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CHEMISTRY AND DUST IN STAR-FORMING REGIONS OF SPACE

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ABSTRACT. Stars form from clouds of gas and dust in the interstellar medium. How the tenuous interstellar gas becomes a relatively dense star, and how a new star interacts with its environment, are currently lively and active fields of astronomical research. Since the ubiquitous cosmic dust makes the gas in denser clouds opaque to visual radiation, the main way that we can probe regions of star formation is by detecting radio emissions from molecules that are formed in the gas during the collapse. About 130 different molecular species have been detected in interstellar clouds. Most of these molecular species are formed in a variety of gas phase reactions, but some species depend on surface reactions for their formation. Understanding these chemical routes helps us to describe in detail the physical conditions in the gas during the collapse that leads to star formation and in the interaction of the new star with the cloud in which it was formed. We give three examples of such interactions:

- (i) We describe how the interaction of a newly-formed hot star interacts with the material close to the star but which was not incorporated in it. We show that the molecules that can be seen in such situations were until recently frozen-out as ices on the surfaces of dust grains.
- (ii) Many young stars have outflows in the form of well-collimated high-velocity jets that impact on nearby interstellar gas to create shocked regions. We show that these shocked regions illuminate and modify the chemistry of those regions. The characteristic chemistry arising enables us to describe the nature of the jet/cloud interaction in detail.
- (iii) Stellar jets widen into general outflows that encounter clumps of denser gas. The outflow from a massive star usually ionised. The interaction between such an outflow and a pre-existing clump creates a characteristic interface chemistry. We describe recent observations that appear to be the first detection of such an interface in a region in which massive stars are forming.

1. Introduction

The formation of stars is one of the most interesting and challenging topics in modern astronomy. Stars are formed deep inside very cold clouds of gas and dust in the interstellar medium. These clouds - or small parts of them, called dense cores - collapse under their own weight, and the gas density in them is strongly concentrated towards the centre of these cores. Eventually, the central parts of the collapsing core become dense enough for gravity to dominate even when hot enough for thermonuclear processes to begin, and a star is formed. The extinction caused by the dust in these cores is generally so high that we cannot observe optically what is happening, and the best approach is to study the radio emissions from molecules that are present in the gas, formed from *in situ* chemical processes. The emissions from these molecules arise from transitions in their rotational spectra.

In this article we shall review the nature and role of both interstellar dust and interstellar molecules in star-forming regions. We shall show that dust is not merely a passive component of the interstellar medium whose function is to extinguish starlight; the dust also has roles that are particularly important in star-forming regions, especially for the chemistry occurring in those regions. We shall describe in general terms the extensive range of molecular species that can be observed in interstellar space, and then we shall discuss the chemistry that gives rise to them. We shall note that the radiation emitted by the molecules by which they are detected is, in fact, a significant energy loss for a collapsing core in which the release of gravitational potential energy as heat would terminate the collapse. The role as coolants is essential for the star-formation process.

With this work as a foundation, we shall illustrate the application of chemistry to astronomy by considering several situations in star-forming regions where the chemistry plays an important role. We shall show that chemistry provides a key to understanding the evolving processes in star-forming regions and the dynamical events occurring there. Thus, a study of the microscopic, i.e. the atoms and molecules, informs us about the macroscopic, i.e. the large-scale gas flows that occur when a star is made.

2. Interstellar dust

The presence of dust in interstellar space is not easily apparent to the naked eye. The first indication of the presence of dust in the interstellar medium was an observation by Sir William Herschel in the 18th century of rich star fields that showed small regions in which there seemed to be an absence of stars. At the time, it was unclear whether this absence was apparent or real. We now know that these regions in which stars seem to be missing are foreground objects containing relatively large amounts of dust that obscures the light of stars behind them. Observations in the infrared, for example, reveal more of the star field than do the images at visual wavelengths (Fig. 1). In fact, there is a general rise in extinction as observations move across the spectrum from infrared, through the visual, to the ultraviolet. This suggests that a range of sizes of dust particles is present, since absorption by dust is usually more effective where the size of the dust particles and the wavelength are comparable.

Dust also scatters the light of stars, and if the dust cloud is close to a bright star the intensity of the scattered light may be large. Such an emission region is called a reflection nebula. Some of these are easily detectable by the naked eye (Fig. 2). Effective scatterers of optical light need to be of a size comparable to the wavelength.

Starlight is often found to be linearly polarized to a small degree. This is interpreted in terms of a differential extinction occurring in the interstellar medium. If the medium contains a population of partially aligned asymmetric dust grains of a size comparable with the wavelength of visible light, then one plane of polarization will be more heavily extinguished than the other. We infer that some of the grains must be asymmetric and capable of being aligned by an interstellar magnetic field, or by some other process.

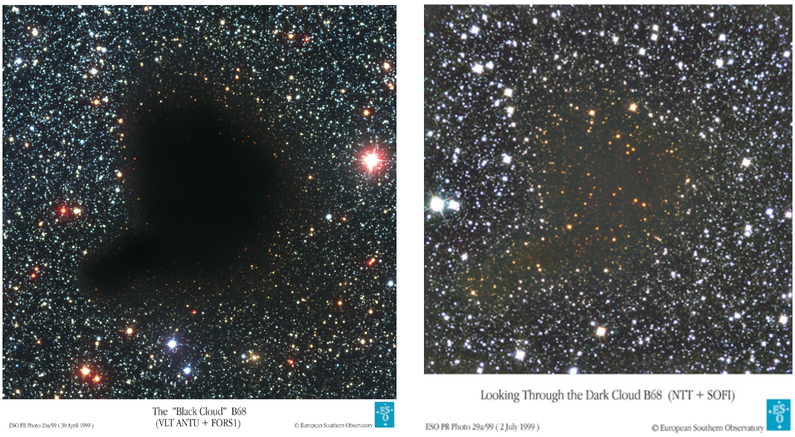


FIGURE 1. Molecular Cloud Barnard 68. The apparent absence of stars in the optical image (left panel) is shown to be incorrect by the infrared image (right panel). Optical image: Credit and ©FORS Team, VLT/ESO. Infrared composite photo: Credit and ©SOFI, NTT/ESO.

Energy from starlight absorbed by dust heats the grains and is then re-emitted thermally, at the temperature of the dust. This radiation is readily detected as a continuum emission. Figures 3 and 4 compare the optical absorption of the familiar Horsehead Nebula with the infrared emission coming from the dust grains in that region. Dust is not limited to the Milky Way Galaxy, but is easily detected in other galaxies (Fig. 5) where the dust extinguishes the light of central bright stars. Evidently, dust is a general phenomenon in the

FIGURE 2. The Pleiades star cluster. Starlight scattered from circumstellar dust creates the reflection nebulae seen around the brightest stars. Credit and ©Robert Gendler.

FIGURE 3. The Horsehead Nebula. ©Daniel Verschatse (Antilhue Observatory-Chile).

