The chemical signature of magnetohydrodynamic waves in molecular clouds

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ABSTRACT
By considering the propagation of low-amplitude magnetohydrodynamic waves in partially ionized plasmas, it is shown that the ion-neutral drift (ambipolar diffusion) induced by the waves can have specific effects on the molecular chemistry of cold material. The chemistry occurring in gas swept by Alfvén waves is described and it is shown that this leads to spatial variations in the deuterium fractionation ratios of, for example, HCO\textsuperscript{+} and N\textsubscript{2}H\textsuperscript{+}, on spatial scales of a few hundredths of a parsec, depending upon the fractional ionization of the ambient medium. The possibility of detecting interstellar Alfvén waves by molecular spectroscopy and their effect of producing small-scale chemical abundance gradients in molecular clouds are briefly discussed.

Key words: MHD – molecular processes – ISM: clouds – ISM: molecules.

1 INTRODUCTION
Magnetohydrodynamic (MHD) waves may be responsible for the superthermal linewidths ($\Delta v$) observed in molecular clouds (Arons \& Max 1975). Theoretically, they are important for the magnetic support of dense cores (Shu, Adams \& Lizano 1987) and in transporting angular momentum during the contraction and collapse of rotating dense cores to form protostars (Mouschovias 1987; Pudritz \& Silk 1987). Clumpy molecular clouds consist of neutral molecular gas, a plasma of ions and electrons, and charged dust grains. Perturbations of this quiescent, dusty plasma (for example, by clump motions, Elmegreen 1985) can also generate a spectrum of MHD waves, the most important of which are fast magnetosonic waves and shear Alfvén waves (Zweibel \& Josafatsson 1983).

Charnley \& Roberge (1991) have pointed out that ambipolar diffusion driven by shear Alfvén waves would increase in the centre-of-mass kinetic energy of those ion–molecular reactions that are either slightly endothermic or which possess small activation energy barriers, allowing them to proceed at enhanced rates and hence transiently alter the molecular chemistry of cold clouds. This process also occurs, for example, in the magnetic precursors of C-type molecular shocks where ion-neutral drift speeds of around 5 km s\textsuperscript{-1} are possible and reactions with large endothermicities can be driven (e.g. Draine 1986; Flower, Pineau des Forêts \& Hartquist 1985). The possible importance of kinetically excited ions in interstellar chemistry has been appreciated for some time (Adams, Smith \& Millar 1984) and the effects of non-thermal N\textsuperscript{+} ions on the synthesis of ammonia in dark clouds have been evaluated (Yee, Lepp \& Dalgarno 1987; Herbst, DeFrees \& McLean 1987).

This Letter presents calculations which suggest that the effects of low-amplitude Alfvén waves on the deuterium chemistry of dark clouds may be detectable by molecular spectroscopy.

2 CHEMISTRY IN ALFVÉN WAVES
2.1 Magnetohydrodynamics

Only the ion-neutral drift speed, $v_{ni}$, is required to compute the coupling between MHD and chemistry. Numerical values were used from a model of MHD disturbances in dense clouds developed by Roberge and co-workers (Roberge \& Hanany 1990; Roberge, Hanany \& Messinger 1995), and kindly made available by Dr W. G. Roberge. Briefly, Roberge et al. consider a Gaussian packet of planar, isothermal, shear Alfvén waves propagating parallel to a uniform magnetic field. The plasma is treated as four interacting fluids – ions, electrons, neutrals, and dust grains. Elastic ion-neutral scattering couples the charged and neutral particles. The structure and evolution of the wave packet are governed by multifluid MHD equations, including dust grains (e.g. Draine 1986; Mouschovias 1987). Solutions of the linearized forms of the MHD equations, valid for small amplitudes, require specification of the amplitude, and $\tau_{\text{ni}}$, the time-scale of the coupling of the neutrals to the wave by collisions with the streaming ions, given numerically by

