

THE ROYAL
SOCIETY

PHILOSOPHICAL
TRANSACTIONS

**MATHEMATICAL,
PHYSICAL
& ENGINEERING**
SCIENCES

THE ROYAL

PHILOSOPHICAL
TRANSACTIONS ō

interstellar molecules The role of H₂D⁺ in the deuteration of

THE ROYAL
SOCIETY

T. J. Millar, H. Roberts, A. J. Markwick and S. B. Charnley

doi: 10.1098/rsta.2000.0666 Phil. Trans. R. Soc. Lond. A 2000 **358**, 2535-2547

Email alerting service

OF

article or click **[here](http://rsta.royalsocietypublishing.org/cgi/alerts/ctalert?alertType=citedby&addAlert=cited_by&saveAlert=no&cited_by_criteria_resid=roypta;358/1774/2535&return_type=article&return_url=http://rsta.royalsocietypublishing.org/content/358/1774/2535.full.pdf)** - sign up in the box at the top right-hand corner of the Receive free email alerts when new articles cite this article

MATHEMATICA PHYSICAL

& ENGINEERIN SCIENCES

<http://rsta.royalsocietypublishing.org/subscriptions> To subscribe to Phil. Trans. R. Soc. Lond. A go to:

THE ROYAL
SOCIETY

PHILOSOPHICAL
TRANSACTIONS

**MATHEMATICAL,
PHYSICAL
& ENGINEERING
SCIENCES**

T he role of H_2D^+ in the deuteration of
interstellar molecules of H_2D^+ in the deuterat
interstellar molecules

interstellar molecules
BY T. J. MILLAR¹, H. ROBERTS¹, A. J. MARKWICK¹ **interstellar molecules**

MILLAR¹, H. ROBERTS¹, A. J. M.

AND S. B. CHARNLEY² $AR¹$, H. ROBERTS¹, A. J.
AND S. B. CHARNLEY²

BY T. J. MILLAR¹, H. ROBERTS¹, A. J. MARKWICK¹
AND S. B. CHARNLEY²
¹Department of Physics, University of Manchester Institute of Science and
Technology, PO Box 88, Manchester M60, 10D, UK *AND* S. B. CHARNLEY²
*Technology, PO Box 88, Manchester Institute of Scien-
<i>Technology, PO Box 88, Manchester M60 1QD, UK*
Sciences Division, MS 915.3, NASA Amer Bessereb Cent Partment of Physics, University of Manchester Institute of Science an
 Technology, PO Box 88, Manchester M60 1QD, UK

² Space Sciences Division, MS 245-3, NASA Ames Research Center,
 Moffett Field, CA 04035, USA Technology, PO Box 88, Manchester M60 1QD, UK
² Space Sciences Division, MS 245-3, NASA Ames Research Center,
Moffett Field, CA 94035, USA

Moffett Field, CA 94055, OSA
Collisions between H_3^+ and HD in molecular clouds lead to the fractionation of deu-
terium in H_2D^+ at temperatures below 20 K. In this article, we describe the chem-Collisions between H_3^+ and HD in molecular clouds lead to the fractionation of deuterium in H_2D^+ at temperatures below 20 K. In this article, we describe the chemistry of H_2D^+ and discuss how variations in tem Collisions between H_3^+ and HD in molecular clouds lead to the fractionation of deu-
terium in H_2D^+ at temperatures below 20 K. In this article, we describe the chem-
istry of H_2D^+ and discuss how variations in terium in H_2D^+ at temperatures below 20 K. In this article, we describe the chemistry of H_2D^+ and discuss how variations in temperature and elemental abundances affect the level of fractionation in H_2D^+ and ot istry of H_2D^+ and discuss how variations in temperature and elemental abundances affect the level of fractionation in H_2D^+ and other species. We describe how accretion of gas-phase molecules on to cold dust grains enhances the deuteration in several tion of gas-phase molecules on to cold dust grains enhances the deuteration in several
molecules including doubly deuterated molecules. We show that the ion-neutral drift
velocities attained in slow Alfvén waves can destr molecules including doubly deuterated molecules. We show that the ion-neutral drift
velocities attained in slow Alfvén waves can destroy H_2D^+ in non-thermal reactions.
As a result, the degree of fractionation can be r velocities attained in slow Alfvén waves can destroy H_2D^+ in normals a result, the degree of fractionation can be reduced and we donsequences of such a model for the dark dust cloud TMC-1. consequences of such a model for the dark dust cloud TMC-1.
Keywords: interstellar; astrochemistry; deuterium

1. Introduction

1. Introduction
Deuterium was made in the first 1000 s of the Universe according to conventional
models of the Big Bang, with an abundance relative to bydrogen, D/H which depends Deuterium was made in the first 1000 s of the Universe according to conventional
models of the Big Bang, with an abundance relative to hydrogen, D/H , which depends
sensitively on the baryon density (Schramm & Turner 1988 Deuterium was made in the first 1000 s of the Universe according to conventional
models of the Big Bang, with an abundance relative to hydrogen, D/H , which depends
sensitively on the baryon density (Schramm & Turner 1988 models of the Big Bang, with an abundance relative to hydrogen, D/H , which depends
sensitively on the baryon density (Schramm & Turner 1988). If the baryon density
is low, the D/H ratio is predicted to be much larger th sensitively on the baryon density (Schramm & Turner 1988). If the baryon density
is low, the D/H ratio is predicted to be much larger than that observed in the local
interstellar medium, 1.5×10^{-5} , whereas if it is la is low, the D/H ratio is predicted to be much larger than that observed in the local
interstellar medium, 1.5×10^{-5} , whereas if it is large, deuterium fuses to form helium
in the early Universe and the D/H ratio shoul interstellar medium, 1.5×10^{-5} , whereas if it is large, deuterium fuses to form helium
in the early Universe and the D/H ratio should be very small. Since the baryon
density is an important parameter in determining wh in the early Universe and the D/H ratio should be very small. Since the baryon density is an important parameter in determining whether the Universe is open or closed, an accurate determination of D/H in as large a volume of the Universe as possible is very important for cosmology. If the D/H ratio can be shown to imply a baryon density less than the critical value needed to c possible is very important for cosmology. If the D/H ratio can be shown to imply a
baryon density less than the critical value needed to close the Universe, it would be
a strong indicator that dark matter must be non-baryo baryon density less than the critical value needed to close the Universe, it would be

a strong indicator that dark matter must be non-baryonic in a closed Universe.
Non-cosmological sources for deuterium have been proposed. In particular, spallation reactions, i.e. photodisintegration of larger nuclei, have Non-cosmological sources for deuterium have been proposed. In particular, spallation reactions, i.e. photodisintegration of larger nuclei, have been suggested but are unlikely to be significant on a global scale; in addit lation reactions, i.e. photodisintegration of larger nuclei, have been suggested but
are unlikely to be significant on a global scale; in addition they tend to produce an
overabundance of lithium (Mullan & Linsky 1999). A are unlikely to be significant on a global scale; in addition they tend to produce an
overabundance of lithium (Mullan & Linsky 1999). Although it is difficult to produce
deuterium in any non-cosmological processes, deuter overabundance of lithium (Mullan & Linsky 1999). Although it is difficult to produce
deuterium in any non-cosmological processes, deuterium is easy to destroy when it
is incorporated into stars, a process known as astrati deuterium in any non-cosmological processes, deuterium is easy to destroy when it
is incorporated into stars, a process known as astration. Hence, local, i.e. galactic,
determinations of the D/H ratio are always a lower l is incorporated into stars, a process known as astration. Hence, local, i.e. galactic,

studies of atomic D and H in diffuse interstellar clouds and give an average ratio of

2535

THE ROYAL PHILOSOPHICAL
TRANSACTIONS

THE ROYAL

PHILOSOPHICAL
TRANSACTIONS

²⁵³⁶ *T.J.Millarandothers* Downloaded from rsta.royalsocietypublishing.org

 $(1.5\pm0.1)\times10^{-5}$ (L T. J. Millar and others
(Linsky *et al.* 1995). The fact that interstellar dust grains absorb UV
ly means that these measurements are restricted to objects within photons efficiently means that these measurements are restricted to objects within $(1.5 \pm 0.1) \times 10^{-5}$ (Linsky *et al.* 1995). The fact that interstellar dust grains absorb UV photons efficiently means that these measurements are restricted to objects within *ca.* 1 kpc $(3 \times 10^{19} \text{ m})$ from the Sun photons efficiently means that these measurements are restricted to objects within ca. 1 kpc $(3 \times 10^{19} \text{ m})$ from the Sun (Linsky *et al.* 1995). More recently, there have been attempts made to determine D/H from obser been attempts made to determine D/H from observations toward distant quasars in which the UV lines are red-shifted into the visible portion of the spectrum. Songaila *et* been attempts made to determine D/H from observations toward distant quasars in which the UV lines are red-shifted into the visible portion of the spectrum. Songaila *et al.* (1994) have claimed that D/H is in the range which the UV lines are red-shifted into the visible portion of the spectrum. Songaila *et* al. (1994) have claimed that D/H is in the range $(1.9-2.4) \times 10^{-4}$ towards the quasar 0014+813 at a redshift of 3.32. However, al. (1994) have claimed that D/H is in the range $(1.9-2.4) \times 10^{-4}$ towards the quasar 0014+813 at a redshift of 3.32. However, the large number of H atom absorption lines towards distant objects make the identification $0014+813$ at a redshift of 3.32. However, the large number of H atom absorption lines towards distant objects make the identification of weak D absorption lines very difficult. Most workers prefer a value about 10 times difficult. Most workers prefer a value about 10 times smaller (see Tytler *et al.* 1996).