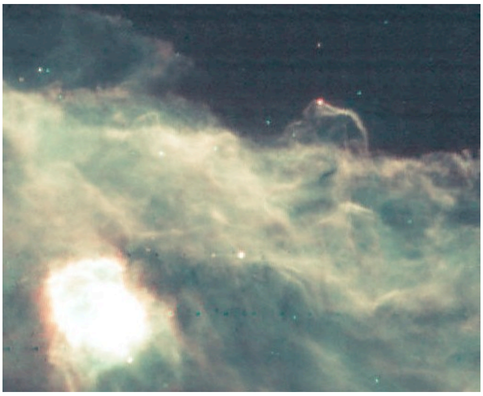


FIGURE 4. Horsehead imaged in infrared light by the European Space Agency's Infrared Space Observatory (ISO) satellite. This false-colour image shows the infrared emission from dust grains that cause the extinction shown in Fig. 3.

FIGURE 5. The Sombrero Galaxy from the Hubble Space Telescope. Dust in the central plane of this galaxy absorbs starlight and creates the dark equatorial band.

Universe, though its properties may vary from one galaxy to another. Further information about the physical and chemical nature of the dust is found in the emission and absorption lines associated with the dust (Figs. 6 and 7) and in the so-called depletions of the elements: the fact that elements present in the dust must be missing from the gas. This missing material is an inventory of the elements that make up the chemical nature of the dust. The depletions are different in different regions of interstellar space. However, in a typical line of sight through a molecular cloud of visual extinction approaching unity, about one half

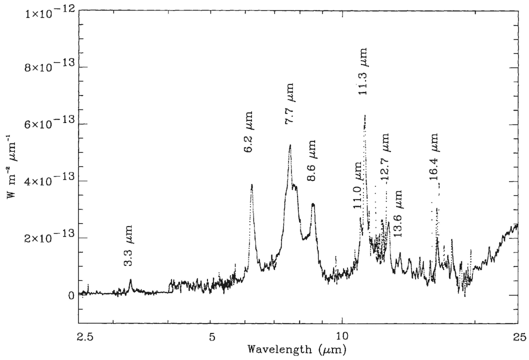


FIGURE 6. Infrared emission spectrum towards a hot star: the Short Wavelength Spectrometer spectrum of the reflection nebula NGC7023 (by the ISO satellite). The indicated peaks are currently unidentified (the so-called Unidentified Infrared Bands, or UIBs), but are characteristic of polycyclic aromatic hydrocarbons. Reproduced from [31] - ©ASP (Astronomical Society of the Pacific) Conference Series.

of the carbon, one tenth of the oxygen, and more than 90% of metals such as silicon are absent from the gas, and are - presumably - locked up in dust grains.

All of this information is combined to produce a model of interstellar dust. A conventional view of the physical and chemical nature of interstellar dust, based on all the evidence to date, is summarized in Box 1.

Further information on GEMS and on grains in primitive meterorites is given in Boxes 2 and 3.

Box 1

Interstellar dust

Distribution

- originates in cooler circumstellar gas
- is well-mixed with quiescent interstellar gas
- is less abundant or even absent from shocked very high temperature gas

Physical nature

- mainly dielectric material
- range of sizes is required, since extinction ranges from UV to IR
- models usually adopt a distribution of radii, a, to be $\mathrm{n(a)da} \sim \mathrm{a}^{-3.5}\mathrm{da}$ with $\mathrm{a_{min}}$ and $\mathrm{a_{max}}$ on the order of 10 nm and 1 micron, respectively
- at least some of the larger grains must by asymmetric and capable of partial alignment; models suggest some grains are oblate spheroids of axial ratio about $\sim 2:1$, and that alignment is caused by partial rotational dissipation in the interstellar magnetic field
- morphology is unknown, but see text

Chemical nature

- spectral features suggest that the material of dust grains includes silicates (both crystalline and amorphous) and amorphous carbons of varying degrees of hydrogenation
- grains in denser clouds become coated with molecular ices (see Table 1 and text)
- collected interplanetary particles contain unprocessed interstellar grains composed of glasses (i.e. amorphous silicates) with embedded metals and sulfides (GEMS)
- primitive meteorites contain diamond, graphite, silicon carbide, aluminium oxides, etc.

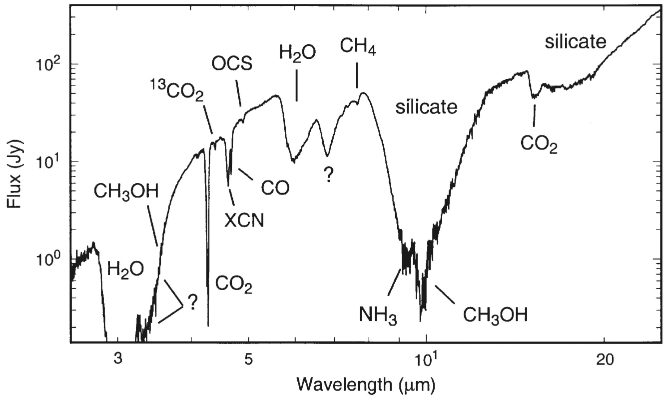


FIGURE 7. Infrared absorption spectra towards a star through a dense cloud: the Short Wavelength Spectrometer flux spectrum of the dust-embedded young stellar object W33A (by the ISO satellite). Solid-state features arising from molecules in the grains are indicated. Reproduced by permission of the American Astronomical Society from [32].

One of the least well-understood aspects of the nature of dust is its morphology. Some collected interplanetary particles - which may contain or have some relation to interstellar particles - have an open, porous nature (Fig. 8). It is difficult to compute the optical properties of such dust particles. Fortunately, the Transition Matrix formalism offers a very good and flexible approach to this problem allowing to build reliable models for dust particles and to study quantitatively their optical behaviour [1, 2].

Box 2

Interstellar GEMS

GEMS: Glass with Embedded Metals and Sulphides
Found in chondritic porous interplanetary dust particles
Embedded in a layer of amorphous carbon
Typical size ~ 0.5 microns
Silicate composition, absorptions at ~ 10 and ~ 20 microns
Contain FeNi and FeS inclusions that are ferromagnetic
Mg-rich and Fe-poor

Interstellar consequences of GEMS

Visual interstellar extinction
IR absorption features
Alignment of large grains for polarization
S, Mg, Fe depletions

We conclude that GEMS are a sample of unprocessed interstellar dust

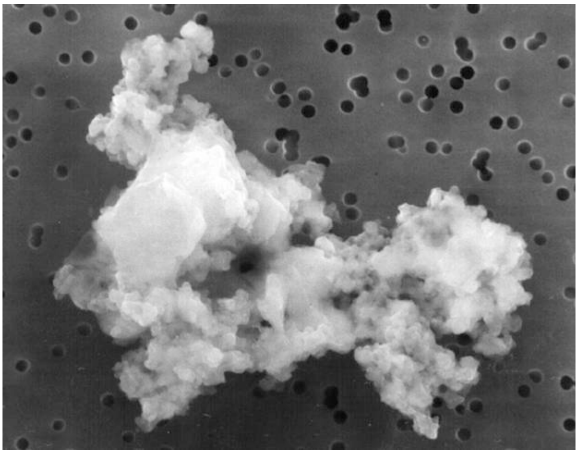


FIGURE 8. A collected interplanetary particle (a so-called Brownlee particle) showing a porous structure. Courtesy of NASA.

Box 3

Interstellar grains in meteorites

Primitive meteorites contain grains of:
diamond
graphite
SiC
Al_2O_3

Isotopic ratios indicate formation in circumstellar environments. These are interstellar grains.

