

## DISCOVERING INTERSTELLAR MOLECULES

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**Abstract.** This paper describes how high resolution spectroscopy has been the key for discovering interstellar molecules and for studying the interstellar medium. The development of radioastronomy in the 1950's has led to the detection of many interstellar molecules in the 1960s and 1970s, and the construction of a new field of research, astrochemistry. The discovery of molecular ions has confirmed the important role of ion-molecule gas phase reactions in interstellar chemistry. Infrared spectroscopy, from the ground and from space, has contributed by enabling an extensive inventory of ice mantles, revealing the complex chemical processes in the solid phase, and for the detection of symmetric species. The field is now mature, and prospects look extremely good with the construction of ALMA starting, and with the Herschel launch expected in the coming years

### 1 The early years : discovery of the interstellar medium and of the first interstellar molecules

The presence of diffuse matter in the space between the stars has been first discussed in the very beginning of the XX<sup>th</sup> century by Hartmann (1904). He describes the detection of a “fixed line”, identified as the calcium K line, in the  $\delta$  Orionis spectrum. The line appears to be weak and narrow, and with a fixed velocity relative to the Sun. Because of the difference in line

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shape and velocity compared to the other stellar lines, he proposed that this Ca line was not associated with the star, but produced in the interstellar medium. Hartmann himself had already detected “fixed” Ca lines in the spectrum of Nova Persei a few years ago. Studies of interstellar Ca and Na lines (and other) steadily developed in the 1920s (e.g. Struve 1927,1928), showing the ubiquitous presence of absorbing material and its association with the Galaxy.

A few years later, imaging surveys conducted by Barnard and others, led to the first catalogues of dark clouds (so-called Barnard’s clouds today) (e.g. Barnard 1919). While it was immediately realized that some obscuring matter was causing these “dark markings in the sky” rather than their being empty places in space, it took longer to identify the particles responsible for the obscuration. Dust grains are now identified as responsible for extinction and scattering. While at that time, atoms and ions had been identified by visible spectroscopy, Eddington (1926,1937) discussed the possibility of forming molecules in the interstellar medium. He considered species based on H, O and N, because they remain neutral in clouds where hydrogen is neutral, and where no photons with energy greater than 13.6 eV can penetrate. Eddington further proposed that, because of the low temperature due to the absence of ionizing radiation, molecules could coagulate, especially water, and form water ice. Nearly simultaneously, new weak interstellar bands were found in stellar spectra. Merrill (1937) reported the discovery of “diffuse interstellar bands (DIBs)”, at  $\lambda 5780$ ,  $\lambda 5797$ ,  $\lambda 6278$  and  $\lambda 6284$  Å. The word diffuse was given because the bands are broader than interstellar atomic lines. These bands were immediately attributed to molecules by Russell (1935). At that time, molecules had already been identified in cometary (comet Halley) and planetary atmospheres spectra. The discussion on the carrier(s) of these DIBs is still vivid, but more and more clues converge toward attributing them to molecules (see e.g; Galazutdinov et al. 2005) ! The presence of molecules in the diffuse interstellar medium was established by the detection and identification of CH (Dunham 1937; Swings & Rosenfeld 1937), CN (Mc Kellar 1940; Adams 1941) and CH<sup>+</sup> (Douglas and Herzberg 1941).

As soon as these molecules were identified, a new field of research opened. Mc Kellar (1941) measured the excitation of the CN molecules to be 2.3 K, a first estimate of the cosmic microwave background (CMB) temperature. Theoretical calculations of the formation and destruction of interstellar molecules were presented by Kramers and Ter Haar (1946) and Bates &

Spitzer (1951). As in modern astrochemistry codes, molecules are formed with two body reactions including radiative association, and are destroyed by photodissociation. Bates & Spitzer (1951) suggested that evaporation of methane from grains could contribute to the formation of CH. While the conclusions on the gas density are correct, the predictions that diatomic species will be solely formed appears erroneous. The role of molecular ions in astrochemistry was not suspected at that time. The next revolution in the field was produced by the development of radioastronomy after the second world war. As rotational level spacings are very small, the frequencies of molecular rotational lines correspond to centimeter or millimeter wavelengths. This was recognized early on by Townes (1957), who gave a list of possible interesting molecules, which could have detectable microwave lines. The same table is reproduced below, with today's status. Molecules on the left side were chosen for their rotational and inversion spectra, while molecules on the right side were chosen for their fine structure and  $\Lambda$  doubling transitions.