difficult. Most workers prefer a value about 10 times smaller (see Tytler *et al.* 1996).
In interstellar molecular clouds, deuterium is in the form of HD and both HD and H_2 are observable only under certain conditions In interstellar molecular clouds, deuterium is in the form of HD and both HD and H_2 are observable only under certain conditions. In diffuse clouds containing some molecular component, although not a dominant one, the H_2 are observable only under certain conditions. In diffuse clouds containing some molecular component, although not a dominant one, the abundance ratio of HD to H_2 is about 10^{-6} (Spitzer *et al.* 1973), co 1.5×10^{-5} , w component, although not a dominant one, the abundance ratio of HD to
ut 10^{-6} (Spitzer *et al.* 1973), consistent with an underlying D/H ratio of
, when the different formation and destruction rates for these molecules H_2 is about 10^{-6} (Spitzer *et al.* 1973), consistent with an underlying D/H ratio of 1.5×10^{-5} , when the different formation and destruction rates for these molecules are considered. More recently, observations 1.5×10^{-5} , when the different formation and destruction rates for these molecules are
considered. More recently, observations of the pure rotational transitions of HD using
the Infrared Space Observatory have given ra considered. More recently, observations of the pure rotational transitions of HD using
the Infrared Space Observatory have given ratios relative to H₂ of $(2.0 \pm 0.6) \times 10^{-5}$
(Wright *et al.* 1999) and $(9.0 \pm 3.5) \times 1$ the Infrared Space Observatory have given ratios relative to H₂ of $(2.0 \pm 0.6) \times 10^{-5}$
(Wright *et al.* 1999) and $(9.0 \pm 3.5) \times 10^{-6}$ (Bertoldi *et al.* 1999) in Orion. In molecular clouds, we expect HD/H₂ \sim 2D (Wright *et al.* 1999) and $(9.0 \pm 3.5) \times 10^{-6}$ (Bertoldi *et al.* 1999) in Orion. In molecular clouds, we expect HD/H₂ \sim 2D/H. The fact that these ratios are slightly less than the value of D/H inferred for diffuse molecular clouds, we expect $HD/H_2 \sim 2D/H$. The fact that these ratios are slightly
less than the value of D/H inferred for diffuse clouds might imply that astration has
destroyed some primordial deuterium in this molecula region. destroyed some primordial deuterium in this molecular cloud, an active star-forming
region.
To date, over a dozen molecules containing deuterium have been detected through

rotational line emission in molecular clouds. These molecules have abundance ratios To date, over a dozen molecules containing deuterium have been detected through
rotational line emission in molecular clouds. These molecules have abundance ratios
relative to their hydrogen analogues that are often enhanc rotational line emission in molecular clouds. These molecules have abundance ratios
relative to their hydrogen analogues that are often enhanced by factors of 100 to
 1000 above the cosmic ratio; enhancements in excess o relative to their hydrogen analogues that are often enhanced by factors of 100 to 1000 above the cosmic ratio; enhancements in excess of 10 000 have been detected.
Table 1 summarizes the molecular D/H abundance ratios fo 1000 above the cosmic ratio; enhancements in excess of $10\,000$ have been detected.
Table 1 summarizes the molecular D/H abundance ratios for a number of molecular clouds in the Galaxy.

2. Fractionation

2. Fractionation
The enhanced ratios observed in interstellar molecules are related to the fractionation
that occurs in chemical reactions due to the fact that molecular bonds containing The enhanced ratios observed in interstellar molecules are related to the fractionation
that occurs in chemical reactions due to the fact that molecular bonds containing
deuterium are slightly stronger than those containin that occurs in chemical reactions due to the fact that molecular bonds containing deuterium are slightly stronger than those containing hydrogen. The most important that occurs in chemical reactions due to the fact that molecular bonds containing
deuterium are slightly stronger than those containing hydrogen. The most important
reactions in extracting deuterium from its reservoir, HD, deuterium are slightly stronger than those containing hydrogen. The most important reactions in extracting deuterium from its reservoir, HD, involve ions which do not react, or react slowly, with H_2 . The three most imp are:

$$
H_3^+ + HD \to H_2D^+ + H_2 + \Delta E_1, \tag{2.1}
$$

$$
CH_3^+ + HD \rightarrow CH_2D^+ + H_2 + \Delta E_2, \qquad (2.2)
$$

$$
C_2H_2^+ + HD \to C_2HD^+ + H_2 + \Delta E_3,
$$
\n(2.3)

 $C_2H_2^+ + HD \rightarrow C_2HD^+ + H_2 + \Delta E_3,$ (2.3)
where the reactions are exoergic to the right by amounts equivalent to $\Delta E_1/k \sim$
220 K (Herbst 1982: Smith *et al.* 1982: Sidbu *et al.* 1992) $\Delta E_2/k \sim 375$ K and where the reactions are excergic to the right by amounts equivalent to $\Delta E_1/k \sim$
220 K (Herbst 1982; Smith *et al.* 1982; Sidhu *et al.* 1992), $\Delta E_2/k \sim 375$ K and
 $\Delta E_2/k \sim 550$ K (Smith *et al.* 1982). Thus at the low where the reactions are exoergic to the right by amounts equivalent to $\Delta E_1/k \sim$ 220 K (Herbst 1982; Smith *et al.* 1982; Sidhu *et al.* 1992), $\Delta E_2/k \sim 375$ K and $\Delta E_3/k \sim 550$ K (Smith *et al.* 1982). Thus, at the lo 220 K (Herbst 1982; Smith *et al.* 1982; Sidhu *et al.* 1992), $\Delta E_2/k \sim 375$ K and $\Delta E_3/k \sim 550$ K (Smith *et al.* 1982). Thus, at the low temperatures of cold interstellar clouds, the reverse reactions do not occur, de $\Delta E_3/k \sim 550$ K (Smith *et al.* 1982). Thus, at the low temperatures of cold interstellar clouds, the reverse reactions do not occur, despite the overwhelming abundance of H_2 , and large fractionations of deuterium in lar clouds, the reverse reactions do not occur, despite the overwhelming abundance of H_2 , and large fractionations of deuterium in H_2D^+ , CH_2D^+ and C_2HD^+ result. Once formed, these ions pass on their enhanced H_2 , and large fractionations of deuterium in H_2D^+ , CH_2D^+ and C_2HD^+ result. Once formed, these ions pass on their enhanced deuterium content in ion–neutral reactions, so that other species are also fractionate *Phil. Trans. R. Soc. Lond.* A (2000)

^H2D⁺ *and deuteration* ²⁵³⁷

Table 1. *Observed deuterium fractionation in interstellar clouds*
(This table shows fractionation observed in a number of molecular clouds. OHC, OCR and
TMC-1 refer to the Orion Hot Core, Orion Compact Ridge and Taurus Mo Table 1. Observed dealervant fuctionation in interstead clouds
TMC-1 refer to the Orion Hot Core, Orion Compact Ridge and Taurus Molecular Cloud-1,
respectively respectively.)

^aThe ratio given is D₂CO/HDCO.
^bObserved in gas surrounding core where $T \sim 70$ K.

spread of fractionation among the species present in interstellar clouds and observaspread of fractionation among the species present in interstellar clouds and observa-
tions of molecular D/H ratios can be used to explore the synthetic paths by which
the molecules are formed the interstellar equivalent spread of fractionation among the species present in interstellar clouds and observa-
tions of molecular D/H ratios can be used to explore the synthetic paths by which
the molecules are formed, the interstellar equivalen experiment. e molecules are formed, the i
periment.
The ions CH₃ and C₂H₂⁺ unc
ures so that H₃⁺ is the most a the interstellar equivalent of a laboratory isotope-labelling
 $\frac{1}{2}$ undergo slow radiative association with H_2 at low temper-
nost abundant of these three jons. As a result, fractionation

 $+$ \ldots experiment.
The ions CH_3^+ and
atures so that H_3^+ is
involving H_2D^+ is of $\text{ind } \text{C}_2\text{H}_2^+$ undergo slow radiative association with H_2 at low temper-
is the most abundant of these three ions. As a result, fractionation
of most importance at low temperatures. However, the relatively The ions CH⁺₃ and C₂H⁺₂ undergo slow radiative association with H₂ at low temperatures so that H₃⁺ is the most abundant of these three ions. As a result, fractionation involving H₂D⁺ is of most importa atures so that H_3^+ is the most abundant of these three ions. As a result, fractionation
involving H_2D^+ is of most importance at low temperatures. However, the relatively
small energy barrier to the reverse reactio involving H_2D^+ is of most importance at low temperatures. However, the relatively
small energy barrier to the reverse reaction in (2.1) means that H_2D^+ is rapidly
destroyed by H_2 once the temperature reaches 25 small energy barrier to the reverse reaction in (2.1) means that H_2D^+ is rapidly
destroyed by H_2 once the temperature reaches 25 K and the fraction of deuterium
in H_2D^+ is simply equal to that in HD at higher t destroyed by H₂ once the temperature reaches 25 K and the fraction of deuterium
in H₂D⁺ is simply equal to that in HD at higher temperatures. Reaction (2.2) can
fractionate CH₂D⁺ up to *ca*. 60 K and reaction (2 in H_2D^+ is simply equal to that in HD at higher temperatures. Reaction (2.2) can
fractionate CH_2D^+ up to *ca*. 60 K and reaction (2.3) can fractionate C_2HD^+ up to
ca. 80 K. Above this temperature, significant fractionate CH_2D^+ up to ca. 60 K a
ca. 80 K. Above this temperature, si
chemistry via exchange reactions.
For the remainder of this paper $ca. 80$ K. Above this temperature, significant fractionation cannot occur in gas-phase chemistry via exchange reactions.

