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+ 3 The astrochemistry of H

Eric Herbst

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$\frac{1}{100}$ The astrochemistry of H_3^+ ${\rm trochemistry\,\, of\,\, }H_{3}^{+}\,$ BY ERIC HERBST

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The reactions of the molecular ion H_3^+ are pivotal to the chemistry of dense inter-
stellar clouds. Produced by the cosmic-ray ionization of molecular hydrogen H_3^+ The reactions of the molecular ion H_3^+ are pivotal to the chemistry of dense inter-
stellar clouds. Produced by the cosmic-ray ionization of molecular hydrogen, H_3^+
reacts with a variety of atoms and molecules to 3 The reactions of the molecular ion H_3^+ are pivotal to the chemistry of dense inter-
stellar clouds. Produced by the cosmic-ray ionization of molecular hydrogen, H_3^+
reacts with a variety of atoms and molecules to stellar clouds. Produced by the cosmic-ray ionization of molecular hydrogen, H_3^+ reacts with a variety of atoms and molecules to produce species that are precursors to many of the detected molecules in dense clouds. F to many of the detected molecules in dense clouds. For example, the reaction of H_3^+ reacts with a variety of atoms and molecules to produce species that are precursors
to many of the detected molecules in dense clouds. For example, the reaction of H_3^+
with atomic O leads, eventually, to the productio with atomic O leads, eventually, to the production of water, while the reaction with with atomic O leads, eventually, to the production of water, while the reaction with
HD leads to the production of a wide variety of deuterated isotopomers. In this arti-
cle, the chemistry of H_3^+ and the products der HD leads to the production of a wich the photon chemistry.

context of interstellar chemistry. context of interstellar chemistry.
Keywords: interstellar clouds; astrochemistry; ion-molecule reactions

1. Introduction

1. Introduction
Matter in galaxies is not confined to stars. Amongst the stars, material exists in a
variety of phases, the best characterized and most massive of which are cool inter-Variety of phases is not confined to stars. Amongst the stars, material exists in a
variety of phases, the best characterized and most massive of which are cool inter-
stellar clouds (Hollenbach & Thronson 1987). These clo Matter in galaxies is not confined to stars. Amongst the stars, material exists in a variety of phases, the best characterized and most massive of which are cool interstellar clouds (Hollenbach $\&$ Thronson 1987). These variety of phases, the best characterized and most massive of which are cool inter-
stellar clouds (Hollenbach & Thronson 1987). These clouds are composed of both
gaseous and particulate matter. The gas is chiefly hydroge stellar clouds (Hollenbach & Thronson 1987). These clouds are composed of both
gaseous and particulate matter. The gas is chiefly hydrogen in one form or another,
while the particles are tiny dust grains constituting $ca.$ gaseous and particulate matter. The gas is chiefly hydrogen in one form or another,
while the particles are tiny dust grains constituting $ca.1\%$ of the mass with a distri-
bution of sizes centred around 0.1 μ m in radi while the particles are tiny dust grains constituting $ca.1\%$ of the mass with a distribution of sizes centred around 0.1 μ m in radius. The matter in clouds derives from previous generations of stars, which, either gen bution of sizes centred around $0.1 \mu m$ in radius. The matter in clouds derives from
previous generations of stars, which, either gently or explosively, eject matter into
interstellar space that eventually collects togeth

At the risk of oversimplification, interstellar clouds can be divided into two classes, interstellar space that eventually collects together via the force of gravity.
At the risk of oversimplification, interstellar clouds can be divided into two classes,
diffuse and dense. Diffuse clouds have gas densities i At the risk of oversimplification, interstellar clouds can be divided into two classes,
diffuse and dense. Diffuse clouds have gas densities in the range $10^{7}-10^{9}$ m⁻³ and
temperatures typically in the range 50-100 K diffuse and dense. Diffuse clouds have gas densities in the range 10^7-10^9 m⁻³ and
temperatures typically in the range 50–100 K. Although partly scattered by dust
particles, visual and ultraviolet radiation from back temperatures typically in the range 50–100 K. Although partly scattered by dust particles, visual and ultraviolet radiation from background stars is able to penetrate at least partly through these sources so that absorptio particles, visual and ultraviolet radiation from background stars is able to penetrate
at least partly through these sources so that absorption spectroscopy can be used to
characterize the gas phase. In diffuse clouds, the at least partly through these sources so that absorption spectroscopy can be used to characterize the gas phase. In diffuse clouds, the gas appears to be mainly atomic in nature, with elements heavier than hydrogen being l characterize the gas phase. In diffuse clouds, the gas appears to be mainly atomic
in nature, with elements heavier than hydrogen being less abundant by a similar or
somewhat greater extent than what is found in stellar a in nature, with elements heavier than hydrogen being less abundant by a similar or somewhat greater extent than what is found in stellar atmospheres. For example, the carbon elemental abundance is $10^{-3.85}$ that of hydro somewhat greater extent than what is found in stellar atmospheres. For example, the carbon elemental abundance is $10^{-3.50}$ that of hydrogen (Meyer 1997). Some diatomic molecules are seen chiefly H_2 . There exists a la carbon elemental abundance is $10^{-3.85}$ that of hydrogen, while the oxygen elemental
abundance is $10^{-3.50}$ that of hydrogen (Meyer 1997). Some diatomic molecules are
seen, chiefly H_2 . There exists a large number of abundance is $10^{-3.50}$ that of hydrogen (Meyer 1997). Some diatomic molecules are
seen, chiefly H_2 . There exists a large number of rather wide absorption features,
known collectively as the diffuse interstellar bands seen, chiefly H₂. There exists a large number of rather wide absorption features, known collectively as the diffuse interstellar bands (DIBs), which are not assigned. Current views of these features are that they arise known collectively as the diffuse interstellar bands (DIBs), which are not assigned.
Current views of these features are that they arise from rather complex molecules
not fully studied in the laboratory (Tielens $\&$ Snow Current views of these features are that they arise from rather complex molecules

not fully studied in the laboratory (Tielens & Snow 1995).
In dense interstellar clouds, the overall gas density is considerably higher than in
diffuse clouds, but is highly heterogeneous in nature. Background starlight d In dense interstellar clouds, the overall gas density is considerably higher than in diffuse clouds, but is highly heterogeneous in nature. Background starlight does not penetrate. Matter is concentrated into regions terme penetrate. Matter is concentrated into regions termed 'cores'. Certain of these cores,
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 $E.$ *Herbst*
also known as dark clouds, are typically characterized by gas densities of *ca*. 10^{10} m⁻³
and temperatures of *ca*. 10 K. Other cores, in which the collapse of material leading also known as dark clouds, are typically characterized by gas densities of ca . 10^{10} m⁻³ and temperatures of ca . 10 K. Other cores, in which the collapse of material leading to the eventual formation of stars is also known as dark clouds, are typically characterized by gas densities of $ca. 10^{10} \text{ m}^{-3}$
and temperatures of $ca. 10 \text{ K}$. Other cores, in which the collapse of material leading
to the eventual formation of stars is and temperatures of $ca. 10$ K. Other cores, in which the collapse of material leading
to the eventual formation of stars is more pronounced, can be considerably warmer
and denser, as can the material surrounding them. Oft to the eventual formation of stars is more pronounced, can be considerably warmer
and denser, as can the material surrounding them. Often the word 'protostar' is
used for these regions, and there is a classification system and denser, as can the material surrounding them. Often the word 'protostar' is
used for these regions, and there is a classification system for such objects. Indeed,
even embedded stars can be found in dense clouds, altho used for these regions, and there is a classification system for such objects. Indeed,
even embedded stars can be found in dense clouds, although their presence is often
well hidden unless they are very warm and light up t even embedded stars can be found in dense clouds, although their presence is often
well hidden unless they are very warm and light up the area around them, forming
so-called H II regions. The formation of stars within dens well hidden unless they are very warm and light up the area around them, forming
so-called H II regions. The formation of stars within dense clouds is in fact the chief
reason why astronomers are very interested in these o so-called H II regions. The formation of stars within dense clouds is in fact the chief
reason why astronomers are very interested in these objects. For astrochemists, on the
other hand, another major source of interest is reason why astronomers are very interested in these objects. For astrochemists, on the other hand, another major source of interest is that molecular development is much more pronounced here than in diffuse clouds. In fact other hand, another m
more pronounced here
(van Dishoeck 1997).
Although molecular