**Table 1.** Molecules with microwave transitions suggested by Townes (1957)

	Detected	Comment		Detected	Comment
CaH	No	Ca depletion	OH	Yes	1963
CO	Yes	1970	AlH	No	Al depletion
CO <sup>+</sup>	Yes	1993	SiH	No <sup>2</sup>	Si depletion
CS	Yes	1971	SH	No <sup>3?</sup>	
NO	Yes	1978	NH	Yes	1991
H <sub>2</sub> O	Yes	1969 (maser)	OH <sup>+</sup>	No	
N <sub>2</sub> O	No	Earth atmosphere	MgH	No	Mg depletion
HCN	Yes	1971			
CH <sub>2</sub>	Yes	1989			
NH <sub>2</sub>	Yes	1992			
NH <sub>3</sub>	Yes	1968			
O <sub>2</sub>	No <sup>1</sup>	Earth atmosphere			

<sup>1</sup> Tentative detection reported by the ODIN team in 2005 <sup>2</sup> Tentative detection reported by Schilke et al. (2001) <sup>3</sup> SH is detected in stellar atmosphere, a tentative detection in the ISM is reported by Goicoechea et al. (2000)

While most of the species selected by Townes have been detected in the

interstellar medium, some notable exceptions remain : metallic hydrides escaped detection, probably because the corresponding metals are severely depleted in molecular regions. The physical conditions, which select the allowed chemical processes, are also important as molecules must reach a certain abundance to be detected. The absence of  $\text{NO}_2$  and  $\text{O}_2$ , two species prominent in the Earth atmosphere, has to be attributed to the absence of efficient formation pathways in the interstellar medium, because many oxygen and nitrogen bearing species have been detected. It is interesting to note that some species were not discovered with the spectral lines suggested by Townes (1957) but with other transitions. For instance rotational transitions of  $\text{CO}^+$  or  $\text{NH}_2$  at millimeter/submillimeter frequencies were first detected.

Table 2 lists detected interstellar and circumstellar species, including deuterated molecules, as of today. Because the majority of detections have been performed using radio telescopes, the inventory of interstellar molecules is biased towards polar molecules. Progresses in UV and infrared spectroscopy have helped in completing the list with symmetric, non-polar, molecules such as  $\text{C}_3$ . While the full list is impressive, it must be recognized that the chemical content of the interstellar medium depends on the environment, some specific regions being more chemically active than others. For instance, the vast majority of complex organic molecules has been detected in the immediate vicinity of massive protostars, in so-called “hot cores”, while deuterated species are most abundant in cold dense cores.

In the following, I discuss a few cases, which illustrate the development of astrochemistry. Other important subjects, such as the water and oxygen chemistry, and hunting for molecules in external galaxies, are discussed extensively elsewhere in this volume.

