that novae ejecta are oxygen rich (e.g. Nussbaumer et al. 1988). If so, then it would seem highly unlikely that carbon dust could condense out of a gas containing no free carbon. Indeed, it would be highly unusual for carbon (as opposed to silicates or SiC) to condense out of an oxygen-rich atmosphere in any event. The abundance measurements may not be representative of the ejecta composition in the region of interest. There are (at least) two possible reasons for this. First, many of the observations from which the abundances have been calculated were made during the ‘nebular’ phase of the ejecta evolution, long after dust condensation has occurred, in which case carbon must be depleted from the gas phase. Secondly, the strong 5-μm excess seen in many novae, and widely attributed to CO emission (e.g. Ney & Hatfield 1978), persists for several days after the nova outburst when we would expect the bulk of the ejecta to be carbon ionized. This indicates (Rawlings 1986) that the source of emission (and hence the region in which grains form) must be density enhanced with respect to the rest of the ejecta for the carbon to remain neutral at these times. It is possible that, as with supernovae, there may be abundance variations across the ejecta envelope as well as density variations.

Here it is assumed that the dust condenses out of this cool, neutral gas consisting mainly of H, H₂, CO, C (N, He, Si, etc.). Homogeneous nucleation and simple radiative association reactions of the type

\[ C_n + C \rightarrow C_{n+1} + h\nu \quad k = 1.0 \times 10^{-17} \text{ cm}^3 \text{ s}^{-1}, \]
\[ H + C \rightarrow CH + h\nu \quad k = 1.0 \times 10^{-17} \text{ cm}^3 \text{ s}^{-1}, \]

are obviously too slow to be significant. Another possibility is that iron atoms/ions may initiate the nucleation process either by simple reactions of the type

\[ \text{Fe}^+ + C \rightarrow \text{FeC}^+ + h\nu \quad k < 10^{15} \text{ cm}^3 \text{ s}^{-1}, \]
\[ \text{Fe}^+ + H \rightarrow \text{FeH}^+ + h\nu \quad k < 10^{15} \text{ cm}^3 \text{ s}^{-1}, \]

or by more complex reactions which create complexes involving CO, such as [Fe(CO)₅] or [Fe₂(CO)₉]²⁺. The simple associative reactions are still too slow to be significant and the products are unlikely to be shielded from the radiation field. The ligand complexes are more stable due to the donation of π bonds into CO anti-bonding orbitals, but they have bond strengths less than that of CO and thus are probably not shielded from the UV radiation field. In all cases one obviously must rely on reactions with simple carbon species to build up graphitic structures, so that we are left with the possibility that the nucleation sites are formed as a result of basic hydrocarbon reactions. In this case the formation and saturation of CO must be regarded as a necessary condition for the formation of nucleation sites to occur (though not a sufficient condition as, for example, in V1500 Cygni a strong 5-μm excess was seen, even though the nova failed to produce dust, e.g. Ferland & Shields 1978). The necessity arises from the fact that the CO ‘locks up’ the oxygen which would otherwise ‘burn’ the hydrocarbons, as is seen to occur in terrestrial situations. The formation of CO and the appearance of the 5-μm excess may thus be a trigger for the formation of nucleation sites.

4 The model of the hydrocarbon chemistry

In order to test the viability of this hydrocarbon nucleation mechanism a time-dependent chemical model based on a limited chemistry has been developed. In any model where one is trying to study the growth of large species it is difficult to decide at what state to terminate the chemistry. In this model, the chemical species included in the scheme are: e⁻, H, He, C, H⁺,
H₂, H₂⁺, H₃⁺, H⁻, C⁺, C⁻, He⁺, HeH⁺ and C₅Hₓ, C₆Hₓ⁺, where x = 1–8 and y = 0–6 (max.).

The choice of C₉Hₓ as the largest species in the scheme is somewhat arbitrary but molecules containing eight carbon atoms probably become more stable as they increase in size, while this is not true for smaller molecules (cf. Gail & Sedlmayr 1987a). C₉ species can thus be regarded as something of a kinetic bottleneck in the route to grain formation. The hydrogenation of the species is also kept low, as it is expected that photodissociation and dissociative recombination reactions will remove hydrogen atoms from the larger species (as required if graphitic dust is to form).