ore pronounced here than in diffuse clouds. In fact, the gas is mainly molecular
an Dishoeck 1997).
Although molecular hydrogen is by far the most dominant gaseous species in dense
puds upwards of 100 other molecules, rang (van Dishoeck 1997).
Although molecular hydrogen is by far the most dominant gaseous species in dense
clouds, upwards of 100 other molecules, ranging in size from 2–13 atoms, and mainly
organic in nature, have been detecte clouds, upwards of 100 other molecules, ranging in size from 2–13 atoms, and mainly organic in nature, have been detected, chiefly by rotational transitions in emission clouds, upwards of 100 other molecules, ranging in size from 2–13 atoms, and mainly organic in nature, have been detected, chiefly by rotational transitions in emission in the microwave and millimetre-wave regions of the in the microwave and millimetre-wave regions of the spectrum (Winnewisser *et al.* 1992). These molecules are listed at http://www.strw.leidenuniv.nl/ ~iau34. The second most abundant molecule, CO, has a concentration 10 1992).These molecules are listed at http://www.strw.leidenuniv.nl/ \sim iau34. The second most abundant molecule, CO, has a concentration 10^{-4} that of H_2 and takes up much of the elemental abundance of carbon. Many ond most abundant molecule, CO, has a concentration 10^{-4} that of H_2 and takes up
much of the elemental abundance of carbon. Many of the molecules are highly unusual
by terrestrial standards, with radicals, three-mem much of the elemental abundance of carbon. Many of the molecules are highly unusual
by terrestrial standards, with radicals, three-membered carbon rings, metastable iso-
mers, and molecular ions prominent. Of chemical inte by terrestrial standards, with radicals, three-membered carbon rings, metastable isomers, and molecular ions prominent. Of chemical interest, these molecules provide, through detailed interpretation of their spectra, a way mers, and molecular ions prominent. Of chemical interest, these molecules provide,
through detailed interpretation of their spectra, a way for astronomers to understand
the physical conditions in clouds. In addition to mol through detailed interpretation of their spectra, a way for astronomers to understand
the physical conditions in clouds. In addition to molecules studied via high-resolution
spectroscopy, there exists a variety of broader the physical conditions in clouds. In addition to molecules studied via high-resolution
spectroscopy, there exists a variety of broader features, mainly in the infrared, inter-
pretable with varying degrees of ambiguity in pretable with varying degrees of ambiguity in terms of species on dust particles as pretable with varying degrees of ambiguity in terms of species on dust particles as
well as individual large molecules known as polycyclic aromatic hydrocarbons (PAHs)
(Millar & Williams 1993). Dust particles in cold regio well as individual large molecules known as polycyclic aromatic hydrocarbons (PAHs)
(Millar & Williams 1993). Dust particles in cold regions of dense clouds appear to
consist of cores of either silicates or carbonaceous ma (Millar & Williams 1993).
consist of cores of either s
of ices, mainly water ice.
Most of the molecular ic consist of cores of either silicates or carbonaceous material surrounded by mantles
of ices, mainly water ice.
Most of the molecular ions seen in clouds have been detected only by rotational

of ices, mainly water ice.
Most of the molecular ions seen in clouds have been detected only by rotational
spectra, but there are exceptions. The ion CH⁺ was detected in diffuse clouds many
vears ago by visible absorpti Most of the molecular ions seen in clouds have been detected only by rotational spectra, but there are exceptions. The ion CH^+ was detected in diffuse clouds many years ago by visible absorption spectroscopy (Douglas & years ago by visible absorption spectroscopy (Douglas & Herzberg 1941). The ion H_3^+ ,
which mainly concerns us here, was detected quite recently in infrared absorption
against continuum radiation emanating from a backg spectra, but there are exceptions. The ion CH⁺ was detected in diffuse clouds many
years ago by visible absorption spectroscopy (Douglas & Herzberg 1941). The ion H_3^+ ,
which mainly concerns us here, was detected qui which mainly concerns us here, was detected quite recently in infrared absorption against continuum radiation emanating from a background protostar (Geballe $\&$ Oka 1996). This ion has since been detected in a variety of against continuum
Oka 1996). This ic
in diffuse clouds.

2. Interstellar chemistry and H_2

2. Interstellar chemistry and H_2
How and where are interstellar molecules produced? Although molecules are formed
in certain types of stellar atmospheres of older stars and blown out into space, their If the stellar molecules produced? Although molecules are formed
in certain types of stellar atmospheres of older stars and blown out into space, their
time of survival in the unshielded interstellar medium is not long by How and where are interstellar molecules produced? Although molecules are formed
in certain types of stellar atmospheres of older stars and blown out into space, their
time of survival in the unshielded interstellar medium in certain types of stellar atmospheres of older stars and blown out into space, their
time of survival in the unshielded interstellar medium is not long by astronomi-
cal standards because of photodissociation. Dust parti time of survival in the unshielded interstellar medium is not long by astronomical standards because of photodissociation. Dust particles, also produced in stellar atmospheres, are different in this regard, since they are cal standards because of photodissociation. Dust particles, also produced in stellar
atmospheres, are different in this regard, since they are reasonably stable against
photodegradation. If quite large molecules, such as P atmospheres, are different in this regard, since they are reasonably stable against
photodegradation. If quite large molecules, such as PAHs, are produced in stellar
atmospheres, they may also be stable against photons, al photodegradation. If quite large molecules, such as PAHs, are produced in stellar atmospheres, they may also be stable against photons, although the minimum size of molecules needed for photostability is presently a matter atmospheres, they may also be stable against photons, although the minimum size

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 $The\ astrochemistry\ of\ H_{3}^{+}$ $The\ astrochemistry\ of\ H_{3}^{+}$ $The\ astrochemistry\ of\ H_{3}^{+}$ $+$

 $The \ astronomistry \ of \ H_3^+$ 2525
sists mainly of atoms and dust particle cores. How then can the gaseous matter be
converted into molecules within a reasonable time by astronomical standards? sists mainly of atoms and dust particle cores. How then can the gaseous matter converted into molecules within a reasonable time by astronomical standards?
There are two types of chemical processes that can occur: reaction ts mainly of atoms and dust particle cores. How then can the gaseous matter be
nverted into molecules within a reasonable time by astronomical standards?
There are two types of chemical processes that can occur: reactions

converted into molecules within a reasonable time by astronomical standards?
There are two types of chemical processes that can occur: reactions in the gas
phase and reactions on the surfaces of dust particles (Herbst 1995 There are two types of chemical processes that can occur: reactions in the gas
phase and reactions on the surfaces of dust particles (Herbst 1995). In the gas phase,
the possible types of reactions are constrained by the l phase and reactions on the surfaces of dust particles (Herbst 1995). In the gas phase, the possible types of reactions are constrained by the low temperatures and densities to binary reactions without activation energy. Al the possible types of reactions are constrained by the low temperatures and densities
to binary reactions without activation energy. Although it was initially thought that
such processes are almost always confined to ion-m to binary reactions without activation energy. Although it was initially thought that
such processes are almost always confined to ion-molecule reactions or reactions
involving neutral atoms and radicals, it is now known t such processes are almost always confined to ion-molecule reactions or reactions
involving neutral atoms and radicals, it is now known that certain neutral reactions
involving one stable species and one radical can also b the involving neutral atoms and radicals, it is now known that certain neutral reactions
involving one stable species and one radical can also be quite rapid at low interstellar
temperatures (Canosa *et al.* 1997). Gas-pha involving one stable species and one radical can also be quite rapid at low interstellar temperatures (Canosa *et al.* 1997). Gas-phase reactions are probably responsible for the syntheses of most of the detected molecule temperatures (Canosa *et al.* 1997). Gas-phase reactions are probably responsible for
the syntheses of most of the detected molecules in dense clouds, but they cannot
explain the formation of molecular hydrogen. The basic the syntheses of most of the detected molecules in dense clouds, but they cannot explain the formation of molecular hydrogen. The basic problem is that in order to form H_2 under interstellar conditions, two hydrogen at explain the formation of molecular hydrogen. The basic problem is that in order to form H_2 under interstellar conditions, two hydrogen atoms must collide and stick together by giving off the excess chemical energy in t form H_2 under interstellar conditions, two hydrogen atoms must collide and stick
together by giving off the excess chemical energy in the form of a photon. This
process, known as radiative association, is thought to be together by giving off the excess chemical energy in the form
process, known as radiative association, is thought to be relatively
classes of larger species, but is very inefficient for two H atoms.
The production of molec process, known as radiative association, is thought to be relatively efficient for certain classes of larger species, but is very inefficient for two H atoms.
The production of molecular hydrogen in interstellar clouds pro

classes of larger species, but is very inefficient for two H atoms.
The production of molecular hydrogen in interstellar clouds probably occurs on
the surfaces of dust particles, presumably via a diffusive, or Langmuir–Hin The production of molecular hydrogen in interstellar clouds probably occurs on
the surfaces of dust particles, presumably via a diffusive, or Langmuir–Hinshelwood,
mechanism. One H atom strikes a dust grain, and sticks eff the surfaces of dust particles, presumably via a diffusive, or Langmuir–Hinshelwood, mechanism. One H atom strikes a dust grain, and sticks efficiently at the low prevailing temperatures. This atom then diffuses over the g mechanism. One H atom strikes a dust grain, and sticks efficiently at the low prevailing temperatures. This atom then diffuses over the grain or evaporates. Meanwhile, a second H atom sticks to the same grain, and there is ing temperatures. This atom then diffuses over the grain or evaporates. Meanwhile,
a second H atom sticks to the same grain, and there is a finite possibility that the
two H atoms can collide with one another to form a hyd a second H atom sticks to the same grain, and there is a finite possibility that the two H atoms can collide with one another to form a hydrogen molecule, with the excess energy this time going into thermal energy of the d two H atoms can collide with one another to form a hydrogen molecule, with the excess energy this time going into thermal energy of the dust particle. Although this process has been studied in the laboratory, our current u excess energy this time going into thermal energy of the dust particle. Although this process has been studied in the laboratory, our current understanding of it is that the H atoms move much more slowly than previously an the H atoms move much more slowly than previously anticipated, and that reaction the H atoms move much more slowly than previously anticipated, and that reaction
before evaporation may take place only over a small temperature range for any given
surface material. Still, in all likelihood, grain format before evaporation may take place only over a small temperature range for any given
surface material. Still, in all likelihood, grain formation of H_2 occurs efficiently and
is able to convert the gas of primarily atomi is able to convert the gas of primarily atomic hydrogen into one of mainly molecular hydrogen within a 'reasonable' time-scale of 10^5 yr.