## 2 Deuterium chemistry

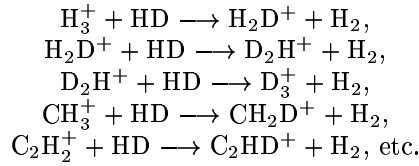
Although  $\text{CH}^+$  was one of the first detected interstellar molecule in the 1940's, the dominant role of molecular ions in interstellar chemistry was recognized later, in the 1970's, following the identification of X-ogen as  $\text{HCO}^+$  (Wahlgren et al. 1973). The detection of several deuterated species ( $\text{DCN}$ ,  $\text{DCO}^+$ ,  $\text{N}_2\text{D}^+$ ) with high abundance (Turner & Zuckerman 1978), has revealed that deuterium fractionation was extremely efficient, and triggered the development of ion-molecule chemistry (Herbst & Klemperer (1973); Watson (1974)). The main deuterium fractionation reactions are exother-

**Table 2.** Interstellar and Circumstellar Molecules

Molecular Hydrogen and Related Ions						
H <sub>2</sub>	<u>HD</u>	H <sub>3</sub> <sup>+</sup>	H <sub>2</sub> D <sup>+</sup>	D <sub>2</sub> H <sup>+</sup>		
<b>Carbon Chains and Cycles</b>						
<u>CH</u>	CH <sup>+</sup>	C <sub>2</sub>	CH <sub>2</sub>	<u>C<sub>2</sub>H</u>	C <sub>3</sub>	CH <sub>3</sub>
C <sub>2</sub> H <sub>2</sub>	<i>l</i> -C <sub>3</sub> H	<i>c</i> -C <sub>3</sub> H	CH <sub>4</sub>	C <sub>4</sub> ?	<i>c</i> -C <sub>3</sub> H <sub>2</sub>	<i>l</i> -C <sub>3</sub> H <sub>2</sub>
C <sub>4</sub> H	C <sub>2</sub> H <sub>4</sub>	C <sub>5</sub>	C <sub>5</sub> H	<i>l</i> -H <sub>2</sub> C <sub>4</sub>	<b>HC<sub>4</sub>H</b>	<b>CH<sub>3</sub>CCH</b>
C <sub>6</sub> H	C <sub>6</sub> H <sub>2</sub>	<b>HC<sub>6</sub>H</b>	C <sub>7</sub> H	CH <sub>3</sub> C <sub>4</sub> H	C <sub>8</sub> H	<u>C<sub>6</sub>H<sub>6</sub></u>
<b>Species with O, and/or H and C</b>						
<u>OH</u>	<u>H<sub>2</sub>O</u>	O <sub>2</sub> ?	<u>CO</u>	CO <sup>+</sup>	<u>HCO<sup>+</sup></u>	HOC <sup>+</sup>
<u>HCO</u>	C <sub>2</sub> O	CO <sub>2</sub>	H <sub>3</sub> O <sup>+</sup>	HOCO <sup>+</sup>	<u>H<sub>2</sub>CO</u>	C <sub>3</sub> O
HCOOH	CH <sub>2</sub> CO	H <sub>2</sub> COH <sup>+</sup>	CH <sub>3</sub> OH	CH <sub>2</sub> CHO	HC <sub>2</sub> CHO	C <sub>5</sub> O
CH <sub>3</sub> CHO	<i>c</i> -C <sub>2</sub> H <sub>4</sub> O	CH <sub>3</sub> OCHO	<u>CH<sub>2</sub>OHCHO</u>			
