Hydrocarbons from shocked carbonaceous dust

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ABSTRACT
Carbonaceous dust is expected to release hydrocarbons upon erosion in interstellar shocks. When released into a predominantly atomic gas, the subsequent chemistry of these hydrocarbons may lead to detectable amounts of CH and CH+. We predict column densities for these molecules and show how the N(CH+)/N(CH) ratio may constrain the shock parameters.

Key words: molecular processes – shock waves – dust, extinction – ISM: molecules.

1 INTRODUCTION
The molecular ion CH+ is detected in diffuse interstellar clouds with column densities ranging from about 10^{12} to more than 10^{13} cm^{-2}. These values are much higher than can be accounted for by cold cloud chemistry (see e.g. Dalgarno 1976), and attention has shifted to explanations of the origin of CH+ in warm regions in which the endothermic reaction

\[ C^+ + H_2 \rightarrow CH^+ + H, \quad \Delta E/k = 4640 \text{ K} \] (1)

is the formation route. However, shock models (Elitzur & Watson 1978; Draine 1986; Draine & Katz 1986a,b; Pineau des Forêts et al. 1986; Hartquist, Flower & Pineau des Forêts 1990) have not proved entirely satisfactory (cf. Hartquist et al. 1990; Duley et al. 1992), and warm interfaces between hot gas and cool molecular gas have been suggested as the location of the CH+ and some other molecules (Duley et al. 1992; Hartquist, Dyson & Williams 1992).

Most attention has been given to those lines of sight for which the CH+ abundances are largest and for which H2 is also abundant. However, little attention has been given to whether CH+ is actually formed in regions containing large amounts of H2, or whether it is formed in regions of low H2 content. Obviously, in regions containing very little H2, formation of CH+ by reaction (1) does not operate. The observations of Hobbs (1972, 1973), in particular, show the presence of a number of weak features, possibly of CH+ (\textgreek{c}> 1 m\text{A}), not attributable to 13CH+, and displaced from the main CH+ lines by velocity shifts of the order of 30 km s^{-1}.

Duley et al. (1992) suggested that CH+ may arise in the shock erosion of carbonaceous dust in regions without H2. Those authors made a crude estimate of abundances that might be expected from this mechanism. The purpose of this paper is to investigate, using a detailed shock model and an adequately extended chemistry, the abundances of CH+ and CH in post-shock gas in which H2 is a very minor constituent. The aim is to identify astrophysical conditions in which detectable amounts of these molecules could be found as a result of the shock injection of hydrocarbons from dust in regions of low H2 content. Shocked regions abundant in H2 are therefore excluded from this study, since formation of CH+ by reaction (1) will dominate there. Current limits of detectability in the optical spectrum are in the range 10^{11}–10^{12} cm^{-2}, but these may be expected to improve [for example, Stahl et al. (1989) have observed 13CH+ at N=4 \times 10^{11} cm^{-2} towards \xi \text{ Oph, and Centurión & Vladilo (1991) have reported a similar result towards \mu \text{ Nor}]. Our results show that currently detectable column densities of CH+ and CH should result from the passage of shocks with speed V, of the order of 30 km s^{-1} through neutral (mainly) atomic regions with nH \sim 1–10 cm^{-3}. A systematic search for such lines in regions in which H2 is of low abundance would, therefore, reveal information about interstellar dynamics in regions of low neutral density, and would confirm the existence of carbonaceous grains containing alkanes in the interstellar medium.

In Section 2 we describe the carbonaceous grain model adopted and the chemistry initiated by the injection of hydrocarbons from the gas. We describe the shock dynamics in Section 3, and give the results of the calculations in Section 4. Section 5 contains a brief discussion of these results.