3. The chemistry of H_3^+

3. The chemistry of H_3^+
Once molecular hydrogen is produced on grain surfaces and either evaporates from
the surface into the gas or is actually eiected during the act of formation, there is a Once molecular hydrogen is produced on grain surfaces and either evaporates from
the surface into the gas or is actually ejected during the act of formation, there is a
finite possibility of ionization. Since the ionizati Once molecular hydrogen is produced on grain surfaces and either evaporates from
the surface into the gas or is actually ejected during the act of formation, there is a
finite possibility of ionization. Since the ionizati the surface into the gas or is actually ejected during the act of formation, there is a finite possibility of ionization. Since the ionization potential of molecular hydrogen is 15.4 eV (1 eV = 96.5 kJ mol⁻¹), direct ph finite possibility of ionization. Since the ionization potential of molecular hydrogen
is 15.4 eV (1 eV = 96.5 kJ mol⁻¹), direct photoionization by the photons present
in interstellar space is impossible, since these ph is 15.4 eV ($1 \text{ eV} = 96.5 \text{ kJ} \text{ mol}^{-1}$), direct photoionization by the photons present
in interstellar space is impossible, since these photons range upwards in energy to
13.6 eV only, and multi-photon events are ineff in interstellar space is impossible, since these photons range upwards in energy to 13.6 eV only, and multi-photon events are inefficient, since relaxation is more rapid than photoexcitation. In any event, the penetr 13.6 eV only, and multi-photon events are inefficient, since relaxation is more rapid than photoexcitation. In any event, the penetration of external photons into the central regions of dense interstellar clouds occurs on than photoexcitation. In any event, the penetration of external photons into the central regions of dense interstellar clouds occurs only to a small extent. The ionization of H_2 occurs via higher energy processes. Throughout galaxies such as our own, high-energy particles known as cosmic rays exist tion of H_2 occurs via higher energy processes. Throughout galaxies such as our own,
high-energy particles known as cosmic rays exist. Travelling at relativistic speeds,
these nuclei, which are in the main protons, are high-energy particles known as cosmic rays exist. Travelling at relativistic speeds, these nuclei, which are in the main protons, are able to penetrate dense clouds and to afford a small degree of ionization upon collision these nuclei, which are in the main protons, are able to penetrate dense clouds and
to afford a small degree of ionization upon collision with gas-phase species, chiefly
molecular hydrogen and helium. The ionization occurs to afford a small degree of ionization upon collision with gas-phase species, chiefly
molecular hydrogen and helium. The ionization occurs both directly and indirectly
through secondary electrons produced in the primary pr molecular hydrogen and helium. The ionization occurs both directly and indirectly through secondary electrons produced in the primary process. In addition, the secondary electrons can excite molecular hydrogen sufficiently ondary electrons can excite molecular hydrogen sufficiently that fluorescence in the

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The total rate (s^{-1}) of ionization/dissociation of H₂ by cosmic rays is labelled ζ ; al. 1996; Millar *et al.* 1997).
The total rate (s⁻¹) of ionization/dissociation of H₂ by cosmic rays is labelled ζ ;
perhaps 90% of ζ leads to H₂⁺. A 'standard' value for ζ of *ca*. 1.3 \times 10⁻¹⁷ s The total rate (s^{-1}) of ionization/dissociation of H₂ by cosmic rays is labelled ζ ;
perhaps 90% of ζ leads to H₂⁺. A 'standard' value for ζ of ca. $1.3 \times 10^{-17} s^{-1}$ is often
used, although recent studi perhaps 90% of ζ leads to H_2^+ . A 'standard' value for ζ of ca. 1.3×10^{-17} s⁻¹ is often used, although recent studies suggest that its value can range more than one order of magnitude in either direction used, although recent studies suggest that its value can range more than one order
of magnitude in either direction from this value (Caselli *et al.* 1998). In addition to
cosmic rays, ionization of molecular hydrogen can of magnitude in either direction from this value (Caselli *et al.* 1998). In addition to cosmic rays, ionization of molecular hydrogen can occur via X-rays in selected regions where there is a high X-ray flux. One such ty cosmic rays, ionization of molecular hydrogen can occur via X-rays in selected regions
where there is a high X-ray flux. One such type of region is a young star known as
a T Tauri object; these stars have not yet settled d where there is a high X-ray flux. One such type of region is a young star known as
a T Tauri object; these stars have not yet settled down to a stable existence and
are capable of high X-ray emission. T Tauri stars embedde a T Tauri object; these stars have not yet settled down to a stable existence and
are capable of high X-ray emission. T Tauri stars embedded in objects enhance the
ionization rate because of their large X-ray emissions; th are capable of high X-ray emission. T Tauri stars embedded in objects enhance the
ionization rate because of their large X-ray emissions; the enhancement can be as
large as orders of magnitude, but the penetrating power of ionization rate because of their large X-ray emissions; the enhancement can be as
large as orders of magnitude, but the penetrating power of X-rays is less than that
of cosmic rays, so the region of enhancement may be smal large as orders of magnitude, but the penetrating power of X-rays is less than that
of cosmic rays, so the region of enhancement may be small. T Tauri stars can be
surrounded by swirling disks of gas and solids known as pr of cosmic rays, so the region of enhancement may be small. T Tauri stars
surrounded by swirling disks of gas and solids known as proto-planetary dis
ionization in parts of these regions is strongly influenced by the X-ray produced by swirling disks of gas and solids known as proto-planetary disks; the nization in parts of these regions is strongly influenced by the X-ray flux.
The H_2^+ produced by cosmic rays and/or X-rays is rather rea

ionization in parts of these regions is strongly influenced by the X-ray flux.
The H_2^+ produced by cosmic rays and/or X-rays is rather reactive and reacts v
the first hydrogen molecule it comes in contact with to form

$$
H_2^+ + H_2 \to H_3^+ + H. \tag{3.1}
$$

This reaction is a classic example of an exothermic ion-molecule reaction, which is known to proceed without activation energy. It occurs with a temperature-indepen-This reaction is a classic example of an κ known to proceed without activation energient $k \approx 2 \times 10^{-15}$ m³ s⁻
simple formula of Langevin. s^{-1}, c % cothermic ion–molecule reaction, which is
gy. It occurs with a temperature-indepen-
, close to what is estimated based on the known to proceed without act
dent rate coefficient $k \approx 2 \times 1$
simple formula of Langevin,

$$
k = \frac{1}{4\pi\epsilon_0} 2\pi e \left(\frac{\alpha}{\mu}\right)^{1/2},\tag{3.2}
$$

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This formula is derived by assuming that reaction occurs with 100% efficiency if the reactants are able to surmount a centrifueal where *e* is the electronic charge, α is the polarizability, and μ is the reduced mass.
This formula is derived by assuming that reaction occurs with 100% efficiency if the reactants are able to surmount a centrifug where e is the electronic charge, α is the polarizability, and μ is the reduced mass. This formula is derived by assuming that reaction occurs with 100% efficiency if the reactants are able to surmount a centrifugal barrier caused by the addition of the rotational kinetic energy to the long-range ion-induc reactants are able to surmount a centrifugal barrier caused by the addition of the rotational kinetic energy to the long-range ion-induced-dipole attractive potential (Herbst 1996). Given a molecular hydrogen density of THE ROYAL rotational kinetic energy to the long-range ion-induced-dipole attractive potential (Herbst 1996). Given a molecular hydrogen density of 10^{10} m^{-3} , the time-scale for the conversion of H_2^+ into H_3^+ is *ca*. (Herbst 1996). Given a
the conversion of H_2^+ in
interstellar standards.
Once H_2^+ is produced e conversion of H_2^+ into H_3^+ is ca. 10⁵ s, or 1 day, which is exceedingly rapid by erstellar standards.
Once H_3^+ is produced, it can be destroyed by a variety of exothermic reactions.
nese reactions are cruc 2 μ muon μ ₃ μ interstellar standards.
Once H_3^+ is produced, it can be destroyed by a variety of exothermic reactions.
These reactions are crucial to the chemistry of dense interstellar clouds, leading to
some if not most of the mor Once H_3^+ is produced, it can be destroyed by a variety of exothermic reactions.