CH <sub>3</sub> COOH	CH <sub>2</sub> CHOH	(CH <sub>3</sub> ) <sub>2</sub> O	CH <sub>3</sub> CH <sub>2</sub> OH	CH <sub>2</sub> CHCHO	CH <sub>3</sub> CH <sub>2</sub> -	HOCH <sub>2</sub> -
(CH <sub>3</sub> ) <sub>2</sub> CO	CO(CH <sub>2</sub> OH) <sub>2</sub>		CH <sub>3</sub> OC <sub>2</sub> H <sub>5</sub>		-CHO	-CH <sub>2</sub> OH
<b>Species with N, and/or H and C</b>						
N <sub>2</sub>	NH	<u>CN</u>	NH <sub>2</sub>	<u>HCN</u>	<u>HNC</u>	<u>N<sub>2</sub>H<sup>+</sup></u>
<u>NH<sub>3</sub></u>	HCNH <sup>+</sup>	H <sub>2</sub> CN	HCCN	C <sub>3</sub> N	CH <sub>2</sub> CN	CH <sub>2</sub> NH
<u>HC<sub>3</sub>N</u>	HC <sub>2</sub> NC	NH <sub>2</sub> CN	C <sub>3</sub> NH	<b>HC<sub>4</sub>N</b>	CH <sub>3</sub> CN	CH <sub>3</sub> NC
HC <sub>3</sub> NH <sup>+</sup>	C <sub>5</sub> N	CH <sub>3</sub> NH <sub>2</sub>	C <sub>2</sub> H <sub>3</sub> CN	HC <sub>5</sub> N	CH <sub>3</sub> C <sub>3</sub> N	C <sub>2</sub> H <sub>5</sub> CN
HC <sub>7</sub> N	CH <sub>3</sub> C <sub>5</sub> N ?	HC <sub>6</sub> N	HC <sub>11</sub> N			
<b>Species with N, O and/or H and C</b>						
NO	HNO	N <sub>2</sub> O	<u>HNCO</u>	NH <sub>2</sub> CHO		
<b>Species with S, Si and Other Elements</b>						
<b>SH</b>	CS	<u>SiS</u>	<b>SO<sup>+</sup></b>	NS	SiH	<b>SiC</b>
SiN	<u>SiO</u>	SiS	HCl	<b>NaCl</b>	<b>AlCl</b>	<b>KCl</b>
HF	<b>AlF</b>	CP	PN	H <sub>2</sub> S	C <sub>2</sub> S	SO <sub>2</sub>
<u>OCS</u>	HCS <sup>+</sup>	<i>c</i> -SiC <sub>2</sub>	<b>SiCN</b>	<b>NaCN</b>	<b>MgCN</b>	<b>MgNC</b>
H <sub>2</sub> CS	HNCS	C <sub>3</sub> S	<i>c</i> -SiC <sub>3</sub>	<b>SiH<sub>4</sub></b>	<b>SiC<sub>4</sub></b>	CH <sub>3</sub> SH
C <sub>5</sub> S	FeO	<b>AlNC</b>	<b>SiNC</b>	CF <sup>+</sup>		
<b>Deuterated species</b>						
HDO	CCD	<u>DCO<sup>+</sup></u>	<b>DCN</b>	DNC	N <sub>2</sub> D <sup>+</sup>	C <sub>4</sub> D
NH <sub>2</sub> D	ND <sub>2</sub> H	ND <sub>3</sub>	HD <sub>2</sub> CO	D <sub>2</sub> CO	DC <sub>3</sub> N	DC <sub>5</sub> N
CH <sub>2</sub> DCCH	CH <sub>3</sub> CCD	CH <sub>2</sub> DCN	HDS	D <sub>2</sub> S	HD <sub>2</sub> S	D <sub>2</sub> CS
CH <sub>2</sub> DOH	CD <sub>2</sub> HOH	CD <sub>3</sub> HOH	CH <sub>3</sub> OD	<i>c</i> -C <sub>3</sub> HD		