2 GRAIN MODEL AND GAS-PHASE CHEMISTRY
We adopt the grain model described by Jones, Duley & Williams (1990), in which the grains are composed of a silicate core and a carbonaceous mantle. The structure of the mantle is sensitive to the nature of the surrounding gas and to
the intensity of the local UV radiation field. Carbon freshly deposited on the core in an environment rich in atomic hydrogen tends to be polymeric, but exposure to UV radiation tends to graphitize the carbon, making it more PAH-like. The chemical structure is, therefore, dependent on the ratio of H atom to UV photon fluxes. The upper layers of the mantle which are the most recently deposited will tend to be mainly polymeric, and it is these layers that will be released by sputtering in weak shocks, while stronger shocks may also release PAH molecules. The alkanes released may be CH₃ or C₂H₆, for example, but for the sake of simplicity only CH₃ is considered here. The subsequent chemistry of CH₃ is shown in Fig. 1. The corresponding rates and rate coefficients are given in the UMIST Rate file (Millar et al. 1991). The rates of photoexcitation (4) and (10) have been increased by a factor of 1.8 in order that they be consistent with the Draine radiation field.

The formation of CH⁺ from CH does not compete with the most favourable route – the ionization of CH₃, which, in the absence of any substantial amount of H₂, is followed by dissociation to CH⁺. Reaction (9) is highly endothermic but has some relevance in hot post-shock gas. Although the hydrocarbons injected into the gas may be in a variety of forms, the outer layers of the dust are expected to be almost entirely small alkanes (see Jones et al. 1990) which are expected to pass rapidly through stages of dissociation and ionization to appear as CH₃⁺, CH₂⁺ or CH⁺. Then the network indicated in Fig. 1 should apply. It should be noted that whichever species are involved in the passage might be expected to have similar column densities to that of CH⁺, so that they may also be observable if the relevant spectroscopic data are available. In fact, alkane ratios may then allow a determination of the mantle alkane concentrations.

The chemistry consists of 38 species, with pre-shock abundances obtained by running a static, time-dependent diffuse cloud model for 10⁶ yr. Cooling is both molecular and atomic and is adopted from the work of Hollenbach & McKee (1979) as described in Taylor & Williams (in preparation).

3 SHOCK MODEL

The total hydrogen column densities, N_H, along lines of sight to bright stars are typically ~10²¹ cm⁻². Much of this material is, however, contained in relatively dense clouds (n_H ≥ 10⁴ cm⁻³) in which the abundances of H and H₂ are comparable. We are not concerned with such regions here. We consider the passage of a shock through diffuse atomic gas along a line of sight which may or may not contain dense H₂ gas. We shall treat the density in these atomic regions as a free parameter; the pre-shock temperature will be taken to be 100 K and the visual extinction A_v = 0.5. Whether or not a magnetic field perpendicular to the shock front is included, shocks in such clouds are likely to be J-type. The possible effects of a magnetic precursor have been ignored here.

The existence of diffuse atomic hydrogen clouds in such lines of sight is well established. They may be of low H₂ abundance because they are optically thin in the Lyman and Werner bands of H₂, so that only a low steady-state abundance of H₂ can be established (typically, 10⁻⁷–10⁻⁵ cm⁻³). It may be that collisional dissociation of the molecular hydrogen by the passage of the same or a previous shock (cf. Lepp & Shull 1983) has left the region almost entirely atomic and that re-association has not yet occurred.

Degradation of grains is assumed to be caused by gas particle sputtering rather than grain–grain collisions. In order to calculate the sputtering, the gas–grain relative velocity is required. Grains are conventionally taken to gyrate about the magnetic field, but we have shown (Taylor & Williams, in preparation) that the dynamics of larger grains (a ≳ 10⁻⁵ cm) are likely to be largely unaffected by magnetic fields of reasonable strength, whereas small grains (a ≲ 10⁻⁶ cm) will probably gyrate about the field. By gyration we mean a = v/ω, where ω is the dust gyrofrequency and ρ is the dust stopping distance (cf. e.g. Havnes, Hartquist & Filipp 1987). Adopting the ‘guiding centre’ approximation (Spitzer 1976) for small grain motion, the gas–grain relative velocity, v_w, can be calculated for the two characteristic grain sizes adopted, a = 10⁻⁵ and 10⁻⁶ cm. In model runs for grains with a = 10⁻⁵ cm, the pre-shock magnetic field strength was taken to be B = 1 × 10⁻² μG (n_H cm⁻³), ensuring that the grains moved through the gas as though no magnetic field were present. In contrast, in runs for grains with a = 10⁻⁶ cm, we took the pre-shock magnetic field strength to be B = 1 × 10⁻² μG (n_H cm⁻³)⁻¹/², and the above approximation is then valid for small grains. In reality, either gyration of small grains or drift of large grains will occur, depending on whether the field is weak or strong. The drag force on the grain is calculated using the formula of Draina & Salpeter (1979). The number densities implied by these grain sizes are