peratures less than 25 K, where fractionation of H_2D^+ is large. Because the proton For the remainder of this paper, we restrict our discussion to clouds having tem-For the remainder of this paper, we restrict our discussion to clouds having temperatures less than 25 K, where fractionation of H_2D^+ is large. Because the proton affinity of H_2 is so low—only He, O₂ and N among peratures less than 25 K, where fractionation of H_2D^+ is large. Because the proton
affinity of H_2 is so low—only He, O_2 and N among the more abundant species have
lower proton affinities— H_2D^+ can transfer a affinity of H_2 is so low—only He, O_2 and N among the more abundant species have
lower proton affinities— H_2D^+ can transfer a proton or a deuteron in collision with
almost all neutral species. By considering the f almost all neutral species. By considering the formation and destruction of H_2D^+ ,

²⁵³⁸ *T.J.Millarandothers* Downloaded from rsta.royalsocietypublishing.org

2538 $T. J.$ *Millar and others* we can write the abundance ratio in steady-state as:

$$
\frac{[H_2D^+]}{[H_3^+]} = S(T)\frac{[HD]}{[H_2]},
$$

where the [M] refers to the number density of species M per unit volume, and the where the [M] refers to the number density of
enhancement factor $S(T)$ can be written as: (T) can be written as:
 $S(T) = k_1/(k_{-1} + \alpha f(e) + \Sigma k_M f(M)).$

$$
S(T) = k_1/(k_{-1} + \alpha f(e) + \Sigma k_M f(M)).
$$

Here, k_1 and k_{-1} are the forward and reverse rate coefficients of reaction (2.1), with

$$
k_{-1} = k_1 e^{-\Delta E_1/kT},
$$

 $k_{-1} = k_1 e^{-\Delta E_1/kT}$,
 α is the dissociative recombination rate coefficient of H₂D⁺, $f(e)$ is the electron

fractional abundance, i.e. the number density of electrons relative to the number $f(x) = \alpha$ is the dissociative recombination rate coefficient of H_2D^+ , $f(e)$ is the electron
fractional abundance, i.e. the number density of electrons relative to the number
density of H_2 and $f(M)$ is the fractional α is the dissociative recombination rate coefficient of H_2D^+ , $f(e)$ is the electron fractional abundance, i.e. the number density of electrons relative to the number density of H_2 , and $f(M)$ is the fractional ab fractional abundance, i.e. the number density of electrons relative to the nu
density of H₂, and $f(M)$ is the fractional abundance of species M which reacts
 H_2D^+ with rate coefficient k_M .
The fractionation resulti

The fractionation resulting from the transfer of a deuteron from H_2D^+ can be H_2D^+ with rate coefficient k_M .
The fractionation resulting from the transfer of a deuteron from H_2D^+ can be exemplified by considering the case of reaction with N₂. Two product channels are possible:

$$
H_2D^+ + N_2 \to N_2D^+ + H_2, \tag{2.4}
$$

$$
H_2D^+ + N_2 \rightarrow N_2H^+ + HD,\tag{2.5}
$$

 $H_2D^+ + N_2 \rightarrow N_2H^+ + HD,$ (2.5)
where the branching ratios of these are taken to be statistical, i.e. the rate coefficient
for (2.4) is taken to be one-half of that of (2.5). Since N_oH⁺ is formed via for (2.4) is taken to be one-half of that of (2.5). Since N_2H^+ is formed via i.e. the rate coef
is formed via

$$
H_3^+ + N_2 \to N_2 H^+ + H_2, \tag{2.6}
$$

we can write, on the assumption that the loss rates of N_2H^+ and N_2D^+ are identical:

$$
\frac{[N_2D^+]}{[N_2H^+]} = \frac{1}{3} \frac{[H_2D^+]}{[H_3^+]} = \frac{S(T)}{3} \frac{[HD]}{[H_2]}.
$$

The expression for $S(T)$ above contains three terms in the denominator, which The expression for $S(T)$ above contains three terms in the denominator, which
can be related to important cloud parameters. By neglecting the final two terms in
the denominator The expression f
can be related to in
the denominator,

 $S(T) = k_1/k_{-1} = e^{\Delta E_1/kT}$.

 $S(T) = k_1/k_{-1} = e^{\Delta E_1/kT}$.
Thus, observations of N₂D⁺ and N₂H⁺ can give an upper limit to the temperature
of the gas. If the first and third terms are neglected, one can derive an upper limit for Thus, observations of N_2D^+ and N_2H^+ can give an upper limit to the temperature
of the gas. If the first and third terms are neglected, one can derive an upper limit for
 $f(e)$ assuming that α is known. The fract Thus, observations of N_2D^+ and N_2H^+ can give an upper limit to the temperature
of the gas. If the first and third terms are neglected, one can derive an upper limit for
 $f(e)$, assuming that α is known. The frac of the gas. If the first and third terms are neglected, one can derive an upper limit for $f(e)$, assuming that α is known. The fractional ionization is an important parameter in determining the coupling of the magnetic f (e), assuming that α is known. The fractional ionization is an important parameter
in determining the coupling of the magnetic field to the gas. If the ionization frac-
tion is high, then the ions are coupled to the in determining the coupling of the magnetic field to the gas. If the ionization fraction is high, then the ions are coupled to the magnetic fieldlines, as are the neutrals through ion-neutral collisions. For low ionization tion is high, then the ions are coupled to the magnetic fieldlines, as are the neutrals
through ion-neutral collisions. For low ionization, the ions and neutrals decouple,
and magnetic field support against gravitational through ion–neutral collisions. For low ionization, the ions and neutrals decouple, and magnetic field support against gravitational collapse can be lost via ambipolar diffusion. Finally, neglect of the first two terms le and magnetic field support against gravitational collapse can be lost via ambipolar diffusion. Finally, neglect of the first two terms leads to an upper limit for $\Sigma f(M)$, which gives information on the elemental abundanc diffusion. Finally, neglect of the first two terms leads to an upper limit for $\Sigma f(M)$, which gives information on the elemental abundances of C, N and O. Likewise, the fractional ionization can be related to the elementa which gives information on the elemental abundances of C, N and O. Likewise, the fractional ionization can be related to the elemental abundances of metals having low ionization potentials, Mg, Fe, Na, etc., abundances th fractional ionization can be related to the elemental abundances of metals having

Phil. Trans. R. Soc. Lond. A (2000)

**MATHEMATICAL,
PHYSICAL**
& ENGINEERING

THE ROYAL

THE ROYAL

PHILOSOPHICAL
TRANSACTIONS

**MATHEMATICAL,
PHYSICAL
& ENGINEERING
SCIENCES**

THE ROYAL

PHILOSOPHICAL
TRANSACTIONS

^H2D⁺ *and deuteration* ²⁵³⁹

 $\rm H_2D^+$ and deuteration
from other observations, then fractionation in molecules can be used to determine from other observations, then fractionation in molecules can be used to determine $[HD]/[H_2]$ and, hence, the D/H ratio in interstellar clouds. Thus, detailed observa-
tions of deuterium-bearing molecules allow one to pro from other observations, then fractionation in molecules can be used to determine $[HD]/[H_2]$ and, hence, the D/H ratio in interstellar clouds. Thus, detailed observations of deuterium-bearing molecules allow one to probe

tions of deuterium-bearing molecules allow one to probe the D/H ratio throughout the volume of our Galaxy and will, in the future, enable us to extend this to other galaxies.

3. Chemical kinetic modelling

Detailed models of deuterium fractionation in interstellar clouds have been studied **by Brown & Rice (1986), Millar** *et al.* (1989), Howe & Millar (1993), Rodgers & Millar (1996) and Willacy & Millar (1998). These models follow the time-dependent Detailed models of deuterium fractionation in interstellar clouds have been studied
by Brown & Rice (1986), Millar *et al.* (1989), Howe & Millar (1993), Rodgers &
Millar (1996) and Willacy & Millar (1998). These models f by Brown & Rice (1986), Millar *et al.* (1989), Howe & Millar (1993), Rodgers & Millar (1996) and Willacy & Millar (1998). These models follow the time-dependent fractionation induced by gas-phase chemistry. It is possibl Millar (1996) and Willacy & Millar (1998). These models follow the time-dependent fractionation induced by gas-phase chemistry. It is possible that reactions on and in ice mantles on interstellar grains also provide a rou fractionation induced by gas-phase chemistry. It is possible that reactions on and in
ice mantles on interstellar grains also provide a route to fractionation (Tielens 1983;
Brown & Millar 1989; Charnley *et al.* 1997), bu ice mantles on interstellar grains also provide a route to fractionation (Tielens 1983;
Brown & Millar 1989; Charnley *et al.* 1997), but it is difficult to make quantitative
predictions. However, the large fractionation Brown & Millar 1989; Charnley *et al.* 1997), but it is difficult to make quantitative predictions. However, the large fractionation observed in hot molecular cores, where the gas kinetic temperature of 150–300 K preclude predictions. However, the large fractionation observed in hot molecular cores, where
the gas kinetic temperature of 150–300 K precludes gas-phase fractionation, indicates
that surfaces do play some part in enhancing molec the gas kinetic temperature of 150–300 K precludes gas-phase fractionation, indicates
that surfaces do play some part in enhancing molecular D/H ratios. The issue is not
entirely clear-cut, since the grain mantles may si that surfaces do play some part in enhancing molecular D/H ratios.
entirely clear-cut, since the grain mantles may simply act as a 'deep fideuterated species formed in the gas at much lower temperatures.
In the remainder

