

CHEMISTRY IN SHOCKS

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ABSTRACT. The column densities of interstellar CH^+ , first detected about fifty years ago, cannot be explained with models of the chemistry in low temperature gas. The resolution of this classic problem is necessary for us to have confidence in our understanding of interstellar chemistry and its role in determining the physical conditions in interstellar clouds and in the utility of molecular abundance measurements as diagnostics. The possibility that the observed CH^+ is formed primarily in shocks in diffuse clouds is addressed. The way in which the chemistry affects the structure of such a diffuse cloud shock is also discussed. The analogous chemical influence on the structures of shocks in dense molecular clouds is also considered as is the possibility that gas in some dense molecular clouds passes repeatedly through dynamical cycles and is shocked frequently enough to influence the global chemical structures in those clouds. Some atomic and molecular data needs are mentioned.

1. Why Shocks?

The high temperatures ($1000 \text{ K} \lesssim T \lesssim 4000 \text{ K}$) in shock heated gas drive many endothermic reactions and reactions with activation barriers which are of no importance in the low temperature interstellar gas. In some types of shocks in weakly ionized magnetized media the relative motion of ions and neutrals is substantial and drives reactions which are normally slow at low temperature. Hence, the chemistry of shock heated gas is potentially rich, and when chemical models of low temperature clouds are incompatible with measured column densities of species, theorists have commonly considered shock chemistry models for the production of those species.

There exists the danger that shocks and dynamics will be invoked to solve outstanding chemical problems which arise not because dynamics have been ignored but rather because fundamental elements are missing in the chemical models. Hence, detailed observational studies (e.g. see the review by Langer (1989)) of the kinematics of the regions in which, for chemical reasons, shocks are supposed to exist are necessary.

Shocks are prevalent in the interstellar medium. On average, each diffuse cloud is engulfed by a supernova remnant once every 10^6 years

(McKee and Ostriker (1977)) leading to the propagation of a shock in it. Dense molecular clouds are regions of star formation, and the young stars have winds which act back on the clouds and drive shocks. The well known shock in Orion and those shocks which may be associated with water maser formation are examples.

2. Shock Structure

The discussions of shock structure in standard texts on fluid mechanics are limited to considerations of one-fluid models. When they are appropriate, the flow is essentially discontinuous. Gas is compressed, heated, and accelerated in a negligibly thin transition zone and is further compressed, at roughly constant pressure, and accelerated in a cooling layer.

Mullan (1971), Draine (1980), and Draine, Roberge, and Dalgarno (1983) have noted that shocks in interstellar clouds often will not have such simple structures and multifluid hydromagnetic models must be used. For diffuse cloud shocks, three fluid models are often constructed. In them, the neutrals, ions, and electrons are treated as separate fluids, and grains are ignored (though grains may contribute significantly to the ion inertia). We will restrict attention to steady plane-parallel models of shocks propagating perpendicularly to the magnetic field. The requirement that no large charge separation induced electric field exists implies that the components of the electron and ion velocities perpendicular to the shock front are equal. However, if the medium is weakly ionized and the shock speed is not too high, the ion and neutral velocities can differ substantially.

Consider a magnetized medium with a nearly vanishing fractional ionization. Assume that a piston acts only on the ions and electrons and moves through the medium at a speed less than $v_{Ai} \equiv B_0 / (4\pi \rho_{i0})^{1/2}$ where B_0 and ρ_{i0} are the upstream magnetic field strength and ion mass density. Then a magnetosonic wave will propagate in the upstream ion and electron fluids as the piston moves; behind its front the pressure of the ion and electron fluids will be increased. The neutrals will be unaffected.

Now, consider a medium which has a small but finite fractional ionization. Assume that a piston which acts on all fluids moves through it at a speed less than v_{Ai} . Because over some range, the ion and electron fluids are effectively decoupled from the neutral fluid, the signal speed in them is about v_{Ai} . Because of the large signal speed in the ion fluid, it responds much further upstream than the neutral fluid does. Hence, an element of ionized and electron fluids is accelerated to a substantial fraction of the shock velocity while the corresponding element of neutral fluid is still little affected by the shock. Eventually, ion-neutral friction will accelerate the neutral fluid to nearly the same velocity as the ions. Often, the lengthscale over which the neutral acceleration occurs is roughly

$$\Delta \equiv B_0^2 / 4\pi \alpha_{in} n_i \rho_0 v_s \quad (1)$$

where α_{in} is the ion-neutral collision rate coefficient, n_i is the ion number density in the neutral acceleration zone and ρ_0 and v_s are the upstream mass density and shock speed. This expression for Δ is obtained by equating the magnetic tension ($\sim B_0^2 / 4\pi \Delta$) to the ion-neutral friction.