Figure 1. Reaction network for released CH₃ molecule. (Reaction 21 represents a further type of reaction that must be included if larger alkanes are released.)
RESULTS

4.1 Large grains

We have considered shock velocities of $V_s = 15-40$ km s$^{-1}$ and taken $x(H_2) = 10^{-5}$ as a representative low molecular hydrogen abundance. With this assumption, grain production always outstrips gas-phase CH$^+$ production. Cooling is then relatively inefficient because in these circumstances H$_2$ is not an important coolant, and neither is it an effective precursor to the formation of other coolant molecules such as OH or CO. For most model parameters, the sputtering yield is drastically reduced for a given $V_s$ compared to that for shocks in gas with high $x(H_2)$, because grains are brought to rest in hot post-shock gas. This means that $v_{\text{rel}}$ has a thermal distribution whereas, for shocks in gas with high molecular hydrogen content, the cooling is rapid enough that $v_{\text{rel}} \sim V_s$. In fact, drift through the cooling zone may occur for larger grains in the lower energy shocks (i.e. $V_s = 15$ km s$^{-1}$ or $n_H = 1$ cm$^{-3}$).

We arbitrarly limit the amount of carbon that can be released per shock to a maximum of 45 per cent of mantled carbon, corresponding to an injection into the gas phase of a carbon fraction of $10^{-4}$ ($\sim 27$ per cent of cosmic carbon). With low H$_2$ content, rather higher values of $V_s$ are required to librate this amount of material than otherwise.

We have set out to parametrize the conditions required for shock-dust production of CH$^+$, and have therefore left the yield parameters as variables, for two reasons. First, as explained above, the physical sputtering coefficients for HAC are not well known. Secondly, the chemical sputtering of HAC is also occurring in such regions. Mantle production of CH$^+$ has most effect when all the available alkanes are released, and then the post-shock chemistry influences the CH$^+$ production. Hence, as the shock velocity is varied, suitable values of $A_s$ and $E_T$ are adopted such that this occurs. These values are indicated for the various cases considered in Table 1. Note that these values are not independent.

Given that, regardless of shock velocity, all the alkanes are assumed to be released, then the chemistry of the injected species, CH$_2$, dictates the CH$^+$ column densities achieved. Reaction (2) dominates the destruction of CH$_2$ for the case in which $n = 100$ cm$^{-3}$ and the interstellar radiation field measured in terms of the standard value is $x = 1$, and hence decreasing $n$ or increasing $x$ helps the formation of CH$^+_2$ and CH$^+$. This can be seen in the model permutations of $n = (100, 100)$ and $x = (1, 5)$. Table 1 also shows the change in the CH$^+$/CH column ratio with decreasing $V_s$. The ratio decreases because, although lower post-shock temperatures mean less CH is formed (since reaction 2 is endothermic), CH$_2$ is also destroyed more slowly at lower temperatures to form neutral carbon by reaction (16) (which is also endothermic). Meanwhile, destruction of CH$^+$ to C$^+$ (reaction 12) has an inverse temperature dependence so that it proceeds more quickly at lower shock velocities.

Hence it would seem that high temperatures and radiation fields and low densities optimize CH$^+$ production. However, it is difficult to achieve column densities considerably above $10^{14}$ cm$^{-2}$ by this mechanism, since the CH$^+$ formed is also rapidly destroyed in such an environment. For example, increasing the radiation intensity to values corresponding to
$\chi > 5$ leads to more $CH_2 \rightarrow CH_3^+$ conversion, but $CH_3^+$ is also photodissociated to $C^+$ more quickly.