Note: Species detected in **circumstellar envelopes** only are written in **boldface**. Species detected in external galaxies are underlined.

mic reactions involving HD (or D<sub>2</sub>) and a molecular ion, where the substitution of an hydrogen atom by a deuterium atom leads to a deuterated molecular ion. By subsequent reactions of deuterated molecular ions with neutrals, deuterated neutral molecules or more complex deuterated molecular ions are efficiently produced (see e.g. Roueff et al. 2005, Roberts et al. 2004) :



$\text{H}_2\text{D}^+$  appeared as a key species for interstellar chemistry. Searches for  $\text{H}_2\text{D}^+$  lines were made using the radio techniques as soon as the technology was ready. The ortho ground state transition of  $\text{H}_2\text{D}^+$  near 372 GHz can be observed from the ground under exceptional conditions as the atmospheric transmission is lowered by a nearby water line. The first searches were therefore attempted using state-of-the-art heterodyne spectrometers on board the Kuiper Airborne Observatory (KAO). Phillips et al. (1985) reported a tentative detection towards NGC2264, which was not confirmed later by more sensitive observations (Pagani et al. 1992). Soon after, Bor-eiko et al. (1993) attempted the detection of the para  $\text{H}_2\text{D}^+$  ground state transition at 1370 GHz from the KAO. New submillimeter telescopes were constructed in the same time on top of the Mauna Kea extinct volcano in Hawaii (USA), the James Clerk Maxwell Telescope (JCMT) and the Cal-Tech Submillimeter Observatory (CSO). Using the CSO, van Dishoeck et al. (1992) also searched for  $\text{H}_2\text{D}^+$ , with no success. The surprise came late, with the detection of a weak feature by Stark et al. (1999) using the JCMT, towards the young protostar NGC1333 IRAS4A, and of a stronger feature towards the protostellar core LDN1544 by Caselli et al. (2003). In fact, the signal towards LDN1544 is so strong that it could have been detected earlier if this source had been surveyed. Previous searches were biased towards star forming regions because of the rather high upper energy level for the ortho  $\text{H}_2\text{D}^+$  transition. As Caselli et al. (2003) pointed out (see also Pagani et al. 1992), the level population and ortho/para ratio of  $\text{H}_2\text{D}^+$  are not necessarily thermalized in cold dense regions, and a significant population remains in the energetically less favorable ortho state. This detection nicely confirmed the theory of gas phase deuterium fractionation, and triggered the search for the next molecular ion,  $\text{D}_2\text{H}^+$  which was found in another protostellar core, LDN1689N, by Vastel et al. (2004).  $\text{H}_2\text{D}^+$  and  $\text{D}_2\text{H}^+$  are found to be extremely abundant relative to  $\text{H}_2$  (and  $\text{H}_3^+$ ) in dense protostellar cores, because these regions combine several factors which all favor the fractionation : i) low temperature, ii) large depletion, iii) low fractional ionization. i) is important to maximize the efficiency of the forward reaction, while ii) and iii) help in lowering the destruction rate of molecular ions (by reactions with CO and other abundant neutrals and by dissociative recombination with electrons).

As seen from Table 2 many multiply deuterated species have been detected including two triply deuterated molecules  $\text{ND}_3$  (Roueff et al. 2005 and references therein) and  $\text{CD}_3\text{OH}$  (Parise et al. 2004). Considering the

low abundance of deuterium ( $D/H \sim 10^{-5}$ ), finding multiply deuterated molecules seems a priori impossible. But, given the high efficiency of fractionation reactions, models succeed in reproducing the observed degree reasonably well (Roberts et al. 2004). Two routes are thought to contribute in the fractionation : i) gas phase ion molecule chemistry is very efficient as described above, especially when depletion of abundant neutrals on grain mantle limit the destruction rate of molecules and molecular ions. ii) substitution of H atoms by D atoms wandering on grain surface is an alternative possibility, first suggested by Tielens (1983). Both routes are considered in most recent calculations as the efficiency of the D fractionation on grain surfaces depends on the actual D/H ratio in the gas phase, which is determined by the gas phase chemistry !

### 3 Reactive and exotic molecules

Interstellar absorption lines due to  $H_3^+$  have been detected in the thermal infrared in the late 1990's (Geballe & Oka 1996) after a long search.  $H_3^+$  belongs to the class of reactive molecules (which includes  $CH^+$ ) which are efficiently destroyed by collisions with electrons and neutrals ( $H_2$ , CO, etc.).  $H_3^+$  is surprisingly abundant in the diffuse interstellar medium (Mc Call et al. 2003), reaching nearly the same abundance level as towards more reddened lines of sight, despite the high destruction rate in the diffuse medium. Other reactive species ( $CO^+$ ,  $HOC^+$ ,  $SO^+$ ) are detected in photodissociation regions (e.g; Rizzo et al. 2003 for MonR2) and in the diffuse interstellar medium (Liszt et al. 2004). Steady state chemical models have difficulties in reproducing the observed abundances, calling for the inclusions of more physical processes in the modeling (see contributions by H. Liszt and by E. Falgarone).