In the remainder of this paper we will illustrate fractionation effects by presenting In the remainder of this paper we will illustrate fractionation effects by presenting deuterated species formed in the gas at much lower temperatures.
In the remainder of this paper we will illustrate fractionation effects by presenting
some results from a new time-dependent chemical kinetic model of deuter In the remainder of this paper we will illustrate fractionation effects by presenting
some results from a new time-dependent chemical kinetic model of deuterium chem-
istry in which we ignore any active effects of grain-s some results from a new time-dependent chemical kinetic model of deuterium chemistry in which we ignore any active effects of grain-surface chemistry. The model, which involves some 5300 reactions among 400 species, uses istry in which we ignore any active effects of grain-surface chemistry. The model,
which involves some 5300 reactions among 400 species, uses the latest laboratory
data on the dissociative recombination of H_3^+ and $H_$ which involves some 5300 reactions among 400 species, uses the latest laboratory
data on the dissociative recombination of H_3^+ and H_2D^+ and includes the deuterium
chemistry of sulphur-bearing molecules for the fir data on the dissociative recombination of H_3^+ and H_2D^+ and includes the deuterium
chemistry of sulphur-bearing molecules for the first time. The detection of doubly
deuterated molecules in hot molecular cores is o face chemistry of sulphur-bearing molecules for the first time. The detection of doubly deuterated molecules in hot molecular cores is often taken as evidence of active surface chemistry in such regions. However, the recen face chemistry in such regions. However, the recent detection of $NHD₂$ (Roueff *et al.*) 2000) in L134N, a cold (10 K) quiescent cloud, implies that this species has not been
processed through an ice mantle, since the physical conditions in L134N make it
unlikely that any significant fraction of the mantle ca processed through an ice mantle, since the physical conditions in L134N make it
unlikely that any significant fraction of the mantle can be returned to the gas phase.
Doubly deuterated formaldehyde, D_2CO , has also been unlikely that any significant fraction of the mantle can be returned to the gas phase.
Doubly deuterated formaldehyde, D_2CO , has also been detected in cold clouds (Cec-
carelli *et al.* 1998) and we have included the ga Doubly deuterated formaldehyde, D_2CO , has also been detected in cold clouds (Ceccarelli *et al.* 1998) and we have included the gas-phase formation of this species as an example of the chemistry of doubly deuterated spe certain conditions, large fractionation in these species can arise in cold clouds. example of the chemistry of doubly deuterated species. We shall see that, under
rtain conditions, large fractionation in these species can arise in cold clouds.
Our new model (Roberts & Millar 2000) has been investigated

certain conditions, large fractionation in
Our new model (Roberts & Millar 200
range of density $(n = 10^{10}-10^{14} \text{ m}^{-3})$,
abundances than the models referred to %) in these species can arise in cold clouds.
2000) has been investigated over a much wider
), temperature $(T = 10{\text -}100 \text{ K})$ and elemental
d to above In addition, we have included the Our new model (Roberts & Millar 2000) has been investigated over a much wider
range of density $(n = 10^{10}-10^{14} \text{ m}^{-3})$, temperature $(T = 10-100 \text{ K})$ and elemental
abundances than the models referred to above. In additio range of density $(n = 10^{10}-10^{14} \text{ m}^{-3})$, temperature $(T = 10-100 \text{ K})$ and elemental abundances than the models referred to above. In addition, we have included the accretion of molecules on to the dust grains in some c abundances than the models refaceretion of molecules on to the greatly enhances fractionation.

(*a*) *Model results*

(a) *Model results*
Figure 1 shows the steady-state abundance ratio for $[DCO^+]/[$
Labundances appropriate to molecular clouds; that is deplete $]/[HCO^+]$ for] for elemen-Figure 1 shows the steady-state abundance ratio for $[DCO^+]/[HCO^+]$ for elemental abundances appropriate to molecular clouds; that is, depleted below their solar values as a function of density and temperature. The low-temp tal abundances appropriate to molecular clouds; that is, depleted below their solar values, as a function of density and temperature. The low-temperature fractionation tal abundances appropriate to molecular clouds; that is, depleted below their solar values, as a function of density and temperature. The low-temperature fractionation evident in this figure is due to the reaction of H_2 values, as a function of density and temperature. The low-temperature fractionation
evident in this figure is due to the reaction of H_2D^+ with CO, which dominates below
20 K. At higher temperatures, the fractionation evident in this figure is due to the reaction of H_2D^+ with 20 K. At higher temperatures, the fractionation decreas H_2 , and the abundance ratio becomes fairly constant. *Phil. Trans. R. Soc. Lond.* A (2000)

**WAITHEWATICAL,
PHYSICAL
& ENGINEERING
SCIENCES ATHEMATICAL**

THE ROYAI

PHILOSOPHICAL
TRANSACTIONS

Figure 1. The DCO⁺/HCO⁺ abundance ratio is shown as a function of density and
temperature for elemental abundances appropriate for dark molecular clouds temperature for elemental abundances appropriate for dark molecular clouds.

Figure 2. The DCO^+/HCO^+ ratio is shown here for the case in which the elemental abundances of C, N and O have been increased by a factor of three from those used in figure 1.

undances of C, N and O have been increased by a factor of three from those used in figure 1.
Figure 2 shows the effect of increasing the C, N and O elemental abundances by a
tor of three, which has the effect of making th Figure 2 shows the effect of increasing the C, N and O elemental abundances by a factor of three, which has the effect of making the third term in the denominator of the expression for $S(T)$ more important. Hence fraction Figure 2 shows the effect of increasing the C, N and O elemental abundances by a factor of three, which has the effect of making the third term in the denominator of the expression for $S(T)$ more important. Hence, fractio factor of three, which has the effect of making the third term in the denominator of
the expression for $S(T)$ more important. Hence, fractionation by H_2D^+ at low tem-
peratures is reduced. At higher temperatures, the the expression for $S(T)$ more important. Hence, fractionation by H_2D^+ at low tem-
peratures is reduced. At higher temperatures, the abundance ratio shows a complex
behaviour, with a value greater than 0.005 over a wid peratures is reduced. At higher temperatures, the abundance ratio shows a complex
behaviour, with a value greater than 0.005 over a wide parameter range. At tem-
peratures greater than $ca. 20 \text{ K}$, fractionation in DCO behaviour, with a value greater than 0.005 over a wide parameter approximation in DCO⁺ is driwhich produces CH_2D^+ , followed by reaction with O atoms:

$$
CH2D+ + O \rightarrow DCO+ + H2.
$$
\n(3.1)

For ^T greater than *ca*. 60 K, the fractionation decreases as the reverse of reac-For T greater than ca. 60 K, the fractionation decreases as the reverse of reaction (2.2) reduces the fractionation in CH_2D^+ . From these figures, it is noticeable that for $T \sim 30{\text -}60$ K fractionation in DCO⁺ is la For T greater than ca. 60 K, the fractionation decreases as the reverse of reaction (2.2) reduces the fractionation in CH_2D^+ . From these figures, it is noticeable that for $T \sim 30{\text -}60$ K, fractionation in DCO⁺ is l tion (2.2) reduces the fractionation in CH_2D^+ . From these figures, it is noticeable that for $T \sim 30{\text -}60 \text{ K}$, fractionation in DCO⁺ is larger for larger elemental abundances. This is due to the increased abundanc that for $T \sim 30{\text -}60$ K, fractionation in DCO⁺ is larger for larger elemental abundances. This is due to the increased abundance of O atoms in the latter model, which drives fractionation through reaction (3.1) more e dances. This is due to the increased abundance of O atoms in the latter model,

of non-reactive metals with low ionization potentials. Figure 3 shows the results of As mentioned previously, the electron abundance is sensitive to the abundance
of non-reactive metals with low ionization potentials. Figure 3 shows the results of
varying the abundances of these elements in a model with t of non-reactive metals with low ionization potentials. Figure 3 shows the results of varying the abundances of these elements in a model with the same C, N and O abundances as in figure 2, and with $T = 10$ K and $n = 2 \times 1$ abundances as in figure 2, and with $T = 10$ K and $n = 2 \times 10^{10}$ m⁻³. One sees that *Phil. Trans. R. Soc. Lond.* A (2000)

**'HYSICAL
k ENGINEERING
c ENGINEERING MATHEMATICAL**
PHYSICAL

THE ROYAL

PHILOSOPHICAL
TRANSACTIONS

**MATHEMATICAL,
PHYSICAL
& ENGINEERING
SCIENCES**

THE ROYAL
SOCIETY

PHILOSOPHICAL
TRANSACTIONS

 log electron abundance
Figure 3. The fractionation in H_2D^+ and DCO^+ is shown as a function of fractional ionization,
calculated using several models as described in the text calculated using several models as described in the text.

the $[H_2D^+]/[H_2D^-]$ calculated using several models as described in the text.
 $]/[\text{H}_3^+]$ ratio has a weak dependence on $f(e)$ when $f(e)$ is less than $10^{-6.5}$.

w ionization level reactions with neutral species M determine the degree . For this low ionization level, reactions with neutral species, M, determine the degree the $[H_2D^+]/[H_3^+]$ ratio has a weak dependence on $f(e)$ when $f(e)$ is less than $10^{-6.5}$.
For this low ionization level, reactions with neutral species, M, determine the degree
of fractionation, and the ratio tends to a For this low ionization level, reactions with neutral species, M, determine the degree
of fractionation, and the ratio tends to a constant value as $f(e)$ decreases. For models
having a larger ionization level, dissociativ of fractionation, and the ratio tends to a constant value as $f(e)$ decreases. For models having a larger ionization level, dissociative recombination of H_2D^+ becomes competitive with the neutral reactions, and the abu as $f^{-0.5}$ (e). petitive with the neutral reactions, and the abundance ratio decreases approximately
as $f^{-0.5}$ (e).
Observations of DCO⁺ and HCO⁺ have been used to derive the ionization fractions

in molecular clouds, most recently by Caselli *et al*. (1998) and Williams *et al*. (1998), Observations of DCO⁺ and HCO⁺ have been used to derive the ionization fractions
in molecular clouds, most recently by Caselli *et al.* (1998) and Williams *et al.* (1998),
with the latter finding that the average valu in molecular
with the latte
20 sources.
Another pi th the latter finding that the average value for $f(e)$ is $10^{-7.1}$ in a sample of around
sources.
Another process that can alter the level of fractionation in cold clouds is accretion,
at is the freezing out of gas-phase