In the acceleration zone, ion-neutral friction leads to heating. Henceforth, the term "dissipation zone" rather than "acceleration zone" will be used in this review; the term "magnetic precursor" is often employed in other papers. We will restrict attention to shocks for which the speed is low enough that the neutral gas does not get so hot that a discontinuous neutral subshock occurs; in other words, we consider only the so-called "C-type shocks" in which all flow variables are continuous. Because the dissipation zones are long for the C-type shocks (The expression given above for Δ is appropriate for them.), they generally have the largest column densities of those chemicals which form only under high temperature conditions.

3. CH⁺ in Diffuse Cloud Shocks

The column density of CH⁺ in the diffuse cloud (The visual extinction of a diffuse cloud is of order unity or less.) towards ζ Oph is about 3×10^{13} cm⁻². The reactions included in low temperature chemistry models produce CH⁺ column densities close to two orders of magnitude less than this. The reason that the cold chemistry model abundances are so low is that the reaction



is so endothermic.

As a consequence, in cold diffuse molecular clouds the ionization balance is determined primarily by the photoionization of C and the radiative recombination of C⁺ and nearly all carbon is contained in C⁺. H⁺ is also an abundant ion with a number density which is about an order of magnitude less than that of C⁺.

Elitzur and Watson (1978) suggested that diffuse cloud CH⁺ is produced in shocks. They considered one fluid models only. The primary production mechanism for CH⁺ is reaction (2) while the primary removal mechanism is the reaction



which initiates the formation of other molecular species.

In all of the discussions in this section we consider regions in which H₂ contains all but a small fraction of the hydrogen. For the moment, ignore photodissociation and photoionization reactions other than the photoionization of C. Reaction (2) is rapid enough that all C⁺ passing through the shock will be removed by it before the shocked gas cools. Reaction (3) is rapid in an analogous sense. Hence, the column density of CH⁺ in the shocked gas will be approximately

$$\frac{n_0(\text{C}^+)v_s}{\alpha_3 n_0(\text{H}_2)} \approx 3 \times 10^{11} \text{ cm}^{-2}$$

for $v_s = 10 \text{ km}^{-1}$. α_3 is the rate coefficient for reaction (3), and $n_0(\text{C}^+)$ and $n_0(\text{H}_2)$ are the upstream number densities of C^+ and H_2 .

Continue to make the same assumptions as those made for the discussion in the preceding paragraph, except now assume that photodissociation and photoionization reactions break CH_2^+ and the larger species formed from it back down to C^+ and CH^+ on a timescale, τ_{ph} . The timescale characterizing cooling in the one fluid shock model is taken to be τ_{cool} . Typically, $\tau_{\text{ph}} < \tau_{\text{cool}}$. Then the resulting column density of CH^+ in the shock heated gas is roughly

$$\frac{n_0(\text{C}^+)v_s}{\alpha_3 n_0(\text{H}_2)} \frac{\tau_{\text{cool}}}{\tau_{\text{ph}}}$$

Shock models for CH^+ formation are constrained by observations of other molecules. Higher lying ($3 \leq J \leq 6$) H_2 rotational levels are collisionally excited in the shock heated gas. OH is produced and removed by the reactions:

$\text{O} + \text{H}_2 \rightarrow \text{OH} + \text{H}$; $\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$; $\text{H}_2\text{O} + h\nu \rightarrow \text{OH} + \text{H}$; $\text{OH} + h\nu \rightarrow \text{O} + \text{H}$. The two neutral-neutral reactions are rapid in shock heated gas but slow in cold gas, and the shock models must be compatible with the OH data. Pineau des Forêts et al. (1986) have found that for reasonable parameters, the one fluid model column densities of CH^+ are at most only about 10^{12} cm^{-2} for shocks which have H_2 rotational level populations that are compatible with the data. The OH column densities do not constrain the one fluid models so severely.