Box 4

Interstellar features assigned to dust grain components

EXTINCTION
UV rise: small (nm) carbon grains
217.5 nm bump: carbons (individual or stacked PAHs)
Visual rise: GEMS, crystalline silicates, carbon grains and coatings
Infrared: carbon grains

Extended Red Emission (a broad red emission): nanoparticles, possibly of silicon, carbon
UIBs: PAHs; small (nm) carbon grains
Infrared absorptions: GEMS, crystalline silicates, ices (H_2O, CO, CO_2, CH_3OH,), saturated hydrocarbons, Hydrogenated Amorphous Carbon (HAC)

Box 5

Roles of interstellar dust

- Deplete elements from the gas
- Extinguish and polarize starlight;
  shield molecules in clouds from photo-dissociation
- Absorb and emit line radiation
- Heat interstellar gas by ejected photoelectrons
- Provide surfaces for heterogeneous catalysis
- Remove atoms and molecules from gas, making ices
- Allow ice processing by UV and fast particles,
  makes complex molecules
- Ices - a reservoir of molecules
- Radiation from cool dust traces cold gas,
  an important cooling mechanism in star forming regions
- Dust - the raw material for planet formation

The roles of dust in the interstellar medium are summarized in Box 4 and 5. Besides the obvious roles of interaction with electromagnetic radiation, the important roles for our present purposes are those that affect the chemistry of star-forming regions. These include the role that dust grains play in providing a surface on which gaseous atoms and molecules can stick, i.e. as a sink for gaseous species. The timescale for this process is typically around $10^9/n_\mathrm{H}$ years, where $n_\mathrm{H} = n(\mathrm{H}) + n(\mathrm{H}_2)$ is the total hydrogen number density in both atoms and molecules in units of number per cm^3. Thus, as density rises during the collapse of a core, the freeze-out timescale becomes shorter and shorter, so that in some regions almost all species (other than H, H_2, and He, which do not stick to the surfaces) are incorporated into molecular ices on the dust surfaces. Figure 9 [3] shows how, for one particular core, the amount of material lost from the gas increases to the centre.

Another important role of the dust depends on the presence of this molecular ice. Solid state chemistry can be induced to occur within this material by either UV photons or by fast particles, such as low energy cosmic rays. Table 1 shows the measured composition of ices along several lines of sight. Evidently, this composition varies widely, and this supports the view that chemical processing of ices is occurring. In fact, the presence in the ices of molecular species such as CO_2, $\mathrm{CH}_3\mathrm{OH}$, and $\mathrm{H}_2\mathrm{CO}$ are strong evidence for the efficiency of chemical processing, since these species cannot be made in the gas phase sufficiently to account for their high abundances in the ice.

A very thorough account of the properties and role of interstellar dust can be found at [4] and a shorter description at [7].

3. Interstellar molecules

In this article we are concerned with molecules in star-forming regions, but it is important to realise that molecules are widespread in the Universe. In star-forming regions, the gas is almost entirely molecular, and its properties are controlled by the molecules. But molecules are present, even if not dominant, in a wide variety of environments in the Universe. Table 2 lists those types of astronomical region where molecules are found. In

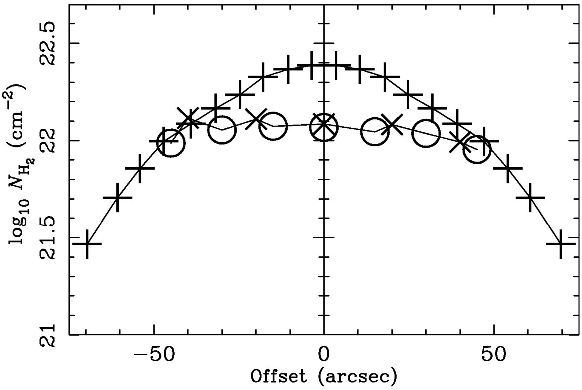


FIGURE 9. Column densities across the pre-stellar core L1689B, measured using the $C^{17}O$ $J = 2 \rightarrow 1$ transition (crosses), $C^{18}O$ data of Jessop & Ward-Thompson [5](circles), and the SCUBA 850-micron radial profile fits of Evans et al. [6] (pluses). This figure shows that molecules of CO are depleted from the gas in the central region of this core, evidently by sticking to the surfaces of interstellar grains. Reproduced by permission of the Royal Astronomical Society from [3].

TABLE 1. An inventory of interstellar ices, given in the lecture by G. A. Blake to the 2006 Nobel Symposium 133. Abundances are expressed as percentage of the H_2O abundance. HH46 is a region of low-mass star formation - a typical molecular cloud; W33A is a region of high-mass star formation; Hale-Bopp is a comet.

	HH46	W33A	Hale-Bopp
H_2O	100	100	100
CO	20	1	23
CO_2	30	3	6
CH_4	4	0.7	0.6
H_2CO	-	2	1
CH_3OH	7	10	2
HCOOH	2	0.5	0.1
NH_3	9	4	0.7
OCS	-	0.05	0.4

general, nearly any region that is not too hot (with temperature less than about 4000 K) and not too tenuous (with density such that there is at least 1 hydrogen atom per cm^3) will exhibit at least some molecules. Since higher-density regions contain most of the non-stellar baryonic mass in the Universe, much of this mass is molecular. For example, most of the

TABLE 2. Where are molecules found?

Interstellar clouds and star-forming regions
circumstellar discs around young stars
cool envelopes around giant stars
stellar atmospheres of relatively cool stars
sunspots
planetary atmospheres
comets and asteroids
ejecta of novae and supernovae
many other galaxies, at least out to a redshift of about 6
the very Early Universe
associated with dust
in ices on dust

TABLE 3. Elemental abundances in the Sun.

H	1
He	8.5×10^{-2}
C	2.5×10^{-4}
N	6.0×10^{-4}
O	4.6×10^{-4}
Mg	3.4×10^{-5}
Si	3.2×10^{-5}
S	1.4×10^{-5}

volume of interstellar space in the Milky Way Galaxy is hot, ionised and molecule-free, but most of the mass of interstellar gas is in the cooler denser parts which occupy a tiny fraction of the whole volume. This cool and dense gas is, of course, the reservoir of matter from which new stars can form. The gas is mainly hydrogen. The elements responsible for forming most of the molecules are a minor component of the gas in the Universe. Table 3 lists the abundances of several elements relative to hydrogen, for the Sun; these are sometimes taken as a standard for the Milky Way, but there are considerable variations from place to place in the Galaxy, not least because of the proportions of some elements that have been incorporated into dust grains (see Section 2). Of course, other galaxies tend to have different elemental abundances.

We show some images of molecular-rich gas in the Milky Way Galaxy: an interstellar cloud (Fig. 10); a dense core within which a low-mass star has formed and has generated an outflow emerging from the core (Fig. 11); molecular-rich gas emerging from a star (Fig. 12); gas ejected from an evolved star and illuminated by it (Fig. 13); molecular discs around young stars that are potential sites of planet formation (Fig. 14); and a comet in our own solar system (Fig. 15).