20 sources.
Another process that can alter the level of fractionation in cold clouds is accretion,
that is the freezing out of gas-phase molecules on to the surfaces of dust particles.
This process, which occurs on a time Another process that can alter the level of fractionation in cold clouds is accretion,
that is the freezing out of gas-phase molecules on to the surfaces of dust particles.
This process, which occurs on a time-scale of ca that is the freezing out of gas-phase molecules on to the surfaces of dust particles.
This process, which occurs on a time-scale of $ca. 3 \times 10^{15}/n$ (m⁻³) years at 10 K,
removes species such as CO, H₂O, N₂ and O, wh This process, which occurs on a time-scale of $ca. 3 \times 10^{15}/n$ (m⁻³) years at 10 K,
removes species such as CO, H₂O, N₂ and O, which destroy H₃⁺ and H₂D⁺. However,
since hydrogen and its isotopes are not fro since hydrogen and its isotopes are not frozen out, H_3^+ remains in the gas phase where
it is destroyed by HD to form H_2D^+ . The result of accretion is an effective decrease removes species such as CO, H_2O , N_2 and O, which destroy H_3^+ and H_2D^+ . However,
since hydrogen and its isotopes are not frozen out, H_3^+ remains in the gas phase where
it is destroyed by HD to form $H_2D^$ since hydrogen and its isotopes are not frozen out, H_3^+ remains in the it is destroyed by HD to form H_2D^+ . The result of accretion is an ef
in the third term in the denominator of the expression for $[H_2D^+]/[$
as he gas phase where
 $]/[H_3^+]$, which can,

cretion in a model it is destroyed by HD to form H_2D^+ . The result of accretion is an effective decrease
in the third term in the denominator of the expression for $[H_2D^+]/[H_3^+]$, which can,
as a result, attain a large value. Figure 4 s in the third term in the denominator of the expression for $[H_2D^+]/[H_3^+]$, which can,
as a result, attain a large value. Figure 4 shows the effects of accretion in a model
having $n = 2 \times 10^{10} \text{ m}^{-3}$ and $T = 10 \text{ K}$. as a result, attain a large value. Figure 4 s
having $n = 2 \times 10^{10} \text{ m}^{-3}$ and $T = 10 \text{ K}$. In t
important after 10^5 years and the $[\text{H}_2\text{D}^+]/[1]$
in the absence of accretion 0.1 to a value 4 shows the effects of accretion in a model
in this figure, the effects of accretion become
 $]/[H_3^+]$ ratio rises from its steady-state value
is greater than 1. The effect of this increase having $n = 2 \times 10^{10} \text{ m}^{-3}$ and $T = 10 \text{ K}$. In this figure, the effects of accretion become
important after 10^5 years and the $[\text{H}_2\text{D}^+]/[\text{H}_3^+]$ ratio rises from its steady-state value
in the absence of accr important after 10^5 years and the $[H_2D^+]/[H_3^+]$ ratio rises from its steady-state value
in the absence of accretion, 0.1, to a value greater than 1. The effect of this increase
is transferred to other species, for ex in the absence of accretion, 0.1, to a value greater than 1. The effect of this increase
is transferred to other species, for example DCO^+ , during the time that accretion is
going on. Eventually, the CO is itself comple going on. Eventually, the CO is itself completely frozen out onto the grains and both

Figure 4. The effects of grain accretion on the fractionation are shown in this figure. The dashed
line shows how the CO abundance varies with time, with removal from the gas occurring on
a time-scale of ca 10^6 years. Figure 4. The effects of grain accretion on the fractionation are shown in this figure. The dashed
line shows how the CO abundance varies with time, with removal from the gas occurring on
a time-scale of *ca*. 10⁶ years. a time-scale of $ca.10^6$ years. As CO is accreted on to the dust grains, fractionation ratios can become very large.

become very large.
a doubly deuterated species, D_2CO , and shows that the ratio of D_2CO to H_2CO can
be substantial i.e. approaching 0.1 a doubly deuterated species, D_2CO , a
be substantial, i.e. approaching 0.1.
The search for enhanced fractionat boubly deuterated species, D_2CO , and shows that the ratio of D_2CO to H_2CO can substantial, i.e. approaching 0.1.
The search for enhanced fractionation in regions in which accretion is important still in its infancy

is still in its infanced fractionation in regions in which accretion is important
is still in its infancy but is likely to be a growing area of research due to the develop-The search for enhanced fractionation in regions in which accretion is important
is still in its infancy but is likely to be a growing area of research due to the develop-
ment of submillimetre bolometer cameras, which ca is still in its infancy but is likely to be a growing area of research due to the development of submillimetre bolometer cameras, which can detect and map dust cores in molecular clouds. Caselli *et al.* (1999) have recen ment of submillimetre bolometer cameras, which can detect and map dust cores in
molecular clouds. Caselli *et al.* (1999) have recently found a dust core in the L1544
cloud that appears to have a reduced CO abundance but cloud that appears to have a reduced CO abundance but a $[DCO^+]/[HCO^+]$ abundance ratio of around 0.12, a factor of 2–3 times larger than expected for cold clouds but consistent with chemistry modified by accretion. Similar molecular clouds. Caselli *et al.* (1999) have recently found a dust core in the L1544 cloud that appears to have a reduced CO abundance but a $[DCO^+]/[HCO^+]$ abundance ratio of around 0.12, a factor of 2–3 times larger tha dance ratio of around 0.12, a factor of 2–3 times larger than expected for cold clouds
but consistent with chemistry modified by accretion. Similarly, we (H. Roberts, L. T.
Little, R. R. Phillips & T. J. Millar, unpublishe but consistent with chemistry modified by accretion. Similarly, we (H. Roberts, L. T.
Little, R. R. Phillips & T. J. Millar, unpublished data) have recently used the James
Clerk Maxwell Telescope to perform similar observa Little, R. R. Phillips & T. J. Millar, unpublished data) have recently used the James
Clerk Maxwell Telescope to perform similar observations in the HH 24–26 dark clouds
in Orion. These objects show peak CO emissions that Clerk Maxwell Telescope to perform similar observations in the HH 24–26 dark clouds
in Orion. These objects show peak CO emissions that are not at the same positions as
the dust clumps, whereas the HCO⁺ and dust peaks c the dust clumps, whereas the $HCO⁺$ and dust peaks coincide. Gibb & Little (1998) the major destruction route for $HCO⁺$ at high densities. We have recently mapped DCO^+ in gued that this can be explained by the removal of H_2O to the dust, H_2O being
jor destruction route for HCO^+ at high densities. We have recently mapped
in these objects, and, although the data are still to be reduc the major destruction route for HCO^+ at high densities. We have recently mapped DCO^+ in these objects, and, although the data are still to be reduced fully, we do find indications of enhanced $[DCO^+]/[HCO^+]$ abundance r]/[HCO⁺] a $DCO⁺$ in these object
find indications of enh
the accretion model.

(*b*) *Non-thermal destruction of* H_2D^+

(b) Non-thermal destruction of H_2D^+
The small energy barrier to the reverse reaction in (2.1) implies that small non-
ermal effects could reduce the fractionation expected in H_2D^+ . One non-thermal thermal effects could reduce the fractionation expected in H_2D^+ . One non-thermal ies that small non-

. One non-thermal

tral velocity differ-The small energy barrier to the reverse reaction in (2.1) implies that small non-
thermal effects could reduce the fractionation expected in H_2D^+ . One non-thermal
process occurring in molecular clouds comes through thermal effects could reduce the fractionation expected in H_2D^+ . One non-thermal
process occurring in molecular clouds comes through the ion-neutral velocity differ-
ence within shear Alfvén waves and may provide the ence within shear Alfvén waves and may provide the non-thermal linewidths observed
in cold clouds. The dissipation time for an Alfvén wave due to ion-neutral damping

**MATHEMATICAL,
PHYSICAL
& ENGINEERING
SCIENCES**

THE ROYAL

PHILOSOPHICAL
TRANSACTIONS p

HYSICAL
· ENGINEERING
· ENGINEERING **ATHEMATICAL**

^H2D⁺ *and deuteration* ²⁵⁴³

 H_2D^+ and deuteration
is, to within 10%, (Charnley 1998)

1998)

$$
\tau_{\rm in} = 2.65 \times 10^{11} n_{10}^{-1} f_{-7}^{-1} \,\rm s,
$$

 $\tau_{\text{in}} = 2.65 \times 10^{11} n_{10}^{-1} f_{-7}^{-1}$ s,
where n_{10} is molecular hydrogen density in units of 10^{10} molecules per m³, and f_{-7}
is the fractional ionization in units of 10^{-7} . Since the Alfvén velocity $v_{$ where n_{10} is molecular hydrogen density in units of 10^{10} molecules per m³, and f_{-7} is the fractional ionization in units of 10^{-7} . Since the Alfvén velocity, v_A , is given by (Zweibel & Josafatsson 1983) is the fractional ionization in units of 10^{-7} . Since the Alfvén velocity, v_A , is given by (Zweibel & Josafatsson 1983) $_{10}^{-1/2}$ km s⁻¹,

s)

$$
v_{A} = 1.3B_{100}n_{10}^{-1/2} \text{ km s}^{-1},
$$

 $v_{\rm A} = 1.3B_{100}n_{10}^{-1/2}$ km s⁻¹,
where B_{100} is the magnetic field in units of 100 μ G, we can define a dissipation length,
 $L_{\rm in} = v_{\rm A} \tau_{\rm in}$ over which we may expect non-thermal effects to be important: where B_{100} is the magnetic field in units of 100 μ G, we can define a dissipation le $L_{\text{in}} = v_A \tau_{\text{in}}$, over which we may expect non-thermal effects to be important: $L_{\text{in}} = v_{A}\tau_{\text{in}}$, over which we may expect non-thermal effects to be important:

$$
L_{\rm in} = 3.45 \times 10^{14} B_{100} n_{10}^{-3/2} f_{-7}^{-1} \text{ m}
$$

For typical values in molecular cores, $B_{100} = 1.5$, $n_{10} = 1$ and $f_{-7} = 0.3$, we find Example 2.10^{1, 1}0 J_{-7} m.