Hydrogen loss from carbon is stimulated by UV in the laboratory (Wild & Koidl 1987) and has been invoked for interstellar amorphous carbon particles (Duley, Jones & Williams 1988). It should be noted that no attempt has been made to differentiate between various molecular structures. This is thought desirable for two reasons. First, the complexity of a network involving all possible isomers would be beyond the range of any existing computer as it would involve many thousands of species; as the structures of even the smaller species are highly uncertain, those of the larger species would be purely conjectural and in any case the differentiation is of no real scientific value since the precise structures are of little specific interest to this problem. Secondly, the extreme uncertainties in the reaction paths and rate coefficients, discussed below, restrict the calculation to being one of a viability study and not a precise quantitative analysis of complex molecular abundances.

The model includes 936 reactions which were collated from a large number of sources. Basic reaction types involving the smaller species were taken from the UMIST Database for Astrochemistry (Bennett 1988) which includes the relevant reactions for astrophysically observed species. Many of the rate coefficients had to be modified so as to take account of the high densities and temperatures in the ejecta (as compared to those encountered in typical interstellar and circumstellar regions). In the case of the larger species, for which no data exist (or else laboratory measurements have been made at much greater gas pressures so that different product branching ratios apply), rate-coefficients and the trends thereof associated with increasing molecular complexity have been estimated in accordance with existing data. Theoretical networks exist for many of the reactions involving larger species (e.g. Schiff & Bohme 1979) and have been included where relevant. However, these networks tend to be based on reactions between complex molecules, i.e. C₅Hₓ + C₉Hₓ → products and thus are more appropriate to the situations where a rich chemistry already exists. In reality we will expect the larger molecules to be suppressed by the intense radiation field so that reactions of the type

C₅Hₓ⁺ + H, H₂, C, Cᵧ⁺ → products

are likely to be more significant in the formation of larger species.

This expectation has been confirmed by preliminary models where it is found that even small species, such as C₆H₂ (and other acetylenes) which photodissociate at wavelengths up to 1550 Å (Nakayama & Watanabe 1964; Suto & Lee 1984) are strongly suppressed by the radiation field. Reactions between complex molecules have therefore been omitted from the scheme. The chemistry of the larger molecules is therefore highly dependent on the stability of the smallest ‘building block’ species and the chemical pathways are determined by the photolytic properties of these species. It has therefore been necessary to do a complete survey of all the data that are available on the photoprocesses, with a view to producing a comprehensive chemical network. The data were taken from a variety of sources and will be presented elsewhere (Rawlings, in preparation). Most molecules have a complicated band/continuum structure in their photodissociation spectrum (e.g. CH₄, C₂H₂ and other acetylenes, C₃H₄ etc.). Dissociation often occurs for wavelengths greater than ~1600 Å, so that these molecules can
only be partially shielded by the carbon continuum ($\lambda \leq 1100$ Å). Other, smaller, species (e.g. CH, C2) have quite well-defined predissociation bands. This is of particular relevance in the case of C2, which has two predissociation bands of interest (Pouilly et al. 1983; one corresponds to the transition $3^1 \Pi_u - x^1 \Sigma_g^+$, which is completely shielded by the carbon continuum and the second (weaker) band corresponds to $2^1 \Pi_u - x^1 \Sigma_g^+$, which is unshielded. C2 is therefore relatively stable and is a very important ‘building block’ in the chemistry. With these considerations in mind a file of reactions additional to the known, measured reactions was generated. The reaction types and representative rate-coefficients are given in Table 1. Helium chemistry has also been included in the model as He$^+$ could prove to be an important reduction agent in the chemistry, especially as helium is seen to be highly overabundant in some novae (e.g. Roche et al. 1984).

The period of time over which the chemistry is to be studied ($t = 30-100$ d post outburst) is comparable to both the chemical and physical time-scales of the ejecta evolution, thus necessitating the use of a time-dependent chemical model (unlike the situation at earlier times when the ejecta is denser and the chemistry achieves steady-state much more quickly). In particular, the ejecta expansion and the temporal evolution of the radiation field must be incorporated into the model. The spectral distribution of the radiation field changes with time as the nova photosphere contracts and its temperature rises, so that the photoreaction rates have to be recalculated for each step in the calculation by integrating over all wavelengths the photodissociation cross-section multiplied by the radiation intensity. This, however, is computationally highly time-consuming so in practice a parameter fit relating the rate to a