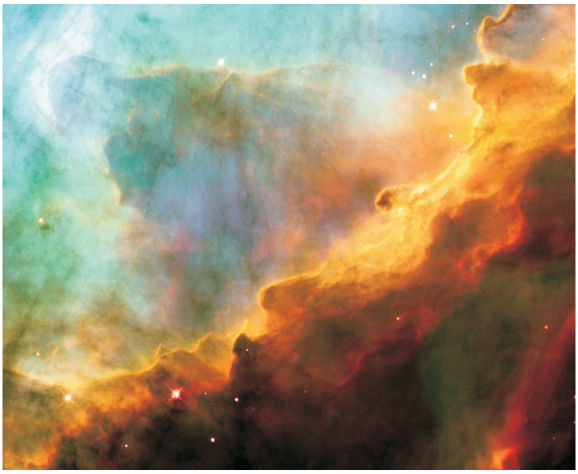


FIGURE 10. M17: A Hubble Close-Up. The picture spans about 3 light-years and was released in the thirteenth year of the Hubble Space Telescope's cosmic voyage of exploration. The figure shows the edge of a large molecular cloud that is being eroded by the radiation and winds of nearby hot stars. Credit: NASA, ESA, J. Hester (Arizona State University).

Interstellar molecules appear in great variety; about 130 different molecular species have been identified; a list appears in Table 4 and an up-to-date list is maintained at the following website: www.cv.nrao.edu/∼wootten/allmols.html. The list is striking in that many of the molecules contain carbon, reflecting that element's remarkable ability to form chemical bonds of various types so that the wealth of organic chemistry is opened up. The detected species are relatively small; the largest known contains only 13 atoms. Some of the species are familiar, but many are highly unsaturated (i.e. poor in hydrogen), and some of these were discovered first in space and later synthesized in the laboratory for confirmation. The list contains species that are radicals, i.e. with unsatisfied valencies and which on Earth would have only a fleeting existence. There are some molecular ions (H_3^+, HCO^+, HCS^+, N_2H^+,etc.), and they give a clue to the type of chemistry that generates these molecules. It is clearly unlike any familiar chemistry on Earth.

What is the chemistry that gives rise to this range of molecules? We note that the physical conditions in much of the interstellar gas are very different to those in the Earth's atmosphere, for example. The number densities are generally in the range of $\sim 10^2$ - $\sim 10^4$ hydrogen atoms per cm^3 (compared to several x $10^{19}\mathrm{cm}^{-3}$ molecules in the air we breathe) and the temperature is generally in the range $10 - 100$ K, although some warmer regions exist. Thus, gas phase chemistry on Earth generally occurs in 3-body interactions in which a third body carries away energy that would otherwise de-stabilise the product molecule

$$\mathrm{A + B + C \rightarrow X + Y + C} \tag{1}$$

FIGURE 11. Molecular cloud BHR 71. A newly-formed star inside this cloud has developed bipolar jets; only one of these points towards us and is visible, the other is embedded within the dense gas. Credit & ©: J. Alves (ESO), E. Tolstoy (Groningen), R. Fosbury (ST-ECF) & R. Hook (ST-ECF), VLT/ESO.

Such reactions can be very efficient in forming products X and Y from reactants A and B. However, in the interstellar gas, 3-body reactions do not occur because the densities are far too low, and the interacting atoms normally bounce off each other without reacting to form a new product

$$\mathrm{A} + \mathrm{B} \rightarrow \mathrm{AB}^* \rightarrow \mathrm{A} + \mathrm{B} \tag{2}$$

The interaction complex, AB^*, must lose some energy if the molecule AB is to remain bound. It can do this by radiating (usually a relatively inefficient process), by giving some energy to a third body such as another atom or to a surface; i.e.

$$\mathrm{A} + \mathrm{BC} \rightarrow \mathrm{AB} + \mathrm{C} \tag{3}$$

in which the exchange reaction between an atom A and a molecule BC gives a product molecule AB while atom C carries away the stabilization energy, or

$$\mathrm{A} + \mathrm{B}{-}\mathrm{grain} \rightarrow \mathrm{AB} + \mathrm{grain} \tag{4}$$

where the grain acts as a sink for the energy, which it subsequently radiates away.

Much of interstellar chemistry depends on exchange reactions of type 3. However, neutral exchange reactions at the very low temperatures of interstellar space can be impeded by small barriers in the reaction path. If one of the reactants is charged, then the ion-neutral reaction

$$\mathrm{A}^+ + \mathrm{BC} \rightarrow \mathrm{AB}^+ + \mathrm{C} \tag{5}$$

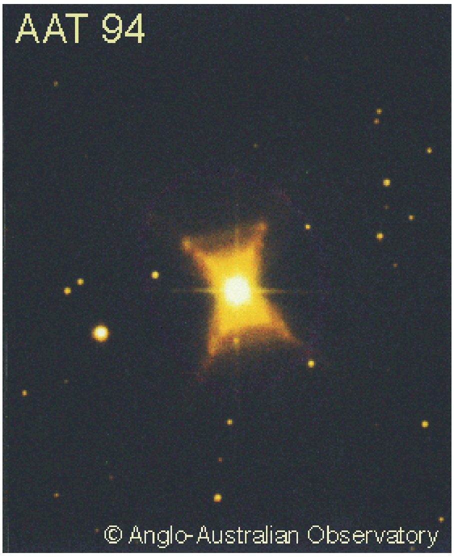


FIGURE 12. The Red Rectangle. The central star is actually a binary. One of these stars ejects an extended envelope that is illuminated by the other star. The nebula is confined by a disk around both stars. ©Anglo-Australian Observatory/David Malin Images.

is often barrier-free. Reaction 5 results in the creation of a new molecular ion, AB^+, which may either undergo further reactions of type 5 or stabilize in recombination reactions with electrons.

So what is needed to drive interstellar chemistry is a source of ionisation. There are two possibilities: photoionisation by UV radiation from stars, e.g.

$$\mathrm{C} + \mathrm{photon} \rightarrow \mathrm{C}^+ + e \tag{6}$$

or collisional ionisation by fast particles, the cosmic rays (the most effective of which are protons of around $1MeV$ in energy)

$$\mathrm{H} + \mathrm{c.r.} \rightarrow \mathrm{H}^+ + e \tag{7}$$

The ionisation of H_2 is quickly followed by an ion molecule reaction with another H_2 molecule to create a new ion, H_3^+

$$\mathrm{H_2} \rightarrow \mathrm{H_2^+}; \quad \mathrm{H_2^+} + \mathrm{H_2} \rightarrow \mathrm{H_3^+} + \mathrm{H} \tag{8}$$

and this stable ion is responsible for driving much of the chemistry; for example

$$\mathrm{H_3^+} + \mathrm{C} \rightarrow \mathrm{CH^+} + \mathrm{H_2} \tag{9}$$

$$\mathrm{CH^+} + \mathrm{H_2} \rightarrow \mathrm{CH_2^+} + \mathrm{H} \tag{10}$$

$$\mathrm{CH_2^+} + \mathrm{H_2} \rightarrow \mathrm{CH_3^+} + \mathrm{H} \tag{11}$$

$$\mathrm{CH_3^+} + \mathrm{O} \rightarrow \mathrm{HCO^+} + \mathrm{H_2} \tag{12}$$

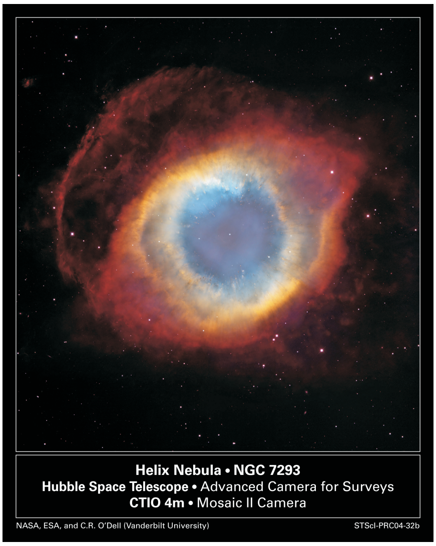


FIGURE 13. The Helix Nebula. An extended envelope of gas and dust, ejected at an earlier phase of evolution of the star, is now being irradiated by the central star that has become hot and bright. Photo by the orbiting Hubble Space Telescope and the 4-meter Blanco Telescope in Chile.