Now consider multifluid models of shocks. Typically, $\Delta > v_s \tau_{\text{cool}}$. This implies that the maximum temperature for a multifluid shock model is not as high as that for a single fluid model of a shock with the same speed. However, for normal shock parameters, the multifluid model temperatures are high enough (The neutral temperature is usually about 1000 K.) to drive reaction (2) at a high rate. In addition, the ion-neutral streaming speed is comparable to the shock speed and can help drive the reaction. Hence, the column density of CH^+ for a multifluid model is roughly

$$\frac{n_0(\text{C}^+)v_s}{\alpha_3 n_0(\text{H}_2)} \frac{\Delta}{v_s \tau_{\text{ph}}}$$

Equation (1) shows that Δ depends on the ion number density in the dissipation zone. In the preshock medium, the most abundant ion is C^+ , but in the dissipation zone C^+ is converted to molecular ions, which recombine four or five orders of magnitude more rapidly than C^+ does. Flower, Pineau des Forêts, and Hartquist (1985) pointed out that the subsequent drop in the flux of carbon bearing ions through the dissipation zone results in it being an order of magnitude longer than one would approximate by using the preshock ion density in equation (1). The drop in the flux of carbon bearing ions results in H^+ -neutral scattering being an important source of ion-neutral coupling.

Two groups have independently investigated the production of CH^+ in multifluid models.

Papers by Pineau des Forêts et al. (1986) and Hartquist, Flower, and Pineau des Forêts (1989) and articles referenced in the latter summarize the results of one group. This group concluded that shocks which would produce column densities of CH⁺ comparable to that measured towards ζOph would contain more H₂ in highly excited rotational levels than observed in that direction.

In contrast, Draine (1986) presented a shock model with CH⁺ and excited H₂ rotational level populations which are comparable to those observed towards ζOph. Draine adopted higher photoionization and photodissociation cross sections for many carbon bearing species and a higher, but acceptable, value for the strength of the radiation field near the ζOph cloud. Hence, the value of τ_{ph} for Draine's model is smaller. Other differences include Draine's adoption of C⁺ and H as the primary products of the photodissociation of CH⁺ and of an incorrect endothermicity for the reaction H⁺ + O → O⁺ + H which dominates the removal of H⁺ in the preshock gas. In reality, the dominant CH⁺ photodissociation products are C and H⁺ (Kirby (1980)). When Draine's "best fit" ζOph model was run again with these two discrepancies removed, the CH⁺ column density dropped by a factor of three (Draine, private communication).

At this date, no shock model which is compatible with the CH⁺ and H₂ observations towards ζOph exists.

4. Chemistry Affecting Dissipation in C-Type Shocks in Dense Clouds

If grains were of uniform radius, *a*, their fractional abundance in a cloud would be roughly $4 \times 10^{-12} (a/10^{-5} \text{ cm})^{-3}$. In low temperature dark clouds, a grain with $a = 10^{-5}$ cm carries on average a charge of -*e*, as a result of the collisions of electrons with neutral grains being much more frequent than collisions of the more slowly moving ions with neutral grains (Spitzer (1978)). The average number of negative charges on grains increases as the electron temperature rises, and $a = 10^{-5}$ cm grains carry of the order of 10² negative charges in shocked gas. Because they are charged the grains may be well-coupled to the magnetic field and, hence, may move with the ions through the neutrals in the dissipation zones of C-type shocks in dense clouds. If so, the grain-neutral friction is roughly

$$10^{-9} \text{ g cm}^{-2} \text{ s}^{-2} \left(\frac{a}{10^{-5} \text{ cm}} \right)^{-1} \left(\frac{v_s}{10 \text{ km s}^{-1}} \right)^2 \left(\frac{\rho_n}{1.4 \times 10^{-12} \text{ g cm}^{-3}} \right)^2$$

In cold dense molecular clouds, the fractional ionization is probably roughly $3 \times 10^{-6} n^{-1/2}$ where *n* is the hydrogen nucleon number density in cm⁻³ (e.g. Elmegreen (1979)). The most abundant ions are metallic ions, such as Mg⁺, which do not react with H₂ (Oppenheimer and Dalgarno (1974)). In low temperature gas, Mg⁺ is formed primarily by the charge transfer of Mg with molecular ions and is removed most rapidly in collisions with grains. Gas phase electrons in low temperature gas are lost mostly by the dissociative recombination of the abundant molecular ions such as HCO⁺. The ion-neutral drag in the dissipation zone of a dense cloud C-type shock is roughly

$$10^{-11} \text{ g cm}^{-2} \text{ s}^{-2} \left(\frac{x_i}{10^{-8}} \right) \left(\frac{v_s}{10 \text{ km s}^{-1}} \right) \left(\frac{\rho_n}{1.4 \times 10^{-12} \text{ g cm}^{-3}} \right)^2$$

where x_i is the fractional ionization.