Once H_3^+ is produced, it can be destroyed by a variety of exothermic reactions.
These reactions are crucial to the chemistry of dense interstellar clouds, leading to some, if not most of, the more abundant species. Th some, if not most of, the more abundant species. The dissociative recombination reaction with electrons is discussed by Larsson in this issue. This reaction is the some, if not most of, the more abundant species. The dissociative recombination
reaction with electrons is discussed by Larsson in this issue. This reaction is the
dominant destruction reaction for H_3^+ in diffuse clou reaction with electrons is discussed by Larsson in this issue. This reaction is the dominant destruction reaction for H_3^+ in diffuse clouds, where the electron fractional abundance is relatively high $(ca. 10^{-4})$. The d abundance is relatively high $(ca. 10^{-4})$. The dominant reaction pathway for reactions with neutral species (X) is proton transfer:

$$
H_3^+ + X \to XH^+ + H_2. \tag{3.3}
$$

 $H_3^+ + X \rightarrow XH^+ + H_2.$ (3.3)
In the early stages of dense-cloud evolution, proton-transfer reactions with certain
neutral atoms are especially important. In the early stages of dense-cloud evolut
neutral atoms are especially important. *Phil. Trans. R. Soc. Lond.* A (2000)

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 $The\ astrochemistry\ of\ H_{3}^{+}$ $The\ astrochemistry\ of\ H_{3}^{+}$ $The\ astrochemistry\ of\ H_{3}^{+}$ $+$ $rac{1}{3}$ 2527

(*a*) *Reaction with atomic* ^O

The reaction with neutral atomic oxygen appears to be a straightforward proton transfer,

$$
H_3^+ + O \to OH^+ + H_2,\tag{3.4}
$$

although the laboratory study is rather old and at room temperature only. A recent $t_1 + t_2$, (3.4)
although the laboratory study is rather old and at room temperature only. A recent
theoretical study by Bettens *et al.* (1999) employing *ab initio* potential surfaces
and classical trajectory calculatio although the laboratory study is rather old and at room temperature only. A recent
theoretical study by Bettens *et al.* (1999) employing *ab initio* potential surfaces
and classical trajectory calculations indicates that theoretical study by Bettens *et al.* (1999) employing *ab initio* potential surfaces and classical trajectory calculations indicates that the reaction proceeds at a rate close to that of the simple Langevin theory, despi and classical trajectory calculations indicates that the reaction proceeds at a rate close to that of the simple Langevin theory, despite the fact that the O atom has a quadrupolar moment that enhances the long-range poten close to that of the simple Langevin theory, despite the fact that the O atom has a

$$
H_3^+ + O \to H_2O^+ + H \tag{3.5}
$$

also occurs, but with a rate coefficient approximately one order of magnitude lower. $\frac{113}{13} + 6 \times \frac{120}{120} + 11$ (0.0)
also occurs, but with a rate coefficient approximately one order of magnitude lower.
This possible reaction channel is not important in interstellar clouds because the
products of re also occurs, but with a rate coefficient approximately one order of magnitude lc
This possible reaction channel is not important in interstellar clouds because
products of reaction (3.4) themselves react efficiently via an

$$
OH^{+} + H_{2} \rightarrow H_{2}O^{+} + H. \tag{3.6}
$$

 $OH^+ + H_2 \rightarrow H_2O^+ + H.$ (3.6)
A subsequent reaction with ubiquitous molecular hydrogen then leads to the hydro-
nium ion: A subseque
nium ion:

$$
H_2O^+ + H_2 \to H_3O^+ + H. \tag{3.7}
$$

 $H_2O^+ + H_2 \rightarrow H_3O^+ + H.$ (3.7)
This ion does not react with molecular hydrogen, and so is relatively abundant. It
has been detected via its rotation-inversion spectrum h_1 has been detected via its rotation-inversion spectrum.
The major destruction process for H_2O^+ is via recombi is ion does not react with molecular hydrogen, and so is relatively abundant. It
s been detected via its rotation-inversion spectrum.
The major destruction process for H_3O^+ is via recombination with electrons, which
e

has been detected via its rotation-inversion spectrum.
The major destruction process for H_3O^+ is via recombination with electrons, which
are produced by cosmic-ray bombardment. The rate coefficients for recombination
 The major destruction process for H_3O^+ is via recombination with electrons, which
are produced by cosmic-ray bombardment. The rate coefficients for recombination
reactions are well known and large, and it is well know are produced by cosmic-ray bombardment. The rate coefficients for recombination
reactions are well known and large, and it is well known that the products are, in the
main, neutral fragments, rather than the parent neutral reactions are well known and large, and it is well known that the products are, in the main, neutral fragments, rather than the parent neutral, but until recently there was little information concerning the branching fract main, neutral fragments, rather than the parent neutral, but until recently there was
little information concerning the branching fractions of the various possible neutral
products. Two methods of measuring the products fo little information concerning the branching fractions of the various possible neutral
products. Two methods of measuring the products for thermal systems are now in
use: spectroscopic detection in a flowing afterglow syste products. Two methods of measuring the products for thermal systems are now in
use: spectroscopic detection in a flowing afterglow system, and particle detection in a
storage ring (see Larsson, this issue). The methods ha use: spectroscopic detection in a flowing afterglow system, and particle detection in a
storage ring (see Larsson, this issue). The methods have been used to fully character-
ize the products of the H_3O^+ -e⁻ reaction storage ring (see Larsson, this issue). The methods have been used to fully character-
ize the products of the H_3O^+ -e⁻ reaction (Williams *et al.* 1996; Vejby-Christensen *et*
al. 1997). Four exothermic channels a ize the products of the H_3O^+ -e⁻ reaction (Williams *et al.* 1996; Vejby-Christensen *et al.* 1997). Four exothermic channels are possible: $H_2O + H$, $OH + H_2$, $OH + 2H$ and $O + H_2 + H$. Although both methods yield the re al. 1997). Four exothermic channels are possible: $H_2O + H$, $OH + H_2$, $OH + 2H$ and $O + H_2 + H$. Although both methods yield the result that OH is the dominant product, they differ quantitatively concerning all four channels. $O + H_2 + H$. Although both methods yield the result that OH is the dominant product, they differ quantitatively concerning all four channels. In particular, the flowing afterglow results indicate that little, if any, water uct, they differ quantitatively concerning all four channels. In particular, the flowing afterglow results indicate that little, if any, water is produced $(0-5\%)$, while the storage-ring results show that water is produc explanation for the discrepancy has been offered. Although the storage-ring results storage-ring results show that water is produced on $33 \pm 8\%$ of reactive collisions. No
explanation for the discrepancy has been offered. Although the storage-ring results
are incorporated into models, recent satellite explanation for the discrepancy has been offered. Although the storage-ring results
are incorporated into models, recent satellite results on water show that there is less
than predicted in dark clouds. A much more efficie are incorporated into models, recent satellite results on water show that there is less
than predicted in dark clouds. A much more efficient synthesis of water occurs on
grain surfaces via successive addition of hydrogen a than predicted in dark clouds. A much more efficient synthesis of water occurs on grain surfaces via successive addition of hydrogen atoms to surface oxygen atoms. The water ice formed tends to remain on the grains in cold sources.
(*b*) *Reaction with atomic* C

The reaction with neutral atomic carbon has not been studied in the laboratory but has been looked at theoretically, most recently by Bettens & Collins (1998a), who ²⁵²⁸ *E. Herbst* Downloaded from rsta.royalsocietypublishing.org

2528 $E.$ Herbst
used classical trajectory studies. This and previous work shows that the dominant
process is proton transfer used classical trajectory stu
process is proton transfer,

$$
H_3^+ + C \to CH^+ + H_2,\tag{3.8}
$$

 $H_3^+ + C \rightarrow CH^+ + H_2,$ (3.8)
and that the rate coefficient is near Langevin at 10 K. Bettens & Collins (1998*a*)
found that the process and that the rate coeffic
found that the process

$$
H_3^+ + C \rightarrow CH_2^+ + H \tag{3.9}
$$

 $H_3^+ + C \rightarrow CH_2^+ + H$ (3.9)
can occur but with a rather small rate coefficient. There are complications in (3.8)
and (3.9) due to the fine structure of atomic carbon and whether or not the collisions can occur but with a rather small rate coefficient. There are complications in (3.8) and (3.9) due to the fine structure of atomic carbon and whether or not the collisions are adiabatic with respect to fine structure. can occur but with a rather small rate coefficient. There are complications in (3.8) and (3.9) due to the fine structure of atomic carbon and whether or not the collisions are adiabatic with respect to fine structure. and (3.9) due to the fine structure of atomic carbon and whether or not the collisions are adiabatic with respect to fine structure. A competing process that also initiates hydrocarbon chemistry is the radiative associa ation reaction
 $\frac{1}{2} + h\nu,$ (3.10)

$$
C^+ + H_2 \to CH_2^+ + h\nu, \tag{3.10}
$$

 $C^+ + H_2 \rightarrow CH_2^+ + h\nu,$ (3.10)
which occurs on roughly one out of every 10^{6-7} collisions according to experiment
and theory (Gerlich & Horning 1992). The carbon ion may be present initially or which occurs on roughly one out of every 10^{6-7} collisions according to experiment
and theory (Gerlich & Horning 1992). The carbon ion may be present initially or
can be produced by the reaction between CO, the second and theory (Gerlich $\&$ Horning 1992). The carbon ion may be present initially or can be produced by the reaction between CO, the second most abundant interstellar and theory (Gerlich & Horning 1992). The carbon ion may be pre
can be produced by the reaction between CO, the second most abune
molecule, and He^+ , an ion produced by cosmic-ray bombardment:

$$
CO + He^{+} \rightarrow C^{+} + O + He.
$$
 (3.11)