<table>
<thead>
<tr>
<th>Reaction type</th>
<th>Rate coefficient ($T$= Temperature)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_2H_2 + H_2 \rightarrow C_6H_6 + H$</td>
<td>$8 \times 10^{-10}$</td>
</tr>
<tr>
<td>$C_2H_2 + C \rightarrow C_6H_6 + H$</td>
<td>$1 \times 10^{-9}$</td>
</tr>
<tr>
<td>$C_2 + C \rightarrow C_2 + h\nu$</td>
<td>$5 \times 10^{-10}$</td>
</tr>
<tr>
<td>$C_2H_2 + H_2 \rightarrow C_6H_5 + H$</td>
<td>$2 \times 10^{-9}$</td>
</tr>
<tr>
<td>$C_2H_2 + C \rightarrow C_6H_5 + H$</td>
<td>$2 \times 10^{-9}$</td>
</tr>
<tr>
<td>$C_2 + C \rightarrow C_2 + h\nu$</td>
<td>$10^{-9}$</td>
</tr>
<tr>
<td>$C_2H_2 + H_2 \rightarrow C_6H_4 + H$</td>
<td>$3 \times 10^{-10}$</td>
</tr>
<tr>
<td>$C_2H_2 + C \rightarrow C_6H_4 + H$</td>
<td>$3 \times 10^{-10}$</td>
</tr>
<tr>
<td>$C_2H_2 + C \rightarrow C_6H_3 + H$</td>
<td>$10^{-9}$</td>
</tr>
<tr>
<td>$C_2H_2 + C \rightarrow C_6H_2 + H$</td>
<td>$10^{-9}$</td>
</tr>
<tr>
<td>$C_2H_2 + C \rightarrow C_6H_1 + H$</td>
<td>$10^{-9}$</td>
</tr>
<tr>
<td>$C_2H_2 + C \rightarrow C_6H_0 + H$</td>
<td>$10^{-9}$</td>
</tr>
<tr>
<td>$C_2H_2 + C \rightarrow C_6H_0 + H$</td>
<td>$10^{-9}$</td>
</tr>
</tbody>
</table>

*Rate coefficients for photoreactions assume an interstellar radiation field.

The values calculated in the model, which are based on the nova radiation field may be some 10 orders of magnitude greater than these values.
polynomial in $T_{\text{PH}}$ (the photospheric temperature) was used. The error incurred by using this method is insignificant compared to the other major sources of error in the model.

5 Results

5.1 The Required Density of Nucleation Sites

Before discussing the results we should consider what the observed number density of nucleation sites is, in the dust-formation zone. If the total number of grains required for an infrared optical depth of unity through the shell is $N_g \sim 7 \times 10^{38}$ (CW) and the dust shell condenses at some radius $r_c \sim 8 \times 10^{14}$ cm and if it is further assumed that the thickness of the shell is about $(r_c/10)$, then the shell volume $V$ is very roughly given by

$$V \sim 4\pi r_c^2 (r_c/10) \sim 6 \times 10^{44} \text{ cm}^3.$$

If the number of nucleation sites is equal to the number of grains then the nucleation site number density is about $10^{-6}$ cm$^{-3}$ (although this figure may be out by a factor of 10 or more, depending upon the ejecta configuration). The total ejecta density in this region is $\approx 10^9$ cm$^{-3}$, so the implied fractional abundance of nucleation sites is $10^{-15}$.

An alternative estimate can be made by assuming that the average (fully condensed) grain size is 2 $\mu$m (CW). Assuming a graphitic composition (i.e. a bulk density of about 2.5 g cm$^{-3}$), each grain consists of $\approx 5 \times 10^{11}$ carbon atoms. If the number of grains is equal to the number of nucleation sites and the total fractional abundance of carbon in the ejecta is $10^{-2}$, then, assuming that all of the carbon is depleted into grains, the implied fractional abundance of nucleation sites is $2 \times 10^{-14}$. In either case, only a small fractional abundance of nucleation sites is required for grain formation to be efficient.

5.2 Results from this Model

The ‘standard’ parameters used in the model are given in Table 2 and the results are illustrated in Figs 1 and 2. Fig. 1 shows the temporal evolution of the abundances of the smaller species