Carbon chains and cycles are the second family of exotic interstellar molecules. While these reactive chains are difficult to isolate in the laboratory, they are rather easily produced (and detected) in the interstellar medium (e.g. the well known dark cloud TMC-1) and in carbon star envelopes (the prototype being IRC 10216). The recent advances of both heterodyne and infrared spectroscopy have led to the identification of long chains, up to  $C_8H$  using radio techniques, and symmetric species ( $C_3$ ,  $C_4H_2$ ), which do not produce millimeter rotational lines because of the absence of dipole moment (Cernicharo et al. 2001), using ISO spectrometers.

The most extreme “molecules” in the interstellar medium are certainly the carriers of the remaining unidentified spectral features. Despite intensive work in the last 70 years, the carriers of the diffuse interstellar bands remain unknown, but the most likely hypothesis is that they are due to large organic molecules. Intense emission bands at  $\lambda = 3.3, 6.2, 7.7, 8.6, 11.3\mu\text{m}$  are ubiquitous in the ISM. After the pioneering work of Sellgren (1984) and Léger & Puget (1984), they are now attributed to organic macromolecules, the Polycyclic Aromatic Hydrocarbons (PAHs) such as coronene  $\text{C}_{24}\text{H}_{10}$ . While many arguments support PAHs as the most likely carriers of these bands, no single molecule of the family has been identified yet. The mid-IR bands are not specific enough for identifying a given molecule, and searches in other spectral regions (in the visible or UV) have not been conclusive. The far infrared spectral region may host the key for identifying the PAHs as low energy bending modes are expected to show up and help in the identification process.

#### 4 The dust gas interplay : ices and complex organic molecules

Complex organic molecules have been steadily discovered over the years in hot cores near massive protostars, following the identification of formaldehyde in 1969 and methanol in 1970. The chemistry of these dense ( $10^7\text{ cm}^{-3}$ ) and warm (150 – 300 K) regions is truly exceptional compared to the bulk of molecular clouds. Families of alcohols ( $\text{CH}_3\text{OH}$ ,  $\text{CH}_3\text{CH}_2\text{OH}$ ,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ , etc.), ethers ( $(\text{CH}_3)_2\text{O}$ ), aldehydes ( $\text{H}_2\text{CO}$ ,  $\text{CH}_2\text{CHCHO}$ ,  $\text{CH}_3\text{CH}_2\text{CHO}$ , etc. ), acetone ( $(\text{CH}_3)_2\text{CO}$ ) have been securely identified. Acetone ( $(\text{CH}_3)_2\text{CO}$ ) was first detected using the IRAM-30m telescope (Combes et al. 1987), and confirmed by higher spatial resolution observations using the BIMA interferometer (Snyder et al. 2002). While the spectral signature of the acetone quadruplets was very clear in the single dish data, spectral confusion was more severe in the large IRAM-30m beam than at higher resolution using BIMA. New detections of complex organic molecules in hot cores have to face the problem of line confusion. Any identification must now be based on the detection of a large number of lines, and with no “missing feature”. The procedure of removing unwanted confusing signals from line forests (due e.g. to  $\text{HCOOCH}_3$ ) is described in Fuchs et al. (2005).