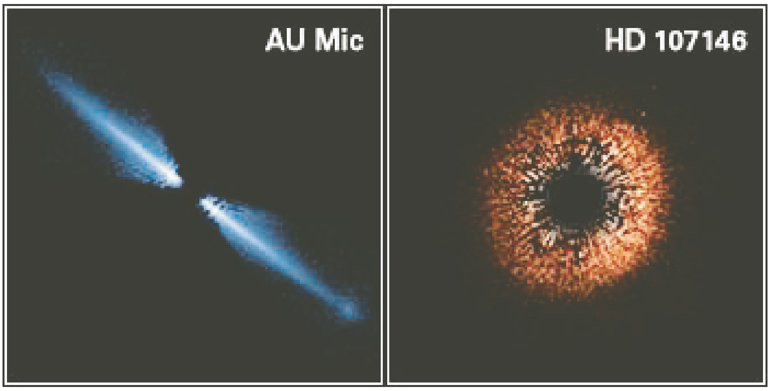


FIGURE 14. Debris Disks Around Sun-Like Stars AU Microscopii and HD 107146. These disks are potentially the sites of planet formation. Credit: NASA, ESA, STScI (Space Telescope Science Institute).

in which HCO^+, a widely observed species, is formed as a result of this sequence of ion-molecule reactions. Reactions of this molecule with H_2 do not occur, and so it usually recombines dissociatively with electrons to make CO, a very abundant molecule

$$HCO^+ + e \rightarrow CO + H \tag{13}$$

FIGURE 15. The Dust and Ion Tails of Comet Hale-Bopp. The tails are created by the erosion of the dusty ice nucleus of the comet by the radiation and wind of the Sun. Credit & ©John Gleason (Celestial Images).

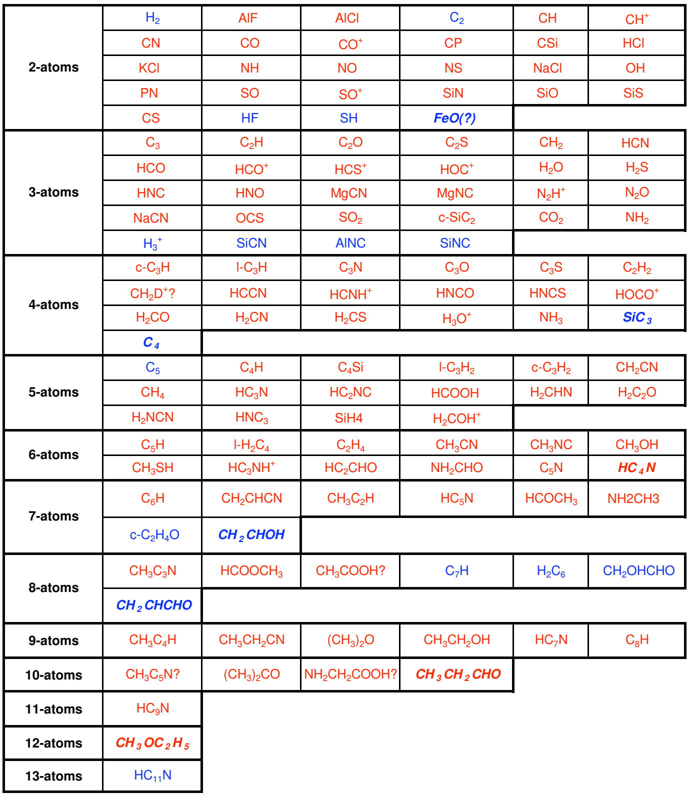
A list of all the types of gas-phase reaction commonly occuring in the interstellar medium is shown in Table 5.

It is evident from these examples that to make molecules such as HCO^+ and CO we need to start with H_2 molecules. How are they made? It turns out that, under the conditions of interstellar space, gas phase reactions are too inefficient to account for the very high abundances of H_2 that are seen in dark clouds such as those illustrated in Figs. 10 and 11. It is now confirmed by laboratory experiments and by fundamental theory that H_2 is formed by reactions of type 4, above, in which both A and B are hydrogen atoms. Further, the H_2 molecules are formed in excited kinetic and rovibrational states. It is also clear that other molecules form in similar reactions and contribute to the gas-phase network. Where the rate of reaction on the surface of dust grains exceeds the rate of desorption of the product molecule, then the excess molecules (principally H_2O ice) accumulate, together with molecules sticking to the grains to form complex molecular ices (see Fig. 7).

In practice, reactions networks describing interstellar chemistry may be rather large and involve hundreds or even thousands of reactions. Compilations of these reactions and their rate coefficients (measured, calculated, or estimated) are available (see the UMIST database website http://www.udfa.net/).

However, it is not sufficient to develop computer models of interstellar chemistry without regard for the dynamical or other timescales affecting the region. In many cases, the

TABLE 4. Molecules found in interstellar clouds of various sorts. Molecules in red have been found in Comet 1995 O1 Hale-Bopp. H_2O^+ and C_2H_6 are seen in the Comet but not in Interstellar Clouds. Molecules in italic have been detected very recently. Reproduced from: www.cv.nrao.edu/∼wootten/allmols.html



2-atoms	H_2	AlF	AlCl	C_2	CH	CH^+
	CN	CO	CO^+	CP	CSi	HCl
	KCl	NH	NO	NS	NaCl	OH
	PN	SO	SO^+	SiN	SiO	SiS
	CS	HF	SH	***FeO(?)***		
3-atoms	C_3	C_2H	C_2O	C_2S	CH_2	HCN
	HCO	HCO^+	HCS^+	HOC^+	H_2O	H_2S
	HNC	HNO	MgCN	MgNC	N_2H^+	N_2O
	NaCN	OCS	SO_2	c-SiC_2	CO_2	NH_2
	H_3^+	SiCN	AlNC	SiNC		
4-atoms	c-C_3H	l-C_3H	C_3N	C_3O	C_3S	C_2H_2
	CH_2D^+?	HCCN	$HCNH^+$	HNCO	HNCS	$HOCO^+$
	H_2CO	H_2CN	H_2CS	H_3O^+	NH_3	***SiC_3***
	C_4					
5-atoms	C_5	C_4H	C_4Si	l-C_3H_2	c-C_3H_2	CH_2CN
	CH_4	HC_3N	HC_2NC	HCOOH	H_2CHN	H_2C_2O
	H_2NCN	HNC_3	SiH4	H_2COH^+		
6-atoms	C_5H	l-H_2C_4	C_2H_4	CH_3CN	CH_3NC	CH_3OH
	CH_3SH	HC_3NH^+	HC_2CHO	NH_2CHO	C_5N	***HC_4N***
7-atoms	C_6H	CH_2CHCN	CH_3C_2H	HC_5N	$HCOCH_3$	NH2CH3
	c-C_2H_4O	***CH_2CHOH***				
8-atoms	CH_3C_3N	$HCOOCH_3$	CH_3COOH?	C_7H	H_2C_6	CH_2OHCHO
	CH_2CHCHO					
9-atoms	CH_3C_4H	CH_3CH_2CN	$(CH_3)_2O$	CH_3CH_2OH	HC_7N	C_8H
10-atoms	CH_3C_5N?	$(CH_3)_2CO$	NH_2CH_2COOH?	***CH_3CH_2CHO***		
11-atoms	HC_9N					
12-atoms	***$CH_3OC_2H_5$***					
13-atoms	$HC_{11}N$					