Table 1 indicates that gas-phase shock production of $CH^+$ in the presence of substantial $H_2$, $x(\text{H}_2)=0.2$, can lead to column densities of up to $\sim 4.5 \times 10^{11}$ cm$^{-2}$, whereas for $x(\text{H}_2)=10^{-2}$ column densities of $CH^+$ are less than about $2 \times 10^{10}$ cm$^{-2}$. Even with such low $H_2$ fractions, reaction (1) is still the important formation route to $CH^+$ in the gas phase. Therefore lower $H_2$ columns ($N \approx 10^{16}$ cm$^{-2}$) will produce even less gas-phase $CH^+$.

Reducing the density to $n = 1$ cm$^{-3}$ might be expected to increase $CH^+$ production. However, at such densities large grains begin to drift through the cooling zone appreciably, as in the high-$H_2$ cases. Sputtering in these cooler regions tends to lead to lower $CH^+$ columns, for the reasons described above.

### 4.2 Small grains

Our shock models show no significant acceleration of small grains about the field lines so that significant non-thermal relative velocities are not obtained. The acceleration is presumably suppressed because the cooling is too slow and the grain mass is small. However, alkanes on these grains are also released by thermal sputtering, and similar alkane quantities to the large-grain case can be released. The $\chi$ and $n$ dependences of $CH^+$ will also be similar to the large-grain case. Hence the results presented in Table 1 are probably not significantly dependent on the presence of a weak transverse magnetic field.

<table>
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<tr>
<th>$V_2$, $n_H$</th>
<th>$x(\text{H}_2)$</th>
<th>$CH^+$</th>
<th>$N(\text{CH}^+)$</th>
<th>$N(\text{CH})$</th>
<th>$N(\text{CH}^+)/N(\text{CH})$</th>
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*H$_2$ allowed to be collisionally dissociated.

### 5 DISCUSSION

Detections of $CH^+$ absorption lines in high signal-to-noise ratio observations along lines of sight known to have low column densities of molecular hydrogen will, according to these results, confirm the presence of shocks in these diffuse neutral regions and their interaction with carbonaceous grains. The $CH^+/CH$ ratio can be used to distinguish between shock parameters if CH is observed simultaneously, since CH will be also formed in the hot gas. Therefore no velocity shift of CH relative to $CH^+$ is expected, unlike the situation in standard gas-phase production in shocks where the presence of H$_2$ means that $CH^+$ and CH do not coincide in velocity (e.g. Draine & Katz 1986b).

The column densities of around $10^{11}$ cm$^{-2}$ predicted here are at the present limit of detection (Federman 1982; Lambert & Danks 1986), but observations along lines of sight with little H$_2$ may be able to test this prediction in the near future. Such lines should have large velocity shifts (20–30 km s$^{-1}$) relative to the atomic hydrogen. Hobbs (1973) detected just such a shift in a number of lines of sight of spectral features that could not be assigned to $^{13}CH^+$ absorption (Hobbs 1972). These features probably arise in separate clouds, so that even lines of sight with H$_2$ present in larger columns may show $CH^+$ absorption in distinct clouds of atomic gas, given a large enough bandpass. Assuming an oscillator strength of $f = 5 \times 10^{-3}$ for the transition at 4232 Å, these separate absorptions detected by Hobbs will have columns well in excess of $10^{10}$ cm$^{-2}$ — inconsistent with gas-phase production in the absence of significant H$_2$.

It is conventional, and more straightforward, to study the strongest spectral features of a particular species. We recommend in this work that observations of $CH^+$ and CH lines, currently at the limit of detection, be made along lines of sight without H$_2$ or in distinct atomic hydrogen clouds. Such observations will allow one to obtain information about the presence of shocks in diffuse neutral atomic interstellar gas and the interaction of these shocks with carbonaceous dust.

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