In shocks, x_i drops below its preshock value. The reactions of species like Mg^+ with H_2 are endothermic by about 2 eV but when they are driven by the high temperatures in shocked gas and ion-neutral streaming, they are followed by rapid dissociative recombination. When the temperatures are high, the grains become very charged and the recombination rate of ions onto them increases due to the enhanced Coulomb attraction as well as the higher ion thermal speeds.

Clearly, if grains remain well-coupled to the magnetic field, grain-neutral drag dominates ion-neutral drag in dense cloud shocks.

When the grains carry an insignificant fraction of the negative charge, they will be decoupled from the magnetic field when

$$\omega_c \tau_{\text{STOP}} = \frac{|\bar{Z}_g| e B}{m_g c} \frac{m_g}{(\pi a^2) \rho v_s} < 1$$

where ω_c , τ_{STOP} , $\bar{Z}_g e$, and m_g are the grain cyclotron frequency, stopping time, average charge, and mass. In all work by Draine and his collaborators on dense cloud shocks, the grain-neutral drag has been evaluated with an expression depending on $\omega_c \tau_{\text{STOP}}$. The expression is appropriate when the grains do not carry a substantial fraction of the negative charge and is a good approximation for the shock parameters which have been considered.

However, in shocks in denser media ($n \geq 10^{7.5} \text{ cm}^{-3}$) such as those which may be associated with interstellar H_2O masers (e.g. Chernoff and McKee (1989)), the grains probably carry most of the negative charge. In such cases, a more complete treatment of the grain-neutral drag is necessary. Work following the suggestions made by Havnes, Hartquist, and Pilipp (1987) is in progress. Preliminary results suggest that in some cases when the grains acquire most of the negative charge, the ExB ion drift velocity, resulting from the electric field which is induced by charge separation between ions and grains subjected to large grain-neutral drag, can become great. The drift velocity may be limited by the onset of ion impact induced ionization of H_2 .

5. Shocks and Global Chemical Structure in B5

Shocks may be prevalent enough in some regions in dense clouds to affect their chemical structures (Williams and Hartquist (1984)). Sputtering of grains in such shocks would constitute a mechanism for returning heavy elements to the gas phase; such elements are depleted onto grains on time scales of $10^6 \text{ yrs } (n/10^3 \text{ cm}^{-3})^{-1}$ which are shorter than average cloud lifetimes.

Goldsmith, Langer, and Wilson (1986) have mapped B5 in optically thin C^{18}O emission, and have delineated its clumpy structure. They argued that the cloud morphology and the presence of four T-Tauri stars are consistent with a dynamical cycling model which is reminiscent of the one proposed by Norman and Silk (1980) for dense molecular regions in general.

Charnley et al. (1988) have studied the time dependent chemical structure of gas which passes repeatedly through dynamical cycles which might be appropriate for B5. One such cycle consists of phases during which interclump material collapses to form clumps in which stars are born, the stars move from the centers of the clumps due to the fact that they are subject to gravitational forces only whereas the gas responds in addition to viscous forces, the stellar winds drive bubbles into the clumpy medium, the winds ablate the clumps and ionized material is mixed with clump molecular material in the wind-clump interfaces, the well mixed gas passes through a terminal bow shock where sputtering occurs, and the shell of shocked wind and ablated material and swept-up interclump gas propagates slowly outwardly and decreases in pressure until it merges with the ambient interclump medium. The mixing of H^+ and He^+ from the wind with clump material would drive the chemistry in the direction of atoms. The chemical model results show that approximate limit cycles obtain, and, hence, point by point mapping of a number of chemical species including C^0 , C^+ , CO , and others can, in principle, be used to diagnose the dynamical cycle in B5.

6. Important Data Needs

The CH^+ column density in diffuse cloud shocks depends on the rates at which photoionization and photodissociation of the species CH_n ($n \geq 1$) and the photodissociation of the species CH_n^+ ($n \geq 1$) occur. Most of the relevant rates are unknown.

The rotational level population distribution of H_2 constrains shock models for the production of CH^+ . Danby, Flower, and Monteiro (1987) have considered H_2 - H_2 collisional excitation. Further such studies are desirable but not as pressing as they once were.

In shocks in dense molecular clouds collisions of heavy ions with H_2 may constitute an important source of ionization. Knowledge of the cross sections near threshold is desirable.

7. References

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