| Table 2. Parameters used in the model whose results are presented in Figs 1 and 2. |
|---------------------------------|------------------|
| Nova luminosity                | $3.1 \times 10^4$ $L_\odot$ |
| Ejecta velocity                | 455 km s$^{-1}$   |
| Initial ejecta/photospheric radius | $1.76 \times 10^{12}$ cm |
| Rate of visual decline from maximum | 0.03 mag d$^{-1}$ |
| Time at start of calculation ($t_0$) | 30 d post-outburst |
| Ejecta density* ($\eta$)       | $5 \times 10^9$ cm$^{-3}$ |
| Ejecta temperature* ($T$)      | 2000 K            |
| Radial dependence of density   | $\eta \propto r^{-2}$ |
| Radial dependence of temperature | $T \propto r^{-0.5}$ |
| Cosmic ray ionization rate ($\xi$) | $1.3 \times 10^{-17}$ s$^{-1}$ |
| Fraction abundances            | $x(\text{C}_{\text{TOTAL}}) = 10^{-2}$ |
|                                | $x(\text{He}_{\text{TOTAL}}) = 0.1$ |
|                                | $x(\text{electrons}_{\text{TOTAL}}) = 10^{-3}$† |
|                                | $x(\text{H}_{\text{TOTAL}}) = 0.9$ |
|                                | $x(\text{H}_2) = 10^{-4}$* |
|                                | $x(\text{H}^+)_0 = 10^{-9}$* |

* At $t = t_0$.
†This is a ‘residual’ abundance corresponding to the contribution to the ionization level from species not included in the scheme (e.g. Mg*, Si*, S* etc).

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(up to C$_2$H/C$_2$H$^+$) and of the 10 largest species whose fractional abundances are greater than $10^{-35}$. The behaviour of the intermediate species tends to be similar to those of other species which have been plotted and in any case are not of any direct relevance to the problem. It is immediately apparent from Fig. 1 that the abundance of the largest species (i.e. C$_7$ and C$_8$ type species) are always far too small for them to be considered as nucleation sites. The sensitivity of the chemistry to the free parameters of the model has been fully investigated and is briefly described below. However, before doing so, we should consider the dominant chemical pathways in the chemistry. Fig. 2 shows the principal formation route of (a) H$_2$ and (b) larger hydrocarbons as deduced from the chemistry at three epochs: log$_{10}$ ($t-t_{\text{START}}$) = 1.9, 5.4 and 6.4 (where $t$ is the time in seconds). In Fig. 2(a) the dominant H$_2$ formation route is via the CH$^+$ molecule and not via H$^+$ as is found at earlier times ($t \sim 1-20$ d post outburst) or via 3-body formation at very early times ($t < 1$ d). Assuming a rate-coefficient of $1 \times 10^{-17}$ cm$^3$ s$^{-1}$ for the rate-limiting stage

C + H $\rightarrow$ CH + hv,
implies a formation time-scale of around $10^5$ d. This is extremely slow indeed so that if, as indicated by Fig. 2(b) and as discussed below, the chemistry is largely dependent on there being a significant amount of hydrogen in the form of H$_2$, then the initial fractional abundance of H$_2$ is a very important parameter. In a shielded (CI) region the only significant H$_2$ loss mechanisms are collisional dissociation and chemical losses.

At the (relatively) low temperatures being considered here (i.e. $T \sim 1000$–3000 K) the collisional dissociation rates are negligible (Roberge & Dalgarno 1982) and in any case the density is not much greater than the critical value below which radiative stabilization of the vibrationally excited H$_2$ is important. Thus chemical loss routes for H$_2$ are the most significant. In the chemical network presented here, the main loss mechanism is

$$
C + H_2 \rightarrow CH + H \quad k = 2.7 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1} \ (T = 2000 \text{ K}).
$$
Dust formation in the eject of novae

Figure 3. Results from the model in which $X(H_2) = 5 \times 10^{-2}$ and $X(e^-) = 10^{-5}$. The plot shows the evolution of the abundances of the seven ‘key’ species, the $C_n/C_n^+$ molecules and the $C_3H/C_4H^+$ molecules.

The carbon abundance is about $5 \times 10^7$ cm$^{-3}$ so that the $H_2$ loss time-scale is $\approx 2 \times 10^5$ s and this is confirmed in Fig. 1 where the $H_2$ abundance drops at $\log (\Delta t) \approx 5$. The importance of this time-scale is reflected in the behaviour of the other curves; the sharp fall in the abundances at $\log (\Delta t) = 5$ is partly due to the physical changes occurring within ejecta; the time-scales for expansion, ejecta cooling and changes in the photospheric temperature are all of the order $10^5$ to $10^6$ s. However, the main cause of the decline is found to be the drop in the $H_2$ abundance. (This is even more dramatically noticeable in Fig. 3, described below.) The importance of $H_2$ and $C_2$ is also apparent in Fig. 2(b), which shows the main types of reaction which lead to the formation of large molecules. The only significant way of making the ‘building block’ molecule $C_2$ is the slow reaction

$$C + C \rightarrow C_2 + h\nu \quad k = 1.0 \times 10^{-17} \text{ cm}^3 \text{s}^{-1},$$