$$\tau_{\text{ni}} = 5.3 \times 10^{11} \left( \frac{n_{\text{H}}}{10^{4} \text{ cm}^{-3}} \right)^{-1} \left( \frac{x_{e}}{10^{-7}} \right)^{-1} \left( 1 + \frac{m_{\text{n}}}{m_{\text{i}}} \right) \text{s}$$

where $n_{\text{H}}$ is the hydrogen nucleon density, $x_{e}$ is the fractional ionization, with $m_{\text{n}}$ and $m_{\text{i}}$ the neutral and ion masses. Hence, physical and chemical conditions in the ambient medium determine $\tau_{\text{ni}}$.\n
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strength is of the order of the Alfven speed, \( v_A \), which chemical reactions are driven non-thermally is \( \sim \tau_{ni} \), equation (1) shows that \( x_c \) is a critical parameter. The most pronounced effects waves will have on the overall molecular chemistry will occur in gas with the lowest values of \( x_c \).

The chemical model used a subset of the deuterium chemistry of Millar et al. (1989) with their ‘old’ rates and elemental depletions (see also Millar et al. 1988) except for the metal fractional abundance which was taken to be ten times less, to examine the effect of a lower \( x_e \) (larger \( \tau_{ni} \)) on the chemistry. Starting from an atomic composition, and all the hydrogen molecular, with a density of \( 2 \times 10^4 \) cm\(^{-3} \) and a neutral temperature of 12 K, the chemistry was allowed to evolve for \( 2 \times 10^5 \) yr, after which time the fractional ionization was \( 4 \times 10^{-8} \), and a significant degree of deuterium fractionation had occurred. This time is much shorter than that required to reach a full chemical steady-state (~\( 10^7 \) yr), however when \( 2 \times 10^5 \) yr the ionized fraction is approximately in a steady-state. The parcel of gas was then swept by an Alfven wave packet and the chemical evolution at the centre, driven by the evolution of \( \tau_{ni} \) depicted in Fig. 1, followed for times \( \sim \tau_{ni} \). The precise chemical state of the gas prior to being swept is not a major concern here since the aim of the calculation is not to model observed abundances, which in any case appear to be better reproduced on this time-scale (e.g. Millar 1990), but to demonstrate the magnitude of the effect that could be expected. As a wave only affects the chemistry transiently, over a time-scale much shorter than either of the above, it does not alter the nature of the final steady-state chemistry.

For endothermic ion–molecule reactions, an ‘effective temperature’, \( T_{eff} \), given by

\[
T_{eff} = T_a + m_{H^+} v_a^2 / 3k_B
\]

(Draine 1980; Flower et al. 1985) where \( m_{H^+} \) is the reduced mass, was used to compute the rate coefficients. This approach has been employed by Pineau des Forêts, Roueff & Flower (1989) to study the destruction of deuterated molecules in C-type MHD shocks; their prescription for the temperature dependence of the rate coefficient of reaction (2), \( 1.7 \times 10^{-6} \exp(-150/T) \) cm\(^3\) s\(^{-1} \) for \( T \approx 20 \) K and \( 3.6 \times 10^{-18} \) cm\(^3\) s\(^{-1} \) otherwise (Smith, Adams & Alge 1982), was also used here. For these isothermal waves, the ion temperature was set equal to \( T_a \).

Heating of the gas is a natural consequence of ambipolar diffusion (Scalo 1977). The temperature evolution in the molecular gas induced by the ion-neutral drift of Fig. 1 was estimated a posteriori taking account of heating by cosmic rays and ambipolar diffusion (see McKee et al. 1993) and CO rotational cooling (Falgarone & Puget 1985). For a peak \( \tau_{ni} \) of 0.5 km s\(^{-1} \), the peak temperature was found to be 25 K (see also Roberge et al. 1995) and so the non-thermal enhancement in the rate coefficient of reaction (2) dominates any contribution from frictional heating.