 $CO + He^+ \rightarrow C^+ + O + He.$ (3.11)
Once CH⁺ and CH₂⁺ are produced, H-atom transfer reactions with H₂ rapidly
ad to the production of the methyl ion CH⁺. This ion does not react rapidly with Once CH⁺ and CH₂⁺ are produced, H-atom transfer reactions with H₂ rapidly lead to the production of the methyl ion, CH₃⁺. This ion does not react rapidly with H₂ since the H-atom transfer channel is endother lead to the production of the methyl ion, CH_3^+ . This ion does not react rapidly with Once CH⁺ and CH₂⁺ are produced, H-atom transfer reactions with H₂ rapidly lead to the production of the methyl ion, CH₃⁺. This ion does not react rapidly with H₂, since the H-atom transfer channel is endothe lead to the production of the methyl ion, CH_3^+ .
 H_2 , since the H-atom transfer channel is endot
radiative association with H_2 produces CH_5^+ : $\frac{+}{5}$: $t_5^+ + h\nu.$ (3.12)

$$
CH_3^+ + H_2 \to CH_5^+ + h\nu. \tag{3.12}
$$

 $CH_3^+ + H_2 \rightarrow CH_5^+ + h\nu.$ (3.12)
This radiative association reaction has been studied in the laboratory (Gerlich &
Horning 1992) as well as theoretically and to within an order of magnitude proceeds This radiative association reaction has been studied in the laboratory (Gerlich & Horning 1992) as well as theoretically, and, to within an order of magnitude, proceeds once out of every 10^4 collisions at low temperatu This radiative association reaction has been studied in the laboratory (Gerlich & Horning 1992) as well as theoretically, and, to within an order of magnitude, proceeds once out of every 10^4 collisions at low temperatu Horning 1992) as well as theoretically, and, to within an order of magnitude, proceeds
once out of every 10^4 collisions at low temperatures. Since the reaction is not very
rapid, the methyl ion retains a significant ab once out of every 10^4 collisions at low temperatures. Since the reaction is not very rapid, the methyl ion retains a significant abundance and is an important precursor for many other species. The dissociative recombin rapid, the methyl ion retains a significant abundance and is an important precursor
for many other species. The dissociative recombination reaction between CH_5^+ and
electrons does not produce large amounts of CH_4 (Se for many other species. The dissociative recombination reaction between CH_5^+ and
electrons does not produce large amounts of CH_4 (Semaniak *et al.* 1998); rather,
the dominant channel leads to $CH_3 + 2H$. Methane can electrons does not produce large amounts of CH₄ (Semaniak *et al.* 1998); rather, the dominant channel leads to CH₃ + 2H. Methane can be formed, however, via the reaction of CH₅⁺ with CO: not produce
thannel leads $_5^+$ with CO:

$$
CH_5^+ + CO \rightarrow CH_4 + HCO^+. \tag{3.13}
$$

The formation of small hydrocarbons such as the methyl ion, methyl and methane The formation of small hydrocarbons such as the methyl ion, methyl and methane
sets the stage for the production of more complex hydrocarbons through three types
of synthetic reactions The formation of sma
sets the stage for the pro
of synthetic reactions, % synthetic reactions,
(i) carbon insertion via either C or C⁺,

- ,
- (ii) condensation reactions between hydrocarbon ions and neutrals, and
- (iii) radiative association reactions,

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The astrochemistry of H_3^+ 2529
many of which have been studied in the laboratory, especially in the first two classes. many of which have been studied in the laboratory, especially in the first two classes.
Examples of each are found in the following sample list of synthetic reactions that occur in dense clouds: many of which have bee:
Examples of each are fo
occur in dense clouds: $^{+}_{2}$ + H₂; C₂H₃⁺ + H₂

$$
C^{+} + CH_{4} \rightarrow C_{2}H_{2}^{+} + H_{2}; C_{2}H_{3}^{+} + H,
$$
\n(3.14)

$$
C^{+} + CH_{4} \rightarrow C_{2}H_{2}^{+} + H_{2}; C_{2}H_{3}^{+} + H,
$$
\n(3.14)
\n
$$
C_{2}H_{3}^{+} + e^{-} \rightarrow C_{2}H_{2} + H(?); C_{2}H + 2H(?),
$$
\n(3.15)
\n
$$
C_{2}H_{2}^{+} + H_{2} \rightarrow C_{2}H_{4}^{+} + h\nu; C_{2}H_{3}^{+} + H(?)
$$
\n(3.16)
\n
$$
H_{1}^{+} + G_{2}H_{3}^{+} + H_{4}^{+} + H_{5}^{+} + H_{6}^{+} + H_{7}^{+}
$$
\n(3.17)

$$
C_2H_2^+ + H_2 \to C_2H_4^+ + h\nu; C_2H_3^+ + H(?)
$$
\n(3.16)

$$
C_2H_2^+ + H_2 \to C_2H_4^+ + h\nu; C_2H_3^+ + H(?)
$$
\n
$$
C_2H_2^+ + C_2H_2 \to C_4H_2^+ + H_2; C_4H_3^+ + H,
$$
\n(3.17)

$$
C^{+} + C_{2}H_{2} \rightarrow C_{3}H^{+} + H,
$$
\n(3.18)
\n
$$
C_{3}H^{+} + H_{2} \rightarrow C_{3}H_{3}^{+} + h\nu; C_{3}H_{2}^{+} + H.
$$
\n(3.19)

$$
C_3H^+ + H_2 \to C_3H_3^+ + h\nu; C_3H_2^+ + H.
$$
\n(3.19)

Controversy still exists concerning the relative rates of radiative association and Controversy still exists concerning the relative rates of radiative association and
normal product channels for several of these reactions (Gerlich & Horning 1992).
It is interesting to note that hydrogen-atom transfer re Controversy still exists concerning the relative rates of radiative association and
normal product channels for several of these reactions (Gerlich & Horning 1992).
It is interesting to note that hydrogen-atom transfer re normal product channels for several of these reactions (Gerlich & Horning 1992).
It is interesting to note that hydrogen-atom transfer reactions between hydrocarbon
ions and H_2 are rarely exothermic or barrier free for It is interesting to note that hydrogen-atom transfer reactions between hydrocarbon
ions and H_2 are rarely exothermic or barrier free for ions with more than a few carbon
atoms, so that even with radiative association the extent of hydrogenation is surprisingly low given the huge abundance of H₂.
It should be mentioned that neutral-neutral reactions involving neutral atomic. the extent of hydrogenation is surprisingly low given the huge abundance of H_2 .

atoms, so that even with radiative association reactions, which can sometimes occur, the extent of hydrogenation is surprisingly low given the huge abundance of H_2 .
It should be mentioned that neutral-neutral reactions

$$
C + C_2H_2 \rightarrow C_3H + H \tag{3.20}
$$

is probably the dominant route to form both known isomers of C_3H , the cyclic and the linear, although neutral{neutral reactions cannot produce the analogous isomers is probably the dominant route to form both known isomers of C_3H , the the linear, although neutral-neutral reactions cannot produce the analogo of C_3H_2 , which are more abundant and ubiquitous in interstellar space. (*c*) *Reaction with other atoms*

(c) Reaction with other atoms
The proton-transfer reaction between H_3^+ and neutral atomic nitrogen is endother-
ic by 98 kJ mol⁻¹ so cannot occur at low temperatures. It has been claimed occa-The proton-transfer reaction between H_3^+ and neutral atomic nitrogen is endother-
mic by 98 kJ mol⁻¹, so cannot occur at low temperatures. It has been claimed occa-
sionally by experimentalists that the reaction The proton-transfer reaction between H_3^+ and n
mic by 98 kJ mol⁻¹, so cannot occur at low tempe
sionally by experimentalists that the reaction

$$
H_3^+ + N \rightarrow NH_2^+ + H \tag{3.21}
$$

 $H_3^+ + N \rightarrow NH_2^+ + H$ (3.21)
occurs without activation energy, but theoretical treatments have never supported
this viewpoint (Bettens & Collins 1998b) and the latest experimental claim has just this viewpoint activation energy, but theoretical treatments have never supported
this viewpoint (Bettens & Collins 1998b), and the latest experimental claim has just
been withdrawn occurs without act
this viewpoint (Be
been withdrawn.
The fact that rea this viewpoint (Bettens & Collins 1998b), and the latest experimental claim has just
been withdrawn.
The fact that reaction (3.21) does not occur in a facile manner has profound impli-

been withdrawn.
The fact that reaction (3.21) does not occur in a facile manner has profound implications for interstellar chemistry, because, if it did occur, the formation of ammonia
via the sequence of reactions The fact that reaction (3.21)
cations for interstellar chemistry
via the sequence of reactions

$$
NH_2^+ + H_2 \to NH_3^+ + H,\tag{3.22}
$$

$$
NH_3^+ + H_2 \to NH_4^+ + H,\tag{3.23}
$$

$$
NH_4^+ + e^- \to NH_3 + H, \tag{3.24}
$$

 $NH_4^+ + e^- \rightarrow NH_3 + H,$ (3.24)
would occur rapidly. Reaction (3.23) has a small entrance channel barrier. Detailed
calculations show however that tunnelling under this barrier becomes enhanced at would occur rapidly. Reaction (3.23) has a small entrance channel barrier. Detailed
calculations show, however, that tunnelling under this barrier becomes enhanced at
low temperatures (Herbst *et al.* 1991), so that the r would occur rapidly. Reaction (3.23) has a small entrance channel barrier. Detailed calculations show, however, that tunnelling under this barrier becomes enhanced at low temperatures (Herbst *et al.* 1991), so that the re calculations show, however, that tunnelling under this barrier becomes enhanced at low temperatures (Herbst *et al.* 1991), so that the reaction is efficient at interstellar temperatures, in agreement with experimental me