although the $C_2$ – once formed – is relatively stable. From Fig. 2(b) it can be seen that in addition to $H_2$ and $C_2$ the other key species are $C$, $C^+$, $C_2^+$, $CH$, $CH^+$ and $C_2H^+$. The main loss routes for the larger species are, as expected, by photodissociation (for the neutral species) and dissociative recombination (for the molecular ions). The chemical routes illustrated in Fig.
2(b) remain valid throughout the calculations, although at the third analysis epoch (log_{10} \Delta t = 6.4), negative ion reactions are significant in the formation of H₂ and CH₂,

\[ \text{H}^- + \text{H} \rightarrow \text{H}_2 + \text{e}^- \]
\[ \text{C}^- + \text{H}_2 \rightarrow \text{CH}_2 + \text{e}^- , \]

and most of the CH is formed by C + H \rightarrow CH + h\nu.

All of the free parameters in the model were varied to see if the chemistry can be enhanced. In general, the chemistry is fairly insensitive to the free parameters (whose values were varied by up to an order of magnitude in either direction), especially when it is considered that an enhancement of the abundances of the larger molecules by several orders of magnitude is required. By increasing the initial ejecta temperature to 3000 K (or by altering the cooling function) the abundances of many of the species are enhanced by about an order of magnitude in the steady-state ‘plateau’ region (i.e. log \Delta t = 2 to 5) but by the end of the calculation the enhancement has practically disappeared. The chemistry is more sensitive to the density so that when n = 5 \times 10^{10} \text{ cm}^{-3} many of the larger species (e.g. C_3, C_5) have fractional abundances of 2–4 orders of magnitude greater than in the standard case (so that the actual abundances are 3–5 orders of magnitude greater). At densities below \approx 5 \times 10^8 \text{ cm}^{-3} the fractional abundances do not reach steady state before the H₂ is absorbed into the chemistry. The initial fractional abundances of H⁺ and He have no effect on the chemical networks at all (except in the case of directly related species, e.g. H₂⁺, HeH⁺). The chemistry is, however, highly sensitive both to the initial ionization level [i.e. X(e⁻) = n(e⁻)/n_{TOTAL}] and to the initial fractional abundance of H₂ [X(H₂)_0]. The sensitivity to the initial fractional ionization arises from the fact that the main loss route for the larger molecular ions is by dissociative recombination, so that a lower ionization results in a richer chemistry [so that if X(e⁻) = 10^-4 then the medium and larger species are substantially enhanced throughout the calculations, e.g. C_3H_2⁺ and C_6H_6 are 4 and 8 orders of magnitude more abundant, respectively]. The sensitivity to the initial fraction of H₂ is even more universal and dramatic; if X(H₂)_0 = 5 \times 10^{-2} the ‘plateau’ abundances of C₂H₂, C₃H and C₅H⁺ (for example) are raised by 8, 12 and 12 orders of magnitude, respectively, over the ‘standard’ values, although the final abundances of most molecules are only enhanced by 7 orders of magnitude (as the H₂ is absorbed into the chemistry). The effects of having a different ionization level and initial H₂ abundance are illustrated in Fig. 3, where the initial H₂ abundance is X(H₂)_0 = 5 \times 10^{-3} and the residual ionization level is X(e⁻) = 10^{-5}. The abundances of the largest species are still a few orders of magnitude smaller than is required for the nucleation sites but the uncertainty in the values of the rate coefficients and the extreme sensitivity of the chemistry of the larger species to the abundances of the smaller species imply that this is probably a ‘positive’ result. The important points to be drawn from the calculations are:

(a) The formation of nucleation sites via a limited hydrocarbon chemistry is possible, provided the fractional abundance of H₂ is high enough (certainly > 10^{-4}) and the residual fractional ionization level is low enough (< 10^{-3}).

(b) Even if nucleation sites can form, they (i.e. the larger molecular species) will only persist on a time-scale which is determined by the rate at which the H₂ is absorbed into the chemistry. The formation of larger molecules/grains must have started within this time limit. In order to test this requirement we can make a simple estimate of the growth rate of a nucleation site. Assuming physical parameters as per Table 2, a bulk grain density of \sim 2.5 \text{ cm}^{-3} then a simple kinetic growth model whereby gas–grain collisions lead to growth (with unit sticking efficiency), yields \( r(t) \sim r_0 + (1.87 \times 10^{-13}) \times t \) where \( r(t) \) is the grain radius (in m), \( r_0 \) is the initial nucleation site radius and \( t \) is the time in seconds. From Fig. 3 it can be seen that the H₂
presents for \( \sim 10^4 \) s. This corresponds to an increase in the nucleation site size for eight carbon atoms to about 3000. Such a cluster is stable against the radiation field. The time required for the grain to grow to a size of 1 \( \mu m \) is about 60 d (inversely proportional to the ejecta density), which is compatible with observations if the density is slightly higher than the value adopted in Table 2 (say \( \sim 10^{10} \) cm\(^{-3} \)).