For typical values in molecular cores, $B_{100} = 1.5$, $n_{10} = 1$ and $f_{-7} = 0.3$, we find
 $L_{\text{in}} = 1.73 \times 10^{15}$ m. It is of interest to note that this scale length is similar to that
 For typical values in molecular cores, $B_{100} = 1.5$, $n_{10} = 1$ and $f_{-7} = 0.3$, we find $L_{\text{in}} = 1.73 \times 10^{15}$ m. It is of interest to note that this scale length is similar to that observed for molecular clumps in T $L_{\text{in}} = 1.73 \times 10^{15}$ m. It is of interest to note that this scale length is similar to that
observed for molecular clumps in TMC-1, where Peng *et al.* (1998) find, through
interferometer maps of dicarbon sulphide, so observed for molecular clumps in TMC-1, where Peng *et al.* (1998) find, through interferometer maps of dicarbon sulphide, some 45 clumps of gas with a typical size of $ca. 10^{15}$ m. It may be that the clump size directly interferometer maps of dicarbon sulphide, some 45 clumps of gas with a typical size
of $ca. 10^{15}$ m. It may be that the clump size directly reflects chemical activity and
evolution in an Alfvén wave, in the sense that th of $ca.10^{15}$ m. It may be that the clu
evolution in an Alfvén wave, in the
determines a chemical length-scale.
The basic effect of the Alfvén wav olution in an Alfvén wave, in the sense that the dissipation length of the wave
termines a chemical length-scale.
The basic effect of the Alfvén wave on fractionation is to provide kinetic energy,
a ion-neutral drift, to

determines a chemical length-scale.
The basic effect of the Alfvén wave on fractionation is to provide kinetic energy,
via ion-neutral drift, to all ion-neutral reactions, including that between H_2D^+ and
 H_2 . We can via ion–neutral drift, to all ion–neutral reactions, including that between H_2D^+ and H_2 . We can define an effective temperature for these non-thermal reactions as:

$$
T_{\text{eff}} = T_n + \frac{m_{\text{in}}v_{\text{in}}^2}{3k},
$$

where v_{in} is the ion-neutral drift speed and m_{in} is the reduced mass of the collision where v_{in} is the ion-neutral drift speed and m_{in} is the reduced mass of the collision
partners. Figure 5 shows the variation of v_{in} in a typical Alfvén wave, together with
the effective temperature for t where v_{in} is the ion-neutral drift speed and m_{in} is the reduced mass of the collision
partners. Figure 5 shows the variation of v_{in} in a typical Alfvén wave, together with
the effective temperature for t partners. Figure 5 shows the variation of v_{in} in a typical Alfvén wave, together with
the effective temperature for the $H_2D^+ + H_2$ reaction. One sees that the effective
temperature can be as large as 25 K in the w the effective temperature for the $H_2D^+ + H_2$ reaction. One sees that the effective
temperature can be as large as 25 K in the wave, which has the result of decreasing
the $[H_2D^+]/[H_3^+]$ abundance ratio. In figure 6, we $]/[\mathrm{H}_3^+]$ a temperature can be as large as 25 K in the w
the $[H_2D^+]/[H_3^+]$ abundance ratio. In figure $(H_2D^+)/[H_3^+]$, $[N_2D^+]/[N_2H^+]$ and $[DCO^+]/[$
is large a factor of 7–8 and slightly less a fa]/[HCO⁺ hich has the result of decreasing
how the abundance variations in
]. The reduction in the first ratio
 $f \rightarrow 4$ for the other two ratios the $[H_2D^+]/[H_3^+]$ abundance ratio. In figure 6, we show the abundance variations in $[H_2D^+]/[H_3^+]$, $[N_2D^+]/[N_2H^+]$ and $[DCO^+]/[HCO^+]$. The reduction in the first ratio
is large, a factor of 7-8, and slightly less, a $T_2D^+]/[H_3^+]$, $[N_2D^+]/[N_2H^+]$ and $[DCO^+]/[HCO^+]$. The reduction in the first ratio large, a factor of 7–8, and slightly less, a factor of 3–4, for the other two ratios.
This ion–neutral drift also affects grain dynamic

is large, a factor of 7–8, and slightly less, a factor of 3–4, for the other two ratios.
This ion–neutral drift also affects grain dynamics, since the dust particles carry
charge. In particular, collisions among the dust This ion–neutral drift also affects grain dynamics, since the dust particles carry charge. In particular, collisions among the dust particles can release ice mantles to the gas with subsequent alterations to the gas-phase charge. In particular, collisions among the dust particles can release ice mantles to the gas with subsequent alterations to the gas-phase chemistry. Markwick *et al.* (2000) have shown that such a model can account quant gas with subsequent alterations to the gas-phase chemistry. Markwick *et al.* (2000) have shown that such a model can account quantitatively for the gradients in molecular abundances observed along the TMC-1 ridge (Pratap have shown that such a model can account quantitatively for the gradients in molecular abundances observed along the TMC-1 ridge (Pratap *et al.* 1997). The return of ice mantle material also affects the deuterium chemist ular abundances observed along the TMC-1 ridge (Pratap *et al.* 1997). The return of
ice mantle material also affects the deuterium chemistry and figure 7 shows the vari-
ation in fractionation that results in such models ice mantle material also affects the deuterium chemistry and figure 7 shows the variation in fractionation that results in such models. Here, the initial decrease in fractionation is caused by the sudden release of materi ation in fractionation that results in such models. Here, the initial decrease in fractionation is caused by the sudden release of material, mostly H_2O , from the grains, which results in the destruction of H_2D^+ , fo tionation is caused by the sudden release of material, mostly H_2O , from the gra
which results in the destruction of H_2D^+ , followed, at *ca*. 10⁴ years, by the effection-neutral drift, as discussed above. The deep of ion–neutral drift, as discussed above. The deep well evident in the $[H_2D^+]/[H_3^+]$
ratio effectively delineates the region in which the effective temperature is larger
than *ca*. 20 K. Finally, for times longer than which results in the destruction of H_2D^+ , followed, at $ca.10^4$ years, by the effects of ion-neutral drift, as discussed above. The deep well evident in the $[H_2D^+]/[H_3^+]$ ratio effectively delineates the region in w ratio effectively delineates the region in which the effective temperature is larger than $ca. 20$ K. Finally, for times longer than $ca. 3 \times 10^5$ years, the effect of the Alfvén wave becomes negligible and the fractionati wave becomes negligible and the fractionation ratios reset to their original values. It fractionation at long times. This occurs because the H_2O injected into the gas is

Phil. Trans. R. Soc. Lond. A (2000)

**MATHEMATICAL,
PHYSICAL**
& ENGINEERING
SCIENCES

THE ROYAL

Figure 5. The ion-neutral drift speed and the effective temperature for the reactive collision between H_2 and H_2D^+ are shown as a function of time in the wave.

Figure 6. The variation in the abundance ratios of H_2D^+/H_3^+ , DCO^+/HCO^+ and N_2D^+/N_2H^+
is shown as a function of time. The rise in effective temperature causes an increase in the
destruction of H_2D^+ in the Al Figure 6. The variation is
is shown as a function
destruction of $H_2 D^+$ in t $+ \cdot \cdot$ in the abundance ratios of H_2D^+/H_3^* , DCO^+/HCO^* and N;
on of time. The rise in effective temperature causes an incre-
in the Alfvén wave, an effect that propagates in other ratios.

destruction of H₂D' in the Alfvén wave, an effect that propagates in other ratios.
processed via ion-neutral reactions into O₂, which, since it does not react with H₃
and H₂D⁺ does not influence the degree of fr processed via ion-neutral reactions into O_2 , which, since it
and H_2D^+ , does not influence the degree of fractionation.
If Alfvén waves do play a significant role in determining to ocessed via ion-neutral reactions into O_2 , which, since it does not react with H_3^+
d H_2D^+ , does not influence the degree of fractionation.
If Alfvén waves do play a significant role in determining the level of

and H_2D^+ , does not influence the degree of fractionation.
If Alfvén waves do play a significant role in determining the level of fractionation,
then one might expect to find observable effects, including gradients in If Alfvén waves do play a significant role in determining the level of fractionation, then one might expect to find observable effects, including gradients in fractionation ratios and correlations between linewidths and fr ratios and correlations between linewidths and fractionation (Charnley 1998). The *Phil. Trans. R. Soc. Lond.* A (2000)