timescales for dynamical events such as the gravitational collapse of a cloud in the process of star formation will be comparable to or shorter than the timescale for the chemistry to reach a steady-state. Time-dependent models that account for physical changes are usually required for computational studies of star-forming regions. Table 6 lists some of the timescales that need to be considered. It is important to notice that these timescales are comparable. Therefore, it is often necessary to include in any model not only the chemical kinetics but also the relevant dynamics, the thermal balance equations, the gas-dust interaction, and in some circumstances the magnetic support that is constrained by ambipolar diffusion. The thermal balance occurs between heating mechanisms (input from starlight; ionisation by cosmic rays; gas dynamics) and cooling mechanisms (thermal emission from dust grains; molecular emissions in rotational transitions). For example, the lowest two

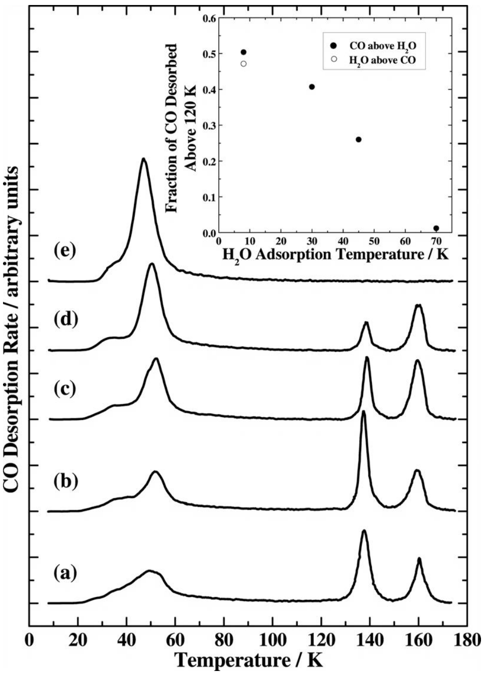


FIGURE 16. Temperature programmed desorption of CO (0.07 $\mu\mathrm{g\,cm^{-2}}$) from H_2O (57 $\mu\mathrm{g\,cm^{-2}}$). Trace *a* for H_2O adsorbed over CO, both adsorbed at 8 K; traces *b–e* for CO adsorbed at 8 K over H_2O adsorbed at 8, 30, 45, and 70 K, respectively. *Inset*: Fraction of the integrated area of desorption traces *a–e* attributable to trapped CO, as a function of H_2O adsorption temperature. Reproduced by permission of the American Astronomical Society from [14].

TABLE 5. Gas-phase reaction in astrochemistry.

Cosmic ray ionization: $\mathrm{H} + \mathrm{c.r.} \rightarrow \mathrm{H^+} + \mathrm{e^-}$
Photoionization: $\mathrm{C} \rightarrow \mathrm{C^+} + \mathrm{e^-}$
Photodissociation: $\mathrm{CH} \rightarrow \mathrm{C} + \mathrm{H}$
Charge exchange: $\mathrm{H^+} + \mathrm{O} \rightarrow \mathrm{H} + \mathrm{O^+}$
Atom exchange: $\mathrm{O^+} + \mathrm{H_2} \rightarrow \mathrm{OH^+} + \mathrm{H}$
Radiative association: $\mathrm{CH_3^+} + \mathrm{O} \rightarrow \mathrm{HCO^+} + \mathrm{H_2}$
Recombination: $\mathrm{H_3O^+} + \mathrm{e^-} \rightarrow \mathrm{H_2O} + \mathrm{H}$

rotational levels of CO are at an energy equivalent to about 5 K apart. Therefore, even in cold molecular clouds, collisions of CO with H_2 may excite the upper rotational level. The CO molecule radiates spontaneously, cools the gas, and is available to be re-excited. This

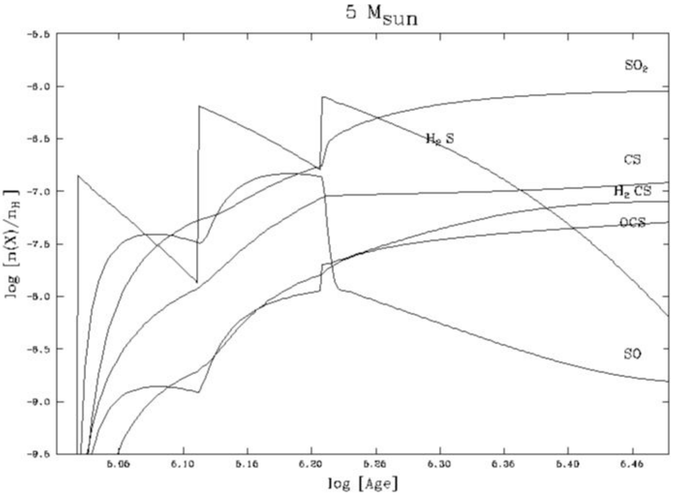


FIGURE 17. Time evolution of hot core chemistry for a dense core illuminated by a five solar mass star. Reproduced by permission of the Royal Astronomical Society from [16].

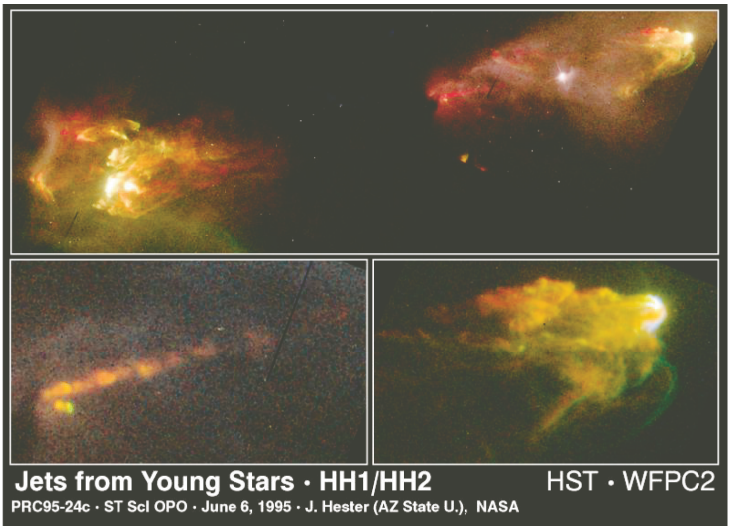


FIGURE 18. Star Jets. This Hubble Space Telescope image shows two nebulosities at the ends of opposing jets from a young star.

particular transition in CO is one of the most important cooling transitions in interstellar clouds.

TABLE 6. Timescales in the interstellar medium.