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 $E.$ *Herbst*
As it is, ammonia is produced much more slowly from OH through N₂ via a very
direct scheme that first leads to the atomic nitrogen ion: As it is, ammonia is produced much more slowly from OH indirect scheme that first leads to the atomic nitrogen ion:

$$
OH + N \rightarrow NO + H, \tag{3.25}
$$

$$
NO + N \rightarrow N_2 + O,
$$
\n
$$
(3.26)
$$

$$
N_2 + He^+ \rightarrow N^+ + N + He. \tag{3.27}
$$

 $N_2 + He^+ \rightarrow N^+ + N + He.$ (3.27)
This ion must then be hydrogenated into NH_4^+ . The H-atom transfer reaction between
 N^+ and H₂ is either slightly endothermic or possesses a small activation energy This ion must then be hydrogenated into NH_4^+ . The H-atom transfer reaction between N^+ and H_2 is either slightly endothermic or possesses a small activation energy of ca 0.01–0.02 eV. This can be overcome because This ion must then be hydrogenated into NH_4^+ . The H-atom transfer reaction between N^+ and H_2 is either slightly endothermic or possesses a small activation energy of $ca. 0.01-0.02$ eV. This can be overcome becaus N^+ and H_2 is either slightly endothermic or possesses a small activation energy of ca. 0.01–0.02 eV. This can be overcome because interstellar species produced in exothermic reactions are not totally thermalized; bo of ca. 0.01–0.02 eV. This can be overcome because interstellar species produced in exothermic reactions are not totally thermalized; both N^+ and H_2 have slightly excess energies, N^+ in its translational and possi exothermic reactions are not totally thermalized; both N^+ and H_2 have slightly excess energies, N^+ in its translational and possibly fine structure states, and H_2 in rotational levels (Galloway & Herbst 1989; excess energies, N^+ in its translational and possibly fine structure states, and H_2 in rotational levels (Galloway & Herbst 1989; Le Bourlot 1991). Since the formation of ammonia takes place so slowly, clouds in whi rotational levels (Galloway & Herbst 1989; Le
of ammonia takes place so slowly, clouds in wh
thought to be old by astronomical standards.
The final H_{α}^{+} reaction with atoms to be consi ammonia takes place so slowly, clouds in which ammonia is highly abundant are
ought to be old by astronomical standards.
The final H_3^+ reaction with atoms to be considered here involves sulphur. Sulphur
emistry is tho

thought to be old by astronomical standards.
The final H_3^+ reaction with atoms to be considered here involves sulph
chemistry is thought to commence with the proton-transfer reaction

$$
H_3^+ + S \to SH^+ + H_2,\tag{3.28}
$$

 $H_3^+ + S \rightarrow SH^+ + H_2,$ (3.2)
which is presumably analogous to its oxygen counterpart. The product ion HS^+ can
not react exothermically with H_2 except for a possible radiative association reaction canwhich is presumably analogous to its oxygen counterpart. The product ion HS^+ cannot react exothermically with H_2 , except for a possible radiative association reaction: not react exothermically with H_2 , except for a possible radiative association reaction:

$$
SH^{+} + H_{2} \rightarrow H_{3}S^{+} + h\nu. \tag{3.29}
$$

 $SH^+ + H_2 \rightarrow H_3S^+ + h\nu.$ (3.29)
The rate of this reaction is uncertain. Although the three-body analogue has been
studied at higher densities, conversion of the three-body to an analogous two-body The rate of this reaction is uncertain. Although the three-body analogue has been
studied at higher densities, conversion of the three-body to an analogous two-body
rate coefficient, which can often be undertaken is comple studied at higher densities, conversion of the three-body to an analogous two-body rate coefficient, which can often be undertaken, is complex here because the reacstudied at higher densities, conversion of the three-body to an ana
rate coefficient, which can often be undertaken, is complex here l
tion must proceed via a spin-flip (Herbst *et al.* 1989). If H₃S⁺ c;
reaction (3.29 $+$ α nalogous two-body
can be formed via
sizeable abundance rate coefficient, which can often be undertaken, is complex here because the reaction must proceed via a spin-flip (Herbst *et al.* 1989). If H_3S^+ can be formed via reaction (3.29), then dissociative recombination mig tion must proceed via a spin-flip (Herbst *et al.* 1989). If H_3S^+ can be formed via
reaction (3.29), then dissociative recombination might lead to a sizeable abundance
of H_2S . The standard assumption, however, is t reaction (3.29), then dissociative recombination might lead to a sizeable abundance
of H_2S . The standard assumption, however, is that gas-phase interstellar H_2S more likely derives from a grain chemistry in which successive H atoms attach to surface. S atoms, followed by some mechanism for desorption from the grain surface.
(*d*) *Reaction with molecules*

(d) Reaction with molecules
In addition to its reactions with atoms, H_3^+ is able to protonate most interstellar
plecules. The protonation of CO In addition to its reactions with a
molecules. The protonation of CO,

$$
H_3^+ + CO \rightarrow HCO^+ + H_2,\tag{3.30}
$$

 $H_3^+ + CO \rightarrow HCO^+ + H_2,$ (3.30)
is important because it produces the polar HCO^+ ion, which is, under most cir-
cumstances the most abundant molecular ion, and is easily detectable by radiois important because it produces the polar HCO^+ ion, which is, under most circumstances, the most abundant molecular ion, and is easily detectable by radio-
astronomical means. The metastable ion HOC^+ is also produced is important because it produces the polar HCO^+ ion, which is, under most circumstances, the most abundant molecular ion, and is easily detectable by radio-astronomical means. The metastable ion HOC^+ is also produced cumstances, the most abundant molecular ion, and is easily detectable by radio-
astronomical means. The metastable ion HOC^+ is also produced in this reaction.
Finally, the protonation of HD ,

$$
H_3^+ + HD \to H_2D^+ + H_2,\tag{3.31}
$$

is especially interesting. This reaction is exothermic by a small amount (*ca*. 230 K is especially interesting. This reaction is exothermic by a small amount $(ca.230 \text{ K}$
or 1.9 kJ mol⁻¹), which is equal to the sum of the zero-point vibrational energy dif-
ference between products and reactants plus the is especially interesting. This reaction is exothermic by a small amount $(ca.230 \text{ K}$ or 1.9 kJ mol^{-1}), which is equal to the sum of the zero-point vibrational energy difference between products and reactants plus the *Phil. Trans. R. Soc. Lond.* A (2000)

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The astrochemistry of H_3^+ 2531
the lowest rotational state of H_3^+ is disallowed by the Pauli principle. At low tem-
peratures, the backwards reaction is very slow, so that the equilibrium lies far to the lowest rotational state of H_3^+ is disallowed by the Pauli principle. At low temperatures, the backwards reaction is very slow, so that the equilibrium lies far to the right, and, even though the HD/H₂ abundance the lowest rotational state of H_3^+ is disallowed by the Pauli principle. At low temperatures, the backwards reaction is very slow, so that the equilibrium lies far to the right, and, even though the HD/H_2 abundance r peratures, the backwards reaction is very slow, so that the equilibrium lies far to
the right, and, even though the HD/H_2 abundance ratio in dense interstellar clouds
is $ca.4 \times 10^{-5}$, the H_2D^+/H_3^+ abundance ratio c the right, and, even though the HD/H_2 abundance ratio in dense interstellar clouds
is $ca. 4 \times 10^{-5}$, the H_2D^+/H_3^+ abundance ratio can become as high as 0.10. The
high abundance of the H_2D^+ ion leads to enhanced is $ca.4 \times 10^{-5}$, the H_2D^+/H_3^+ abundance ratio can become as high as 0.10. The high abundance of the H_2D^+ ion leads to enhanced abundances of many other singly deuterated isotopomers through ion–molecule reaction high abundance of the H_2D
deuterated isotopomers thr
Millar *et al*. in this issue.