**'HYSICAL
k ENGINEERING
c ENGINEERING MATHEMATICAL**
PHYSICAL

THE ROYAI

THE ROYAL

PHILOSOPHICAL
TRANSACTIONS p

log time (years)
Figure 7. The variation in the abundance ratios of H_2D^+/H_3^+ , DCO⁺/HCO⁺ and N_2D^+/N_2H^+
are shown as a function of time for the case in which the Alfvén wave causes liberation of ice Figure 7. The variation in the abundance ratios of H_2D^+/H_3^+ , DCO^+/HCO^+ and N_2D^+/N_2H^+
are shown as a function of time for the case in which the Alfvén wave causes liberation of ice
mantles from dust grains. The are shown as a function of time for the case in which the Alfvén wave causes liberation of ice mantles from dust grains. The release of this material causes the sharp decrease in fractionation at $ca. 1000$ years. mantles from dust grains. The release of this material causes the sharp decrease in fractionation

former will be the topic of a separate paper. However, it is already evident that some correlations between linewidth and fractionation exist. In TMC-1, both C_3HD former will be the topic of a separate paper. However, it is already evident that
some correlations between linewidth and fractionation exist. In TMC-1, both C_3HD
(Bell *et al.* 1988) and N_2D^+ (H. M. Butner & S. B. some correlations between linewidth and fractionation exist. In TMC-1, both C₃HD (Bell *et al.* 1988) and N₂D⁺ (H. M. Butner & S. B. Charnley, unpublished data) have fractionation levels that are greatest in regions (Bell *et al.* 1988) and N_2D^+ (H. M. Butner & S. B. Charnley, unpublished data) have fractionation levels that are greatest in regions with the narrowest linewidths, exactly as expected in the Alfvén wave model. We no have fractionation levels that are greatest in regions with the narrowest linewidths, exactly as expected in the Alfvén wave model. We note that not all deuterated species will be affected in an identical manner. Species exactly as expected in the Alfvén wave model. We note that not all deuterated species exactly as expected in the Alfvén wave model. We note that not all deuterated species
will be affected in an identical manner. Species formed from C_2HD^+ , which has the
largest energy barrier against destruction by H_2 will be affected in an identical manner
largest energy barrier against destruct
drift speed is large (Charnley 1998).

drift speed is large (Charnley 1998).
Astrophysics at University of Manchester Institute of Science and Technology is supported by a
grant from the PPARC S B C is funded by the NASA's Origins of Solar Systems and Exobiolog Astrophysics at University of Manchester Institute of Science and Technology is supported by a
grant from the PPARC. S.B.C. is funded by the NASA's Origins of Solar Systems and Exobiology
Programs Programs.

References

- References
Bell, M. B., Avery, L. W., Matthews, H. E., Feldman, P. A., Watson, J. K. G., Madden, S. C. &
Irvine W. M. 1988. A study of CaHD in cold interstellar clouds. A stranbus. J. 326. 924–930. II, M. B., Avery, L. W., Matthews, H. E., Feldman, P. A., Watson, J. K. G., Madden, S. C. &
Irvine, W. M. 1988 A study of C₃HD in cold interstellar clouds. *Astrophys. J.* **326**, 924–930.
Irteldi E. Timmerman, B. Becenth Bell, M. B., Avery, L. W., Matthews, H. E., Feldman, P. A., Watson, J. K. G., Madden, S. C. &
Irvine, W. M. 1988 A study of C₃HD in cold interstellar clouds. Astrophys. J. **326**, 924–930.
Bertoldi, F., Timmermann, R., Ro
- Irvine, W. M. 1988 A study of C₃HD in cold interstellar clouds. *Astroph*
rtoldi, F., Timmermann, R., Rosenthal, D., Drapatz, S. & Wright, C. I
HD in the Orion molecular outflow. *Astron. Astrophys.* **346**, 267–277.
cum, Bertoldi, F., Timmermann, R., Rosenthal, D., Drapatz, S. & Wright, C. M. 1999 Detection of

HD in the Orion molecular outflow. Astron. Astrophys. **346**, 267–277.

Brown, P. D. & Millar, T. J. 1989 Models of the gas-grain
- *HD* in the Orion molecular outflow. *Astr.* Own, P. D. & Millar, T. J. 1989 Models *Mon. Not. R. Astr. Soc.* 237, 661–671. Brown, P. D. & Millar, T. J. 1989 Models of the gas-grain interaction: deuterium chemistry.
 Mon. Not. R. Astr. Soc. **237**, 661–671.

Brown, R. D. & Rice, E. H. N. 1986 Galactochemistry. Part 2. Deuterium chemistry. *Mon*
- *Mon. Not. R. Astr. Soc.* **237**, 661–671.
Brown, R. D. & Rice, E. H. N. 1986 Galactochemistry. Part 2. Deuterium chemistry. *Mon. Not.* R. Astr. Soc. **223**, 429–442.
- Caselli, P., Walmsley, C. M., Terzieva, R. & Herbst, E. 1998 The ionization fraction in dense cloud cores. $A \, stronglys. J. 499, 234-249.$ Caselli, P., Walmsley, C. M., Terzieva, R. & Herbst, E. 1998 The ionization fraction in dense
cloud cores. Astrophys. J. 499, 234–249.
Caselli, P., Walmsley, C. M., Tafalla, M., Dore, L. & Myers, P. C. 1999 CO depletion in
- cloud cores. *Astrophys. J.* **499**, 234–249.
selli, P., Walmsley, C. M., Tafalla, M., Dore, L. & Myers,
starless cloud core L1544. *Astrophys. J.* **523**, L165–L169. *starless cloud core L1544. Astrophys. J.* **523**, L165–L169.
Phil. Trans. R. Soc. Lond. A (2000)

- 2546 *T. J. Mutar and others*
Ceccarelli, C., Castets, A., Loinard, L., Caux, E. & Tielens, A. G. G. M. 1998 Detection of doubly
deuterated formaldebyde towards the low-luminosity protostar IRAS 16293-2422. Astron ccarelli, C., Castets, A., Loinard, L., Caux, E. & Tielens, A. G. G. M. 1998 Detection of doubly deuterated formaldehyde towards the low-luminosity protostar IRAS 16293-2422. *Astron.*
Astronhys 338 L43–L46 deuterated formaldehyde towards the low-luminosity protostar IRAS 16293-2422. Astron.
Astrophys. 338, L43-L46. deuterated formaldehyde towards the low-luminosity protostar IRAS 16293-2422. Astron.
Astrophys. 338, L43–L46.
Charnley, S. B. 1998 The chemical signature of magnetohydrodynamic waves in molecular clouds.
Mon. Not. R. Astr
- *Astrophys.* **338**, L43–L46.
 Mon. Not. R. Astr. Soc. **298**, L25–L28.
 Mon. Not. R. Astr. Soc. **298**, L25–L28.
 Annally S. B. Ticlops. A. G. G. M. & Rod. Charnley, S. B. 1998 The chemical signature of magnetohydrodynamic waves in molecular clouds.
 Mon. Not. R. Astr. Soc. 298, L25–L28.

Charnley, S. B., Tielens, A. G. G. M. & Rodgers, S. D. 1997 Deuterated methanol in the
- *Mon. Not. R. Astr. Soc.* **298**, L25–L28.

arnley, S. B., Tielens, A. G. G. M. & Rodgers, S.

Compact Ridge. *Astrophys. J.* **482**, L203–L206.

bb. A. G. & Little, L. T. 1998 Probing the struct Gompact Ridge. Astrophys. J. 482, L203–L206.
Gibb, A. G. & Little, L. T. 1998 Probing the structure of molecular cloud cores: observations
- and modelling of CI and $C^{18}O$ in HH 24-26. *Mon. Not. R. Astr. Soc.* 295, 299-311. Gibb, A. G. & Little, L. T. 1998 Probing the structure of molecular cloud cores: observations
and modelling of CI and $C^{18}O$ in HH 24-26. Mon. Not. R. Astr. Soc. 295, 299-311.
Herbst, E. 1982 The temperature dependence
- and modelling of CI and C¹⁸O in HH 24–26. *Mon. 1*
rbst, E. 1982 The temperature dependence of the I
interstellar clouds. *Astron. Astrophys.* 111, 76–80.
wg D. A. & Millar, T. I. 1993 Alternative routes to Herbst, E. 1982 The temperature dependence of the HCO⁺/DCO⁺ abundance ratio in dense
interstellar clouds. *Astron. Astrophys.* **111**, 76–80.
Howe, D. A. & Millar, T. J. 1993 Alternative routes to deuteration in dark cl
- interstellar clouds. *Astron. As*
 R. Astr. Soc. **262**, 868–880.
 R. Astr. Soc. 262, 868–880. Howe, D. A. & Millar, T. J. 1993 Alternative routes to deuteration in dark clouds. Mon. Not.

R. Astr. Soc. 262, 868–880.

Linsky, J. L., Diplas, A., Wood, B. E., Brown, A., Ayres, T. R. & Savage, B. D. 1995 Deuterium and
- *K. Astr. Soc.* **262**, 868–880.

1sky, J. L., Diplas, A., Wood, B. E., Brown, A., Ayres, T. R. & Savage, B. D. 1995 Deu-

terium and the local interstellar medium properties for the Procyon and Capella lines of

sight Astr terium and the local interstellar medium properties for the Procyon and Capella lines of sight. *Astrophys. J.* 451, 335–351. terium and the local interstellar medium properties for the Procyon and Capella lines of sight. Astrophys. J. 451, 335–351.
Markwick, A. J., Millar, T. J. & Charnley, S. B. 2000 On the abundance gradients of organic molec
- sight. *Astrophys. J.* 451, 335–351.
arkwick, A. J., Millar, T. J. & Charnley, S. B. 2000 On the abu
molecules along the TMC-1 ridge. *Astrophys. J.* 535, 256–265.
llar T. J. Bonnett A. & Harbet E. 1989 Douterium frectiona molecules along the TMC-1 ridge. *Astrophys. J.* 535, 256–265.
Millar T. J., Bennett A. & Herbst E. 1989 Deuterium fractionation in dense interstellar clouds.
- *Astrophys. J.* 340, 906-920. Millar T. J., Bennett A. & Herbst E. 1989 Deuterium fractionation in dense interstellar clouds.
 Astrophys. J. **340**, 906–920.