(c) Since the maximum abundance of the nucleation sites as predicted by this model is about the same as the minimum abundance required to fit the observations (Section 5.1), it is a conclusion of this model that nova dust is characterized by a small population of large grains, rather than a large population of small grains.

Two possible approaches to enhance the richness of the chemistry have been investigated:

(i) A separate model has been developed which examines the H\(_2\) chemistry from early times up to the time at which the calculations in the main model start. Calculations were performed many times with different values for the various free parameters. The results indicate that the significant H\(_2\) abundances can be achieved if the ejecta temperature (at \( t_0 \)) is slightly lower, i.e. 1000–1500 K, and that it was cooler at earlier times than might be expected if the ejecta were optically thick. A similar enhancement can be obtained by increasing the ejecta density by about an order of magnitude.

(ii) An alternative possibility is that the ejecta may be in a lower state of ionization, i.e. with S, Si, Mg or Fe neutral. In such cases the fractional ionization will obviously be lower and the photodissociation UV flux will be substantially blocked by the ionization continua. It might be expected, therefore, that the chemistry would be enhanced in such regions. However, in all calculations where the ionization is lower than in the standard case, it is found that the chemistry is very severely inhibited and the abundances of the larger species are lower by more than 10 orders of magnitude. This is because the ionization level of the smaller molecular species is reduced and many of the important ion–molecule reactions (e.g. as illustrated in Fig. 2) are suppressed.

6 Summary of conclusions

The conclusions of this paper are briefly summarized below:

(i) Grain nucleation occurs in a region that is not in LTE so that the nucleation mechanism is not solely determined by condensation temperatures and partial vapour pressures.

(ii) The intense nova radiation field and the inefficiency of homogeneous nucleation reactions imply that the grains must form in a CI region.

(iii) In such a region all oxygen is locked up in CO (the assumed source of the 5-\( \mu \)m excess). As the only efficient nucleation mechanism seems to involve hydrocarbon reactions with the larger hydrocarbons acting as nucleation sites, the formation of CO and hence the depletion of oxygen is an essential prerequisite for the formation of nucleation sites.

(iv) A limited time-dependent model of the hydrocarbon chemistry has been developed which takes account of the physical conditions within the envelope. Preliminary investigations show that only simple reactions with small species (e.g. C\(_2\)) are of significance with respect to the formation of large molecules. The stability of these small species is of vital importance to the chemistry.

(v) In favourable conditions (\( x(\text{H}_2) \geq 10^{-3}, x(e^-) \leq 10^{-3} \)) the largest species (i.e. C\(_4\) species in this scheme) can reach fractional abundances of greater than \( 10^{-18} \). While the required fractional abundance of nucleation sites is \( 10^{-15} \), the uncertainties in the chemistry imply that these abundances are compatible with the observations. This is apparent from the fact that
small variations (e.g. a few tens of per cent) in the rate-coefficients for the reactions involving the smallest species can affect the abundances of the largest species by a few orders of magnitude.

(vi) As a consequence of (v), the model predicts that the nova dust primarily consists of a small population of large grains (∼μm) rather than a larger population of smaller grains.

(vii) The chemistry is insensitive to the parameters in the model other than the H₂ and electron abundances to which it is extremely sensitive. Models of the chemistry at early times show that the dust-forming region must be fairly cool at early times (T < 1500 K at t₀) and that the ionization must be appropriate to a CI region where the other, heavier metals are essentially ionized. This is a very important point as it implies that if the ejecta is too neutral then dust nucleation sites cannot form. This may help to explain why the very slow nova HR Del, whose ejecta maintained a low ionization level, failed to produce dust (Gallagher 1977), while slow novae are generally regarded as the most efficient dust producers. In all cases, the ejecta configuration, elemental composition and ionization structure are the most important factors which determine whether or not dust will form. These factors probably depend on the nova speed class in which case the correlation between speed class and dust formation may be more complicated than has been previously suggested (e.g. Gallagher 1977).

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