in this issue.
4. The concentration of $\rm{H_3^+}$ in interstellar clouds

4. The concentration of H_3^+ in interstellar clouds
What is the concentration of H_3^+ in interstellar clouds? In dense clouds, the destruc-
tion of this ion is controlled by reactions with abundant neutrals, mainly What is the concentration of H_3^+ in interstellar clouds? In dense clouds, the destruction of this ion is controlled by reactions with abundant neutrals, mainly CO, and by reaction with electrons. The competition betwe What is the concentration of H_3^+ in interstellar clouds? In dense clouds, the destruction of this ion is controlled by reactions with abundant neutrals, mainly CO, and by reaction with electrons. The competition betwe tion of this ion is controlled by reactions with abundant neutrals, mainly CO, and
by reaction with electrons. The competition between these two destruction mecha-
nisms is important in determining the region of bistabili by reaction with electrons. The competition between these two destruction mechanisms is important in determining the region of bistability, as discussed by Pineau des Forêts & Roueff in this issue. The electron abundance i nisms is important in determining the region of bistability, as discussed by Pineau des Forêts $\&$ Roueff in this issue. The electron abundance is determined principally by the abundance of so-called 'metals' in the gas des Forêts & Roueff in this issue. The electron abundance is determined principally
by the abundance of so-called 'metals' in the gas phase. The word 'metal' in astron-
omy often refers to every element heavier than helium by the abundance of so-called 'metals' in the gas phase. The word 'metal' in astron-
omy often refers to every element heavier than helium (to be fair, astronomers refer
mainly to the concept of 'metallicity'), although he omy often refers to every element heavier than helium (to be fair, astronomers refer mainly to the concept of 'metallicity'), although here we use it in a more restrictive sense as a group of elements consisting of actual mainly to the concept of 'metallicity'), although here we use it in a more restrictive
sense as a group of elements consisting of actual metals as well as sulphur and silicon.
Some of the typical stellar abundance of these sense as a group of elements consisting of actual metals as well as sulphur and silicon.
Some of the typical stellar abundance of these elements is to be found on dust par-
ticles in the interstellar medium, and not in th Some of the typical stellar abundance of these elements is to be found on dust particles in the interstellar medium, and not in the gas phase. In standard dense-cloud models (Lee *et al.* 1996; Millar *et al.* 1997), the g ticles in the interstellar medium, and not in the gas phase. In standard dense-cloud models (Lee *et al.* 1996; Millar *et al.* 1997), the gas-phase concentrations of these elements relative to hydrogen are reduced strongl models (Lee *et al.* 1996; Millar *et al.* 1997), the gas-phase concentrations of these elements relative to hydrogen are reduced strongly, since this reduction leads to better agreement with observation for many molecule ments relative to hydrogen are reduced strongly, since this reduction leads to better agreement with observation for many molecules and makes sense physically. Under these circumstances, the fractional electron abundance (agreement with observation for many molecules and makes sense physically. Under
these circumstances, the fractional electron abundance (with respect to hydrogen)
is, typically, 3×10^{-8} and H_3^+ is depleted mainly b these circumstances, the fractional electron abundance (with respect to hydrogen)
is, typically, 3×10^{-8} and H_3^+ is depleted mainly by reaction with abundant neutrals
such as CO. In our time-dependent models of ty is, typically, 3×10^{-8} and H₃⁺ is depleted mainly by reaction with abundant neutrals
such as CO. In our time-dependent models of typical cold dense-cloud cores, the con-
centration of H₃⁺ quickly reaches a val such as CO. In our time-dependent models of typical cold dense-cloud cores, the concentration of H_3^+ quickly reaches a value of $ca. 20 \text{ m}^{-3}$. For a cloud of length 10 pc $(ca. 3 \times 10^{17} \text{ m})$, the predicted column d centration of H_3^+ quickly reaches a value of $ca. 20 \text{ m}^{-3}$. For a cloud of length 10 pc $(ca. 3 \times 10^{17} \text{ m})$, the predicted column density is $6 \times 10^{18} \text{ m}^{-2}$. For a cloud of length 1 pc, the column density is o $(ca. 3 \times 10^{17} \text{ m})$, the predicted column density is $6 \times 10^{18} \text{ m}^{-2}$. For a cloud of length 1 pc, the column density is one-tenth of this amount. Use of a simple steady-state model in which H_3^+ is only depleted model in which H_3^+ is only depleted by reaction with CO leads to an ion concentra-1 pc, the column density is one-tenth of this amount. Use of a simple steady-state model in which H_3^+ is only depleted by reaction with CO leads to an ion concentration and column density a factor of a few greater. Th model in which H_3^+ is only depleted by reaction with CO leads to an ion concentra-
tion and column density a factor of a few greater. The agreement with observation
(see the paper by Geballe in this issue) is good. Wi tion and column density a factor of a few greater. The agreement with observation (see the paper by Geballe in this issue) is good. With a reasonably high abundance for an ion, H_3^+ is a principal (if not dominant) des for an ion, H_3^+ is a principal (if not dominant) destroyer of neutral species by pro-(see the paper by Geballe in this issue) is good. With a reasonably high abundance
for an ion, H_3^+ is a principal (if not dominant) destroyer of neutral species by pro-
tonation reactions followed by dissociative reco for an ion, H_3^+ is a principal (if not dominant) destroy tonation reactions followed by dissociative recombinations to form species other than the original neutrals.
In diffuse interstellar clouds, the ion is depleted In diffuse interstellar clouds, the ion is depleted mainly by recombination with
In diffuse interstellar clouds, the ion is depleted mainly by recombination with
ectrons. The calculated concentration and column density dep

ions to form species other than the original neutrals.
In diffuse interstellar clouds, the ion is depleted mainly by recombination with
electrons. The calculated concentration and column density depend on how much of
the In diffuse interstellar clouds, the ion is depleted mainly by recombination with
electrons. The calculated concentration and column density depend on how much of
the hydrogen in the gas is in molecular form. Assuming that electrons. The calculated concentration and column density depend on how much of
the hydrogen in the gas is in molecular form. Assuming that much of the gas in inner
regions is molecular, it is easy to estimate that the the hydrogen in the gas is in molecular form. Assuming that much of the gas in inner
regions is molecular, it is easy to estimate that the H_3^+ concentration is perhaps two
orders of magnitude less than in dense clouds regions is molecular, it is easy to estimate that the H_3^+ concentration is perhaps two
orders of magnitude less than in dense clouds. This result does not appear to be in
agreement with the observations of Geballe *et* orders of magnitude less than in dense clouds. This result does not appear to be in
agreement with the observations of Geballe *et al.* (1999), as discussed by Geballe in
this issue. The interstellar chemistry of H_3^+ agreement with the observations of Geballe *et al.* (1999), as disc
this issue. The interstellar chemistry of H_3^+ is still not completely
is much more this most simple of polyatomic ions is telling us.

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Discussion

Discussion
I. W. M. SMITH (*School of Chemistry, University of Birmingham, UK*). Can you
please say a little more about the starting conditions for your time-dependent calcula- B because the same of B inversity of B irmingham, UK). Can your please say a little more about the starting conditions for your time-dependent calcula-
tions and how these are chosen? Can you also comment on how the please say a little more about the starting conditions for your time-dependent calculations and how these are chosen? Can you also comment on how the elemental atomic please say a little more about the starting conditions for your time-dependent calculations and how these are chosen? Can you also comment on how the elemental atomic abundances change with time? Is there any allowance for from and how these are cho
abundances change with the
from outside the cloud? from outside the cloud?
E. HERBST. For quiescent cores in dense clouds, several sets of initial conditions are

E. HERBST. For quiescent cores in dense clouds, several sets of initial conditions are
used for gas-phase models. A standard density is $1{\text -}3 \times 10^4$ molecules cm⁻³ and a
typical temperature is 10 K. These conditions E. HERBST. For quiescent cores in dense clouds, several sets of initial conditions are used for gas-phase models. A standard density is $1-3 \times 10^4$ molecules cm⁻³ and a typical temperature is 10 K. These conditions are used for gas-phase models. A standard density is $1-3 \times 10^4$ molecules cm^{-3} and a typical temperature is 10 K. These conditions are normally fixed. The overall gas density is divided among the various elements, the rel typical temperature is 10 K. These conditions are normally fixed. The overall gas
density is divided among the various elements, the relative proportions of which are
given by so-called 'cosmic' (near-solar) abundances wit some extent to account for the dust particles. A typical set of elemental abundances given by so-called 'cosmic' (near-solar) abundances with heavy elements depleted to some extent to account for the dust particles. A typical set of elemental abundances for the gas would be: $H = 1$, $He = 0.1$, $C = 7(-5)$, some extent to account for the dust particles. A typical set of elemental abundances
for the gas would be: $H = 1$, $He = 0.1$, $C = 7(-5)$, $O = 2(-4)$, $N = 2(-5)$. Variations in
these uncertain abundances can lead to very diffe for the gas would be: $H = 1$, $He = 0.1$, $C = 7(-5)$, $O = 2(-4)$, $N = 2(-5)$. Variations in these uncertain abundances can lead to very different results. If the material is carbon rich $(C > 0)$, it is far easier to synthesize these uncertain abundances can lead to very different results. If the material is carbon rich $(C > 0)$, it is far easier to synthesize organic molecules. A high abundance of sulphur is conducive to the phenomenon of bistability (see the paper by Pineau des Forêts $\&$ Roueff in this issue). One can start off with the elements in the form of neutral atoms. An alternative possibility often favo sulphur is conducive to the phenomenon of bistability (see the paper by Pineau des
Forêts & Roueff in this issue). One can start off with the elements in the form of
neutral atoms. An alternative possibility often favoured Forêts & Roueff in this issue). One can start off with the elements in the form of
neutral atoms. An alternative possibility often favoured is to start with abundances
that pertain to diffuse clouds; the main differences neutral atoms. An alternative possibility often favoured is to start with abundances
that pertain to diffuse clouds; the main differences with the first view are that much
of the hydrogen has already been converted into th that pertain to diffuse clouds; the main differences with the first view are that much
of the hydrogen has already been converted into the molecular form and the carbon
is in the form of the singly charged atomic cation. I of the hydrogen has already been converted into the molecular form and the carbon
is in the form of the singly charged atomic cation. In truth, the real initial species
are unknown, since they depend on the formation of t is in the form of the singly charged atomic cation. In truth, the real initial species
are unknown, since they depend on the formation of the molecular clouds from
the primeval stellar ejecta. Typical steady-state results are unknown, since they depend on the formation of the molecular clouds from
the primeval stellar ejecta. Typical steady-state results (reached after 10^7 yr or so)
are insensitive to the choices of initial conditions, the primeval stellar ejecta. Typical steady-state results (reached after 10⁷ yr or so)
are insensitive to the choices of initial conditions, although the so-called early time
results, where organic molecular abundances p are insensitive to the choices of initial conditions, although the so-called early time
results, where organic molecular abundances peak, are more prominent if one starts results, where organic molecular abundances peak, are more prominent if one starts
with H_2 . Although there are no models that contain replenishment of material from
external sources, there are models in which large-sca with H_2 . Although there are no models that contain replenishment of material from external sources, there are models in which large-scale motions inside clouds mix heterogeneous material from inner and outer regions. A external sources, there are models in which large-scale motions inside clouds mix
heterogeneous material from inner and outer regions. Also, there are models in which
grain-surface chemistry is also included, as are the ad heterogeneous material from inner and outer regions. Also, there are models in which

gram-surface chemistry is also included, as are the adsorption and desorption of
material from the grains.
S. LEPP (*UNLV, Las Vegas, NV, USA*). Regarding H₃O⁺ recombination, the results
may be consistent if one assume S. LEPP (*UNLV, Las Vegas, NV, USA*). Regarding H_3O^+ recombination, the results may be consistent if one assumes the ring experiments are measuring predissociated states states.