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2.2 Chemistry

As only the rate coefficients of reactions which have small endothermicities or activation energy barriers will be significantly affected, the high degree of deuterium fractionation observed (Langer et al. 1979; Guélin, Langer & Wilson 1982; Gerin et al. 1987; Bell et al. 1988). In ion–molecule theories of interstellar deuteration, each of the above three deuterated ions is important for the formation of particular deuterated species, for example, \( \text{H}_2\text{D}^+ \) leads to \( \text{N}_2\text{D}^+ \), \( \text{DCO}^+ \) and \( \text{H}_2\text{D}^+ \); \( \text{CH}_3\text{D}^+ \) leads to HDCHO and DCN; and \( \text{C}_2\text{HD}^+ \) to \( \text{C}_2\text{D} \) and \( \text{C}_2\text{HD} \) (see Howe & Millar 1993 for an alternative view). Millar et al. (1989) have shown that the fractionation chemistry is, as expected, sensitive to temperature and exhibits a strong time-dependence in the abundance ratios, \( R(\text{XD}) = n(\text{XD})/n(\text{XH}) \), of several species. The reactions most sensitive to wave-induced ion-neutral streaming are those of deuterated molecular ions with hydrogen molecules. Since the time-scale over which chemical reactions are driven non-thermally is \( \sim \tau_{ni} \), equation (1) shows that \( x_c \) is a critical parameter. The most pronounced effects waves will have on the overall molecular chemistry will occur in gas with the lowest values of \( x_c \).

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3 RESULTS

The low amplitude waves considered here yield a non-thermal enhancement in the rate coefficient of reaction (2) which produces significant chemical effects. Fig. 2 shows the evolution of the three molecular ions primarily responsible for interstellar deuteration. As expected, the effect of the wave in depressing $R(XD)$ is most pronounced for the least endothermic reactions. Fig. 3 shows the effect on $R(XD)$ for some observable molecules. As shown in Fig. 2, $H_2D^+$ is the most severely depleted ion and, as it is the primary source of deuteration in HCO$^+$, and the sole source for $N_2H^+$, the deuteration in these ions also experiences significant depletion. At these low drift speeds, deuteration in molecules such as NH$_2D^+$, DCN, and DNC can still be retained by reactions involving CH$_2D^+$ and C$_2$HD$^+$. To significantly affect $R(XD)$ in these molecules, and in other neutrals such as HDO, and C$_2$D, would require an increase in the depletion of C$_2$HD$^+$, attainable only at drift speeds, and hence amplitudes, beyond the range of validity of the MHD solution. The persistence of deuteration by CH$_2D^+$ and C$_2$HD$^+$ at drift speeds sufficient to deplete H$_2D^+$ is analogous to the temperature dependence of $R(XD)$ found by Millar et al. (1989).

4 DISCUSSION

Even the conservative ion-neutral drift speeds attained in the waves considered here are sufficient to alter the deuterium fractionation ratios of several molecules over linear scales $\sim \tau_{in}\nu_A$, depending upon the fractional ionization and density of the gas.

The observed velocity dispersion in molecular clouds is a result of large-amplitude, long-wavelength Alfvén waves which are the longest-lived wave motions (Zweibel & Josafatson 1983). In these low-frequency waves (e.g. Martin, Heyraerts & Priest 1997), the coupling between the ionized and neutral fluids is good and so, although they can contribute to the cloud magnetic support, despite their large amplitude they possess almost zero drift speeds – they do not play any part in producing the chemical effects described here. Those waves which could affect the chemistry must have higher frequencies. However, according to the scaling law relating the velocity dispersion and size scale of molecular clouds (Larson 1981), at the shorter wavelength region of the wave spectrum, in which ion and neutral velocities are dissimilar, the waves have intrinsically lower amplitudes.

In molecular clouds, a source will produce many waves of differing wavelengths and orientations to the magnetic field (Zweibel & Josafatsson 1983). Apart from those Alfvén waves which contribute to the bulk of the velocity dispersion, the others will dissipate closer to the source and these, including shorter wavelength Alfvén waves, might provide the modest drift speeds that are needed to affect $R(H_2D^+)$ and $R(N_2D^+)(> 0.2 \text{ km s}^{-1})$. We might therefore expect there to be some weak but observable correlation between $R(XD)$ and $\Delta \nu$ since, to first order, the chemistry in gas where, hypothetically, no mechanism can produce...
suprathermal linewidths, should be distinct from that case in which a spectrum of MHD waves is present. A more quantitative discussion of this point is beyond the scope of a Letter, but some observational consequences of the theory are outlined below.