	Timescales (y)
Chemistry	3×10^5
Collapse	10×10^5
Cooling	3×10^5
Freeze-out	3×10^5
Ambipolar diffusion	4×10^5

Assuming $n_H = 10^4 \mathrm{cm}^{-3}$

TABLE 7. Typical physical parameters of hot cores.

Small: $10^{-1} - 10^{-2}$ pc
Dense: $>\sim 10^7 \mathrm{H}_2 \ \mathrm{cm}^{-3}$
Warm: $>\sim 10^2$ K
Opaque: $A_V > 10^2$ mag
Transient: $<\sim 10^5$ y
Location: < 0.1 pc from star

Interstellar chemistry is well reviewed in the books by Duley & Williams [8], Dyson & Williams [9], Hartquist & Williams [10], and by Tielens [11].

4. Applications of astrochemistry to the study of star-forming regions

In this section we shall describe some recent work on regions of high mass star formation, on the interaction of stellar jets from young stars with molecular clouds, and on the dynamical interaction between outflows of hot ionised gas from stars with the cold molecular gas from which the stars were formed.

4.1. Dense gas near very young stars. In the collapse of a core to form a star, not all the material in the core becomes incorporated into the star. As soon as the star begins to radiate and to generate an outflow, the continuing infall of material from the core on to the star will be inhibited and eventually arrested. Therefore, dense material that was in the collapsing core is now located close to a star of rapidly increasing intensity. Of course, it cannot survive very long in such a location. Its temperature and pressure rise because of the stellar radiation, and stellar winds will erode it. Nevertheless, such situations survive for long enough for us to be able to observe them, and in them we find a chemistry that is anomalous when compared to lower density clouds in which star formation is not occuring. These regions are given the name "hot cores" since they are considerably warmer ($\sim 200 - 300$ K) than the normal temperature of dark clouds, ~ 10 K. Their typical observed physical properties are summarised in Table 7, and the characteristic chemistry that they show is summarized in Table 8 [12, 13]. Why are these objects of interest? What can they tell us?

TABLE 8. Hot cores: resulting chemistry.

The long low-temperature collapse promotes:
Hydrogenation:
e.g., formation of NH_3, CH_4, etc.
Fractionation:
e.g., insertion of D for H to make NH_2D, NHD_2, and even ND_3
e.g.,insertion of 13C for 12C in CO, and other isotopic changes
Solid state chemistry:
e.g., conversion of CO to CH_3OH,
formation of complex species such as C_2H_5OH, CH_3COOH, $(CH_3)_2O$

When the star begins to radiate and the dust grains in the hot core begin to warm up, the ices that have accumulated on their surfaces during the long slow collapse that formed the star evaporate. These are the molecules that we observe in the hot core. These molecules formed by gas phase reactions during the collapse, frozen on to the grain surfaces, and in some cases underwent a solid state chemical processing. Therefore, the nature of the molecules tells us something about the physical conditions during the collapse process. The molecules we detect in the gas phase reflect the speed of the warming of the dust; some molecules desorb earlier than others, so we should be able to use the chemistry to describe the speed of warming - which is related to the speed of warming of the star itself.

In fact, the desorption of ices of mixed composition during warming from very low temperatures is a complex process that has only recently been studied in the laboratory. Figure 16 [14] shows the desorption flux from a mixed amorphous ice of CO in H_2O that has been prepared in various ways, as the ice is warmed from about 10 K to about 200 K. All the curves show a similar structure that arises because the CO molecules are in different sites in the ice. The CO molecules may be attached directly to H_2O molcules in the ice; they may be in multilayers of pure CO; they may be trapped in cavities within the amorphous ice and released only when the ice becomes crystalline; and finally any CO trapped in cavities within crystalline ice is released only when the ice itself evaporates. In fact, molecules of all types share some or all of these charactistics, and their behaviour with respect to desorption can be studied similarly to that of CO, or estimated [15].

Assuming that interstellar ices formed in the collapsing cloud are also mixed and amorphous then similar effects can be expected in the hot core chemistry. Figure 17 shows the predicted chemical behaviour for some species in a hot core heated by a 5 solar mass star [16]. The stepped behaviour of H_2S arises because that molecule behaves rather like CO in a mixed ice; some of the H_2S desorbs at several temperatures. Such structure has not yet been observed in any hot core. But in principle it offers a way of measuring directly the temperature rise in a hot core through the chemistry.

Emissions from hot cores are very strong in the millimetre and submillimetre wavelength range in the Milky Way Galaxy. Such emissions are likely to be very powerful in galaxies that have much higher star-forming rates, i.e. in starburst or colliding galaxies. In fact, the emissions should be so powerful that we should be able to detect them in galaxies at very high redshift. This means that we should be able to probe, through the inferred chemistry, the elemental abundances in the gas that give rise to the hot cores. In effect, this means probing the previous generation of stars that provided the "heavy" elements of carbon, nitrogen, oxygen, etc. So through chemistry we should be able to say something about the thermonuclear models of some of the very earliest stars in the Universe. Theoretical studies indicates that molecules such as CO, CH_3OH, H_2S, SO, SO_2, and H_2CO should be detectable with the largest radio telescopes currently available at a red-shift of 6, and with new technology now being built this should be straightforward [17].

4.2. Stellar jets and their impact on interstellar clouds. It is a remarkable yet well-established fact that many young stars of modest mass have associated with them powerful and well-collimated jets (Fig. 18) The processes that initiate these jets are still unclear, but are most likely related to the magnetic fields and angular momentum of the star. These jets are of fast particles which have velocities on the order of 100 km s^{-1}. The jets may travel considerable distances through the interstellar medium before they encounter a molecular cloud. The impact of the jet on the cloud creates a strong shock behind which the gas is fully ionised and radiates strongly in the visual region of the spectrum. These radiating regions are known as Herbig-Haro objects (HHOs), after the two astronomers who studied these objects most intensively. The HHOs can create a source of radiation in a molecular cloud which would otherwise be dark [18].

Radio observations in the vicinity of many HHOs have demonstrated the presence of molecular clumps, detected first in strong lines of HCO^+ and NH_3 but subsequently in lines of many other molecules [19, 20, 21, 22]. However, the chemistry is not that expected for a quiescent region. These radio lines are narrow, implying that the molecules have not been shocked, so what is it that has caused an anomalous chemistry to appear? The HCO^+ lines are important in that it is generally difficult to make large abundances of this ion; since the presence of more ions implies more electrons and faster recombination.

A model has been suggested in which the HHO acts as a powerful source of radiation in a regions that should otherwise be dark. If this radiation impinges on a dense core within the cloud, then it may act to desorb the ices that will be present on the grains, and to promote a photochemistry which produces a variety of molecular species (Fig. 19). This model has now been tested observationally and theoretically, and found to be satisfactory [23].

The HCO^+ is believed to arise from the desorption of CO molecules from the ices (along with H_2O and NH_3); the CO is dissociatively ionized and the resulting C^+ ions react with water molecules in the gas to give HCO^+. A wide range molecules not normally enhanced in molecular clouds (including CH_3OH, H_2S, C_3H_4, H_2CO, SO, SO_2, H_2CS, and NS) is also produced by this kind of photochemistry, and these species have also been detected in the environments of HHOs [24].