may be consistent if one assumes the ring experiments are measuring predissociated
states.
E. HERBST. It is certainly true that given the speed of the particles in a storage ring,
they are sampled by the detector within a E. HERBST. It is certainly true that given the speed of the particles in a storage ring,
they are sampled by the detector within a much shorter time than in the flowing
afterglow apparatus. Thus, if the water formed by the E. HERBST. It is certainly true that given the speed of the particles in a storage ring, they are sampled by the detector within a much shorter time than in the flowing afterglow apparatus. Thus, if the water formed by the afterglow apparatus. Thus, if the water formed by the dissociative recombination of *Phil. Trans. R. Soc. Lond.* A (2000)

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 $E.$ Herbst
H₃O⁺ + e is metastable and predissociates in some manner, it might be detectable
in the storage ring but not detectable in the flowing afterflow. For a species as H_3O^+ + e is metastable and predissociates in some manner, it might be detectable
in the storage ring but not detectable in the flowing afterflow. For a species as
small as water, however, a typical lifetime against vi in the storage ring but not detectable in the flowing afterflow. For a species as small as water, however, a typical lifetime against vibrational predissociation (uniin the storage ring but not detectable in the flowing afterflow. For a species as
small as water, however, a typical lifetime against vibrational predissociation (uni-
molecular decomposition) is only 10^{-13} s, so that small as water, however, a typical lifetime against vibrational predissociation (uni-
molecular decomposition) is only 10^{-13} s, so that it would not be seen in either
apparatus. A larger neutral species, with more degr molecular decomposition) is only 10^{-13} s, so that it would not be seen in either
apparatus. A larger neutral species, with more degrees of freedom, might be suffi-
ciently metastable against vibrational predissociation ciently metastable against vibrational predissociation to live for the ca . 10^{-6} s needed
to reach the neutral detector in a storage ring. There remains the possibility that
the water is produced in a bound but prediss ciently metastable against vibrational predissociation to live for the ca. 10^{-6} s needed
to reach the neutral detector in a storage ring. There remains the possibility that
the water is produced in a bound but predisso to reach the neutral detector in a storage ring. There remains the possibility that
the water is produced in a bound but predissociative excited electronic state (e.g. a
triplet state) that lives longer than the 10^{-6} s the water is produced in a bound but predissociative excited electronic state (e.g. a
triplet state) that lives longer than the 10^{-6} s but not long enough to be detected
in the flowing afterglow. This hyothesis could p triplet state) that lives longer than the 10^{-6} s but not
in the flowing afterglow. This hyothesis could possibly b
phosphorescence, which would undoubtedly be weak. I. B. B. A. MITCHELL (*PALMS, Université de Rennes, France*). In your talk, you is also have phosphorescence, which would undoubtedly be weak.

J. B. A. MITCHELL (*PALMS, Université de Rennes, France*). In your talk, you

J. B. A. MITCHELL (*PALMS*, *Universite*
showed a transparency with the $C_3H_3^+$ ion
rich flames and is seen ubiquitously in hyd versité de Rennes, France). In your talk, you
 $\frac{1}{3}$ ion on it. This is the dominant ion in fuel-

in hydrocarbon plasmas but its mechanism of J. B. A. MITCHELL (*PALMS, Université de Rennes, France*). In your talk, you showed a transparency with the $C_3H_3^+$ ion on it. This is the dominant ion in fuel-
rich flames and is seen ubiquitously in hydrocarbon plasm rich flames and is seen ubiquitously in hydrocarbon plasmas but its mechanism of formation is not understood. Do you have a viable scheme to form it?

Fich flames and is seen ubiquitously in hydrocarbon plasmas but
formation is not understood. Do you have a viable scheme to form
E. HERBST. The dominant formation mechanism for $C_3H_3^+$ in
starts with the reaction betwe $\frac{1}{3}$ in interstellar clouds E. HERBST. The dominant formation mechanism for
starts with the reaction between acetylene and C^+ , starts with the reaction between acetylene and C^+ ,

 $C^+ + C_2H_2 \to C_3H^+ + H$,

and is followed by the radiative association of C_3H^+ with H_2 :

 $^+ + H_2 \rightarrow C_3 H_3^+$.

 $C_3H^+ + H_2 \rightarrow C_3H_3^+$.
A. SUZOR-WEINER (*Laboratoire de Photophysique Moléculaire, Université Paris-*
Seed France) In diffuse introstaller aloude you point out that two jons. CH^+ and *A.* SUZOR-WEINER (*Laboratoire de Photophysique Moléculaire, Université Paris-
<i>Sud, France*). In diffuse intrestellar clouds, you point out that two ions, CH⁺ and
 H_{α}^+ have unexplained high abundances at least wi H_3^+ , ha $Sud, France$). In diffuse intrestellar clouds, you point out that two ions, CH^+ and Sud, France). In diffuse intrestellar clouds, you point out that two ions, CH^+ and H_3^+ , have unexplained high abundances, at least with the fast rate measured for their dissociative recombination. Is there a special H_3^+ , have unexplained high a dissociative recombination. It wo unrelated problems?

two unrelated problems?
E. HERBST. At present, they do appear to be unrelated problems. The ion CH^+ must E. HERBST. At present, they do appear to be unrelated problems. The ion CH^+ must
be produced under high energy/temperature conditions, either in a shock wave or in
a region of turbulence of some sort. In either situatio E. HERBST. At present, they do appear to be unrelated problems. The ion CH⁺ must
be produced under high energy/temperature conditions, either in a shock wave or in
a region of turbulence of some sort. In either situation

$$
C^+ + H_2 \rightarrow CH^+ + H,
$$

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which is endothermic by 0.4 eV. The H_3^+ ion is easily produced at low temperatures.
It is difficult to see how high energies/temperatures can enhance its abundance sigwhich is endothermic by 0.4 eV . The H_3^+ ion is easily produced at low temperatures.
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nificantly although I have not done a detai which is endothermic by 0.4 eV . The H_3^+ ion is easily produced at low temperatures that is difficult to see how high energies/temperatures can enhance its abundantificantly, although I have not done a detailed

It is difficult to see how high energies/temperatures can enhance its abundance significantly, although I have not done a detailed calculation on the subject.
E. F. vAN DISHOECK (*Leiden Observatory, The Netherlands*). It to observe the H₃ line profile with high spectral resolution on the subject.

E. F. VAN DISHOECK (*Leiden Observatory, The Netherlands*). It would be interesting

to observe the H₃ line profile with high spectral reso 3 H. E. F. VAN DISHOECK (*Leiden Observatory, The Netherlands*). It would be interesting
to observe the H_3^+ line profile with high spectral resolution (a few km s⁻¹) in diffuse
clouds. It would then be possible to determ clouds. It would then be possible to determine observationally whether CH^+ and H_3^+ to observe the H_3^+ line profile with high spectral resolution (a few km s⁻¹) in di
clouds. It would then be possible to determine observationally whether CH⁺ and
are related, since the CH⁺ profile is much broade clouds. It would then be possible to determine observationally whether CH^+ and H_3
are related, since the CH^+ profile is much broader than that of other species.
M. LARSSON (*Department of Physics, Stockholm Univers*

ing related, since the CH profile is fluid broader than that of other species.

M. LARSSON (*Department of Physics, Stockholm University, Sweden*). The branch-

ing ratios for dissociative recombination of H_3O^+/D_3O^+ ing ratios for dissociative recombination of H_3O^+/D_3O^+ have been measured in CRYRING. The production of H_2O/D_2O was found to be 17–18%.

E. HERBST. Now that we have somewhat different values for the branching fraction CRTRING. The production of H_2O/D_2O was found to be $11–1876$.
E. HERBST. Now that we have somewhat different values for the branching fraction
of H_2O product from two different storage rings (ASTRID and CRYRING), it E. HERBST. Now that we have somewhat different values for the branclof H_2O product from two different storage rings (ASTRID and CRYRIN be useful to look carefully at the sources of uncertainty in the values. *Phil. Trans. R. Soc. Lond.* A (2000)