It is now believed that complex organic molecules in hot cores are chemically related to the ice mantles. Indeed, ISO has revealed the chemical richness of ice mantles by performing sensitive absorption spectroscopy in



the thermal infrared. A summary of the ice composition towards massive protostars is given by Gibb et al. (2004) and Dartois (2005). While water ice is the main constituent, fractions of several tens of percent have been measured for CO, CO<sub>2</sub> and CH<sub>3</sub>OH, and few percent for CH<sub>4</sub>, H<sub>2</sub>CO and possibly HCOOH. Ammonia is present at the few percent level, although an accurate determination of the ammonia fraction is difficult because of blending of ammonia ice lines with other spectral features. The presence of OCN<sup>-</sup> and OCS indicates that more complex molecules may be present at a low level but they remain undetectable in the solid state. When a protostar forms, the dense matter surrounding the star is heated and ices sublimate, liberating their constituents in the gas phase. The gas chemistry is modified and new species may form in this transient phase (see models by Doty et al. (2002) for instance). It is not completely understood which species are formed in situ in the ice mantles, and are simply liberated in the gas during the hot core phase, and which species require additional chemical processing. The detection of deuterated species (HDO, DCN, CH<sub>2</sub>DCN, Wright et al. 1996 ) with fractionation ratio in excess of the equilibrium value at the hot temperature suggests that some species can survive in the gas. Laboratory experiments succeed extremely well in synthesizing analogues of interstellar solids, and in reproducing their processing mechanisms. The laboratory study of ice evaporation products for further astronomical searches is the next challenge as laboratory experiments are performed in well controlled conditions. It is expected that evaporation products may be used to better understand the chemical history of ice mantles.

## 5 Looking towards the future

Looking back at the past, discoveries of interstellar species have been performed using three different methods :

- Deep searches with no a priori have often been rewarding. Spectral line surveys covering hundreds of GHz will be routinely performed in the near future with the increase of receiver bandwidth and sensitivity.
- Chemical reasoning may help in selecting interesting targets (family of molecules). This method has been applied successfully for detecting isomers (e.g. HCOOCH<sub>3</sub> and CH<sub>3</sub>COOH) or studying interstellar alcohols. Non detections should be reported as they bring interesting information for modelers.
- Chemical models may also be used for identifying interesting interstellar

species. The successful detections of  $\text{H}_3^+$  and of  $\text{H}_2\text{D}^+$  in space have put gas phase ion-molecule chemistry on a firm basis, although some problems remain open.

Can these methods be used and applied in the future? The launch of the Herschel satellite will fully open the submillimeter wavelength domain. As very few data are known, it is expected that sensitive spectral line surveys will be carried out over the accessible frequency range, to uncover all spectral features. Dedicated deep searches for individual chemical species should also be performed. Carbon clusters are an obvious target as  $\text{C}_2$  and  $\text{C}_3$  are known to be abundant in the ISM. Spectral lines from PAHs are also expected to be found in this spectral range, carrying key information on their carriers (size, geometry) and leaving open the possibility of identifying some molecules of this important ISM family.

Line confusion is a severe barrier for finding new species, especially in hot cores. With the improved spatial resolution accessible with ALMA, combined with unprecedented sensitivity, the different sources of molecules will be spatially separated, lowering the line confusion. The recent confirmation of acetone in space (Snyder et al. 2002) shows how using an interferometer helps in discovering complex interstellar molecules securely.

Given the rich harvest of ISO spectrometers, it is expected that the bias towards polar molecules will be lowered by using sensitive mid-infrared spectrometers on 8m class telescopes. Because solid state and gas features can be observed simultaneously in the infrared, this technique is best suited for studying the complex interplay of gas phase and solid state processes in synthesizing the many interstellar molecules which have been detected.

Finally, a tight collaboration between physicists, chemists and astronomers remains the key for success. Laboratory spectroscopy and theoretical calculations remain the most valuable tools for both spectroscopic identification, and extraction of meaningful information from the line profile, while astrophysical observations provide challenging problems to physicists.

I warmly thank the organizers of this meeting for their excellent and cheerful organization, and the broad range of topics covered. I am indebted to P. Encrenaz for having welcomed me in his group when I started my PhD, and suggested to work on interstellar chemistry.

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