Is this simply an interesting but unimportant aspect of astrochemistry? No; we can learn from these observations, guided by the models, about the molecular clouds where these interactions take place. Firstly, the HHOs are a probe of molecular clouds. They act as a "searchlight", identifying the denser clumps where grains are coated with ice. By using the data in a statistical sense we can discover the clumpiness of molecular clouds. This is an important parameter, since clumpiness is related to the star-forming propensity of molecular clouds. The intensity of the HHO radiation is a measure of the shock which

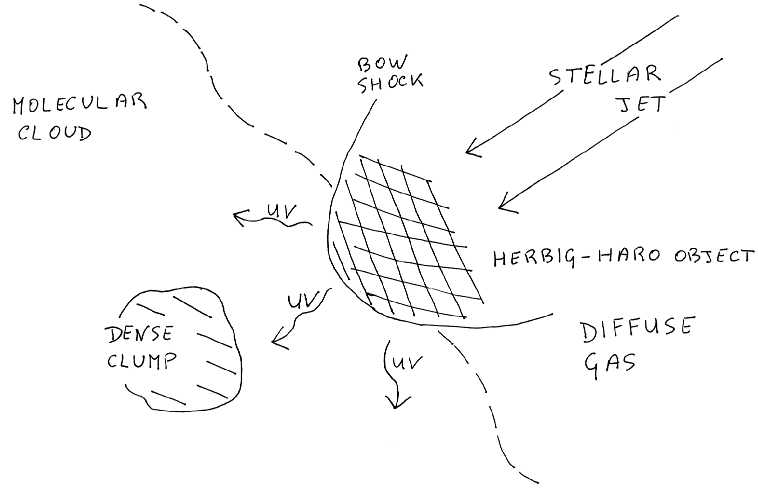


FIGURE 19. A schematic diagram indicating the interaction of a stellar jet with a clumpy molecular cloud.

itself is determined by the velocity of the jet; so the velocity of the stellar jet can also be determined.

4.3. Interfaces between stellar winds and dense core gas. All young stars have outflows which may or may not be collimated into jets. Young stars are still to a large extent embedded in the dense core from which they were formed. Thus, the outflow has to force its passage through the dense core until it reaches lower density gas that does not impede the outflow significantly. The passage of a fast gas past a slow one is a situation in which a turbulent interface is likely to arise. The turbulence introduces a mixing of the two fluids with a size scale on the order of 10% of the size of the outflow diameter.

In the case of a stellar outflow close to the star, the gas is ionised while the gas in the dense core is almost entirely neutral. Therefore, the result of turbulent mixing of the gases is in part to increase abruptly the level of ionisation of the molecular gas. As we have seen, above, it is the ionisation that drives the chemistry, so we expect that this mixing may produce a chemical signature of the mixing zone which advertises the fact that mixing is occurring. Chemical models have explored this new type of environment and have predicted the range of molecules that should be observable [25, 26, 27, 28].

Recently, observations [29] of a star-forming region have been made in which an extended feature is found to exist in the lines of several species (H_2CS, OCS, CH_3OH, and HDO) but to be absent in the lines of conventional tracers of star-forming regions H_2S, SO_2, SO, and CS (Fig. 20). The feature is large enough that it seems unlikely to be a hot core - since a hot core is usually compact. In any case, the chemistry exhibited by this object is not like that of a hot core.

It may, however, be an interface between the outflow from the star and the dense core from which the star was formed. It is possible to find agreement between the interface model and the observations of this feature, but for this to be possible the ice originally on the dust grains in the dense core gas must have a significant amount of sulfur in the form of OCS. While it is known that OCS can be a component of interstellar ices (Table 1), it is a surprise to find this prediction that a significant fraction of sulfur must be in this form in the ices.

However, perhaps it is not so unreasonable. It is known that CO_2 is an abundant component of interstellar ice, even though it is absent from the gas in cold clouds. It is assumed, therefore, that CO_2 is formed by solid state chemical processing of CO (which is abundant

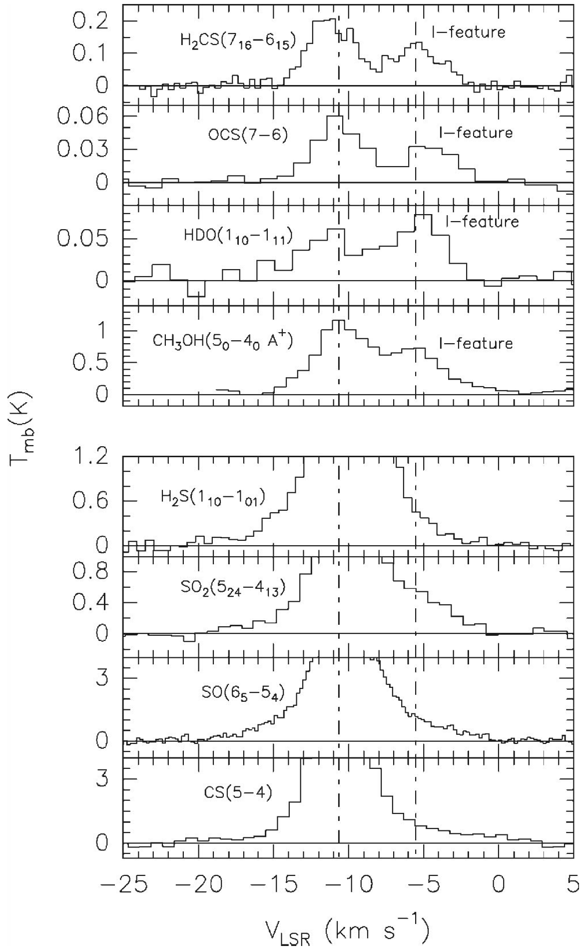


FIGURE 20. Spetra of various molecules detected towards the star-forming region Cepheus A. In the top four spectra an additional peak, denoted I-feature, is evident. It is absent from the lower four spectra. The I-feature is emission from the suspected interface. Reproduced by permission of the American Astronomical Society from [29].

in the gas and ice) into CO_2 by a reaction such as $CO + OH \rightarrow CO_2 + H$. Here, the OH arises from water molecules. If H_2S is abundant in the ices, the reaction of SH and CO should similarly produce OCS, since S and O are chemically similar. These speculations are currently about to be tested by observations of the chemistry in the supposed interface.

The result of this study is that we understand better the nature of dynamical mixing through chemical tracers of the process, and of the evolving chemistry of ices on dust grains in the gas.

5. Conclusions

The more one considers the role of chemistry in astronomy, the more one becomes persuaded that molecules are playing an important role. It is not merely that the chemistry produces molecules that by their emissions allow us to trace interstellar in a variety of situations. The radiation emitted by molecules is a major energy loss of gas at low temperatures and this cooling ability of molecules is the physical property that allows the formation of galaxies and stars. In the early Universe, some 300000 years after the Big Bang, molecules of hydrogen were present and allowed the formation of the first structures, from which galaxies emerged [29]. Within those structures, the first stars formed, thanks again to molecular hydrogen, and from those stars the Universe was seeded by heavy elements of carbon, nitrogen, oxygen, etc. so that a more complex chemistry gave rise to a new set of coolants, notably carbon monoxide. As we have seen from the few examples in Section 4, molecules play an interesting and important role in many aspects of star formation in galaxies, but perhaps the most important role is in the formation of dusty molecular disks around young stars. From these disks planetary systems emerge, and the dust, the ices they carry and the gas are all the feedstock from which planets are forming [33]. In this sense, one might argue that chemistry plays a fundamental role in the evolution of the Universe.

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