The theory predicts a weak dependence of $R(\text{XD})$ on $1/\Delta v$, at least on the length-scale $\tau_{ud} \ll \tau_A$. Observations of deuterium fractionation in TMC-1 by Guélin et al. (1982) show that a spatial abundance gradient in deuterium does exist in this cloud. Bell et al. (1988) have shown that C$_3$HD is one of the most deuterated interstellar molecules and that $R(\text{C}_3\text{HD})$ is the greatest in material with the narrowest $\Delta v$. This $R(\text{C}_3\text{HD})$ versus $\Delta v$ dependence is as the theory predicts, since C$_3$HD is formed from C$_3$H$^+$ which is relatively unaffected by low-amplitude waves (Fig. 2) and could only be significantly depleted at higher drift speeds. At epochs when conventional ion–molecule models of interstellar deuterium chemistry give reasonable agreement with the observed $R(\text{XD})$, they fail to explain the C$_3$HD observations and reproduce $R(\text{C}_3\text{HD})$ values that are smaller than observed by about an order of magnitude (Millar et al. 1989). It is conceivable that the effect of MHD turbulence in the chemical models of Millar et al. (1989) would be such that the correct epoch for comparison with observation is one when, in their model, many of the $R(\text{XD})$ are too large but that of C$_3$HD is close to the observed value: ion-neutral drift could possibly depress the $R(\text{XD})$ closer to that observed for many molecules, but not $R(\text{C}_3\text{HD})$.

As observations have been unable to detect $\text{H}_2\text{D}^+$ in molecular clouds (e.g. van Dishoeck et al. 1992), it appears that seeking spatial variations of $R(\text{C}_3\text{HD}) \approx 1/\Delta v$, in gas that is ostensibly too cold to be destroying $\text{H}_2\text{D}^+$ thermally, currently offers the best prospect of testing this theory. For $\chi$ in the range $4 \times 10^{-8} - 1 \times 10^{-7}$, variations in $R(\text{DCO}^+)\approx R(\text{C}_3\text{HD})$ should occur on spatial scales of $\tau_{ud} \approx 0.03 - 0.08 \text{ pc}$. For clouds 140 pc distant in Taurus, the corresponding angular sizes are well within the capabilities of current millimetre and submillimetre telescopes (van Dishoeck et al. 1993). For example, mapping of cold molecular clouds, such as TMC-1 or L134N, in the high frequency $J = 3 - 2$ and $J = 4 - 3$ transitions of $\text{N}_2\text{D}^+$ and $\text{N}_2\text{H}^+$ would probably have sufficient resolution to identify spatial variations of $R(\text{C}_3\text{HD})$ on the smaller scale. Measurement of their hyperfine components would enable accurate determination of optical depths, and hence of the relevant column densities (Womack, Ziurys & Wyckoff 1992). Some fractionation ratios may be unaffected (e.g. $R(\text{DCN})$ and $R(\text{DNC})$; Fig. 3), and so could provide an additional chemical check on any variations observed in $R(\text{C}_3\text{HD})$.

MHD waves may play a significant part in interstellar chemistry and could tentatively be responsible for some of the small-scale molecular abundance gradients observed in dark clouds (e.g. Olano, Walmsley & Wilson 1988; Swade & Schloerb 1992) since several other reactions could also have their rates transiently increased. In reality, a parcel of gas may experience this effect periodically; it is, however, a long way from the simple model studied here to the inclusion of MHD turbulence in astrochemical models. Both the non-linear regime, in which parallel propagating Alfvén waves steepen into tiny C-shocks, and the effect of wave trains, will each have interesting chemical effects; these issues will be treated elsewhere (Roberge & Charnley, in preparation).

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