Mullan, D. J. & Linsky, J. L. 1999 Non-primordial deuterium in the interstellar medium. *Ast*
- *Astrophys. J.* **340**, 906–9

illan, D. J. & Linsky, J. J
 phys. J. **511**, 502–512.

ng B. Janger W. D. V. phys. J. 511, 502–512.
Peng, R., Langer, W. D., Velusamy, T., Kuiper, T. B. H. & Levin, S. 1998 Low-mass clumps in
- TMC-1: scaling laws in the small-scale regime. *Astrophys. J.* 497, 842-849. Peng, R., Langer, W. D., Velusamy, T., Kuiper, T. B. H. & Levin, S. 1998 Low-mass clumps in TMC-1: scaling laws in the small-scale regime. *Astrophys. J.* **497**, 842–849.
Pratap, P., Dickens, J. E., Snell, R. L., Miralles,
- FMC-1: scaling laws in the small-scale regime. A strophys. J. 497, 842–849.
atap, P., Dickens, J. E., Snell, R. L., Miralles, M. P., Bergin, E. A., Irvine, W. M. & Schloer
F. P. 1997 A study of the physics and chemistry of Pratap, P., Dickens, J. E., Snell, R. L., Miralles, M. P., Bergin, E. A., Irvine, W. M. & Schloerb,
F. P. 1997 A study of the physics and chemistry of TMC-1. Astrophys. J. 486, 862–885.
Roberts, H. & Millar, T. J. 2000 Mod
- F. P. 1997 A study of the physics and chemistry of T
berts, H. & Millar, T. J. 2000 Modelling of deuter
molecular clouds. *Astron. Astrophys.* (Submitted.) molecular clouds. Astron. Astrophys. (Submitted.)
- Rodgers, S. D. & Millar, T. J. 1996 The chemistry of deuterium in hot molecular cores. *Mon.* Rodgers, S. D. & Millar, T. J. 1996 The chemistry of deuterium in hot molecular cores. Mon.
 Not. R. Astr. Soc. 280, 1046–1054.

Roueff, E., Tiné, S., Coudert, L. H., Pineau des Fôrets, G., Falgarone, E. & Gerin, M. 2000
- Not. R. Astr. Soc. 280, 1046–1054.
ueff, E., Tiné, S., Coudert, L. H., Pineau des Fôrets, G., Falgarone, E. & Gerin, M. 2
Detection of doubly deuterated ammonia in L134N. *Astron. Astrophys.* 354, L63–L66.
hromm D. N. & Tu Detection of doubly deuterated ammonia in L134N. Astron. Astrophys. 354, L63-L66.
- Schramm, D. N. & Turner, M. S. 1988 Big Bang nucleosynthesis enters the precision era. *[Rev.](http://matilde.ingentaselect.com/nw=1/rpsv/cgi-bin/linker?ext=a&reqidx=/0034-6861^28^2970L.303[aid=540471])* Schramm,D. N. & Turner, M. S. 1988 Big Bang nucleosynthesis enters the precision era. *Rev.*
 Mod. Phys. **70**, 303–318.

Sidhu, K. S., Miller, S. & Tennyson, J. 1992 Partition functions and equilibrium constants for

- ${\rm H_3^+}$ and ${\rm H_2D^+}$. A *fod. Phys.* **70**, 303–318.

u, K. S., Miller, S. & Tennyson, J. 1992 Partition
 $\frac{1}{3}$ and H_2D^+ . *Astron. Astrophys.* **255**, 453–456.
 $\frac{1}{3}$ b. D. Adoms. N. C. & Alge E. 1982 Some H/D.
- Smith, D., Adams, N. G. & Alge, E. 1982 Some H/D exchange reactions involved in the deuteration of interstellar molecules. *Astrophys. J.* 263, 123-129. Smith, D., Adams, N. G. & Alge, E. 1982 Some H/D exchange reactions involved in the deuteration of interstellar molecules. Astrophys. J. 263, 123–129.
Songaila, A., Cowie, L. L., Hogan, C. J. & Rugers, M. 1994 Deuterium ab
- ation of interstellar molecules. *Astrophys. J.* 263, 123–129.
ngaila, A., Cowie, L. L., Hogan, C. J. & Rugers, M. 1994 Deuterium abundance and ba
ground radiation temperature in high redshift primordial clouds. *Nature* 3 groundradiation temperature in high redshift primordial clouds. Nature 368, 599–604.
Spitzer, L., Drake, J. F., Jenkins, E. B., Morton, D. C., Rogerson, J. B. & York, D. G. 1973 Spec-
- ground radiation temperature in high redshift primordial clouds. *Nature* 368, 599–604.
itzer, L., Drake, J. F., Jenkins, E. B., Morton, D. C., Rogerson, J. B. & York, D. G. 1973 Spec-
trophotometric results from the Coper itzer, L., Drake, J. F., Jenkins, E. B., Motophotometric results from the Copern
space. *Astrophys. J.* **181**, L116-L121.
plans. A. G. G. M. 1983 Surface chamic
- trophotometric results from the Copernicus satellite. IV. Molecular hydrogen in interstellar space. *Astrophys. J.* **181**, L116–L121. Tielens, A. G. G. M. 1983 Surface chemistry of deuterated molecules. *Astron. Astrophys.* Tielens, A. G. G. M. 1983 Surface chemistry of deuterated molecules. Astron. Astrophys. 119, 177–184.
Tytler, D., Fan, X.-M. & Burles, S. 1996 Cosmological baryon density derived from the deuterium
- 177–184.
tler, D., Fan, X.-M. & Burles, S. 1996 Cosmological baryc
abundance at redshift $z = 3.57$. *Nature* **381**, 207–209.
illacy K. & Millar, T. J. 1998 Descrition processes and t
- Willacy,K. & Millar, T. J. 1998 Desorption processes and the deuterium fractionation in molec-
ular clouds. Mon. Not. R. Astr. Soc. 298, 562–568. abundance at redshift $z = 3.57$. *Nature* **381**, 207–209
illacy, K. & Millar, T. J. 1998 Desorption processes an
ular clouds. *Mon. Not. R. Astr. Soc.* **298**, 562–568.
illiams. J. B. Borgin F. A. Casolli, B. Muera, B. C. Willacy, K. & Millar, T. J. 1998 Desorption processes and the deuterium fractionation in molec-
ular clouds. Mon. Not. R. Astr. Soc. 298, 562-568.
Williams, J. P., Bergin, E. A., Caselli, P., Myers, P. C. & Plume, R. 1998
- ular clouds. *Mon. Not. R. Astr. Soc.* 298, 562–568.
illiams, J. P., Bergin, E. A., Caselli, P., Myers, P. C. & Plume, R. 1998 Th
in dense molecular gas. I. Low-mass cores. *Astrophys. J.* 503, 689–699. in dense molecular gas. I. Low-mass cores. *Astrophys. J.* 503, 689–699.
Phil. Trans. R. Soc. Lond. A (2000)

THE ROYAL

Downloaded from rsta.royalsocietypublishing.org

^H2D⁺ *and deuteration* ²⁵⁴⁷

 H_2D^+ and deuteration H_2D^+ and deuteration H_2D^+ and deuteration H_2N .
Wright, C. M., van Dishoeck, E. F., Cox, P., Sidher, S. D. & Kessler, M. F. 1999 Infrared Space Observatory–Long Wavelength Spectrometer d right, C. M., van Dishoeck, E. F., Cox, P., Sidher, S. D. & Kessler, M. F. 1999 Infrared Space
Observatory–Long Wavelength Spectrometer detection of the 112 micron HD $J = 1{\text -}0$ line
toward the Orion Bar, Astronbus, J. 5 right, C. M., van Dishoeck, E. F., Cox, P., Sidher, S. I.
Observatory-Long Wavelength Spectrometer detectic
toward the Orion Bar. *Astrophys. J.* 515, L29-L33.
reibel, F. C. & Leepfetsson, K. 1983, Hydromagnetic Observatory–Long Wavelength Spectrometer detection of the 112 micron HD $J = 1-0$ line
toward the Orion Bar. Astrophys. J. 515, L29–L33.
Zweibel, E. G. & Josafatsson, K. 1983 Hydromagnetic wave dissipation in molecular clo

Letting to Bar. Astrop
 Astrophys. J. 270, 511–518.
 Astrophys. J. 270, 511–518.

Discussion

E. F. van Dishoeck (*Leiden Observatory, Germany*). First, Stark *et al*. (1999) $E.$ F. VAN DISHOECK (*Leiden Observatory, Germany*). First, Stark *et al.* (1999) have directly detected the H₂D⁺ ion in a region with significant CO depletion, NGC 1333 IRAS 4A consistent with the models. Second the E. F. VAN DISHOECK (*Leiden Observatory, Germany*). First, Stark *et al.* (1999) have directly detected the H_2D^+ ion in a region with significant CO depletion, NGC 1333 IRAS 4A, consistent with the models. Second, the have directly detected the H_2D^+ ion in a region with significant CO depletion,
NGC 1333 IRAS 4A, consistent with the models. Second, there have been two direct
determinations of the overall deuterium abundance $[D]/[H]$ NGC 1333 IRAS 4A, consistent with the models. Second, there have been two direct determinations of the overall deuterium abundance $[D]/[H]$ in warm molecular gas from observations of the pure rotational lines of HD. Specif determinations of the overall deuterium abundance [D]/[H] in warm molecular gas
from observations of the pure rotational lines of HD. Specifically, Wright *et al.* (1999)
detected the HD $J = 1{\text -}0$ line at 112 μ m towa detected the HD $J = 1-0$ line at 112 μ m toward the Orion Bar, and Bertoldi *et al.* (1999) detected the HD $J = 6-5$ line at 19 μ m in the Orion shock. In both cases, the inferred [D]/[H] ratio is a factor of approxim (1999) detected the HD $J = 6-5$ line at 19 μ m in the Orion shock. In both cases, the inferred [D]/[H] ratio is a factor of approximately two below the local interstellar medium value, suggesting some astration in activ the inferred $[D]/[H]$ ratio is a factor of approxima
medium value, suggesting some astration in act
affect the abundances of deuterated molecules. *Additional reference*

Stark, R., van der Tak, F. S. & van Dishoeck, E. F. 1999 *Astrophys. J.* ⁵²¹, L67.

**MATHEMATICAL,
PHYSICAL**
& ENGINEERING
SCIENCES

THE ROYAL