

PRISMAS : PRobing InterStellar Molecules with Absorption line Studies

ABSTRACT

We will carry out a comprehensive spectroscopic study of key molecular line carriers, probing interstellar hydrides and carbon chains. Our investigation will entail high-resolution HIFI spectroscopy of some 25 molecules towards 8 sources, and full spectral scans with PACS. The target hydrides contain the elements H, D, C, N, O, F and Cl. We will take advantage of the strong dust emission from massive star forming regions to detect multiple absorption components from foreground clouds of diverse properties that are known to intersect the selected sight-lines, along with emission and absorption intrinsic to the background sources. Our investigation will provide a wealth of new information about interstellar hydrides – addressing key puzzles posed by previous observations from the ground since the 1940’s, and recently with ISO, SWAS, and ODIN – and leaving an important Herschel legacy to astrochemistry and ISM science. We will address the role of high temperature chemical reactions in the formation of interstellar molecules, and the question of how such reactions might be driven. We will also investigate the role of grain surface reactions in interstellar chemistry, and the growth of carbon molecules, bridging the gap between molecules and aggregates, as unique spectroscopic signatures of carbon chains and rings, are accessible in the FIR.

Many of the lines that are detectable with Herschel in the local Universe become accessible to ground-based observatories for redshifted sources. Our programme will provide an unique benchmark for the studies of molecular gas at high redshift with ALMA.

List of proposers and Institutions

*M. Gerin*¹, *T. Bell*², *J. Black*³, *F. Boulanger*⁴, *J. Cernicharo*⁵, *E. Dartois*⁴, *P. Encrenaz*¹, *E. Falgarone*¹, *T. Giesen*⁶, *J. R. Goicoechea*^{1,5}, *P. Goldsmith*⁷, *C. Gry*⁸, *P. Hennebelle*¹, *E. Herbst*¹⁰, *P. Hily-Blant*^{9,1}, *C. Joblin*¹¹, *R. Kolos*¹², *J. Krelowski*¹³, *D. C. Lis*², *J. Martin-Pintado*⁵, *B. Mookerjee*¹⁴, *D. Neufeld*¹⁵, *J. Pearson*⁷, *M. Perault*¹, *T. G. Phillips*², *R. Plume*¹⁶, *M. Salez*¹, *M. Schmidt*²¹, *J. Stutzki*⁶, *D. Teyssier*¹⁷, *C. Vastel*¹¹, *A. Contursi*¹⁸, *K. Menten*¹⁹, *T. Geballe*²⁰

¹ LERMA, CNRS, Observatoire de Paris, Ecole Normale Supérieure, Universités Paris 6 and Cergy-Pontoise, Paris, France.

² California Institute of Technology, Pasadena, USA.

³ Chalmers University of Technology, Göteborg, Sweden.

⁴ Institut d'Astrophysique Spatiale (IAS), CNRS and Université Paris 11, Orsay, France.

⁵ DAMIR, Instituto de Estructura de la Materia, CSIC, Madrid, Spain.

⁶ I. Physikalisches Institut, University of Cologne, Germany.

⁷ Jet Propulsion Laboratory (JPL), California Institute of Technology, Pasadena, USA.

⁸ Laboratoire d'Astrophysique de Marseille (LAM), CNRS, Marseille, France.

⁹ IRAM, Grenoble, France.

¹⁰ Department of Physics, Astronomy and Chemistry, Ohio State University, USA.

¹¹ CESR, Université Toulouse 3 and CNRS, Toulouse, France

¹² Institute of Physical Chemistry, Polish Academy of Sciences, Poland

¹³ Toruń Center for Astronomy, Nicolaus Copernicus University, Toruń, Poland.

¹⁴ Department of Astronomy, University of Maryland, USA.

¹⁵ Department of Physics and Astronomy of the Johns Hopkins University, USA.

¹⁶ Department of Physics and Astronomy, University of Calgary, Canada.

¹⁷ European Space Astronomy Centre, ESA, Vilspa, Spain.

¹⁸ Max Planck Institute für Extraterrestrische Physik, Garching, Germany.

¹⁹ Max Planck Institute für Radioastronomie, Bonn, Germany.

²⁰ Gemini telescope, Hilo Hawaii.

²¹ Nicolaus Copernicus Astronomical Center, Torun, Poland.

Contents

1	Scientific goals	4
1.1	Introduction	4
1.2	The astrochemical importance of hydride molecules	4
1.3	Carbon chains and rings	6
1.4	Why Herschel is essential	7
1.5	Summary of proposed observations	8
2	Science exploitation	8
3	Relation to past or future observations	9
4	Technical implementation	10
4.1	Observing strategy and time requirements	10
4.1.1	HIFI Observations of hydride lines	10
4.1.2	HIFI observations of carbon chains	12
4.1.3	PACS Observations	12
4.2	Special requirements and constraints	12
4.3	Impact of different instrument sensitivity	12
5	Description of data processing plan and archival data products and tools that will be produced	13
5.1	Data processing	13
5.2	Science exploitation and advanced data analysis	13
5.3	Archive and data products	14
6	Management and Outreach plan	14
6.1	Organization and Management Plan	14
6.2	Consortium resources	15
6.3	Outreach	15
A	Observing time estimate	18
B	Curriculum Vitae	21
C	The chemistry of interstellar hydrides	25
C.1	Oxygen chemistry	25
C.2	Fluorine chemistry	26
C.3	Carbon chemistry	27
C.4	Nitrogen chemistry	28
C.5	HCl	28
C.6	Deuterium fractionation and interstellar deuterides	28

1 Scientific goals

1.1 Introduction

The opening of the full far-infrared and submillimeter wavelength domains by Herschel will provide a unique opportunity for progress in astrochemistry, because it gives access to important classes of interstellar species, which have not been studied before with high spectral resolution heterodyne techniques. The list includes the rovibrational transitions of carbon molecules and carbon clusters (carbon chains, possibly rings), together with the ground state transitions of most hydrides. Among the many molecules identified in the interstellar medium and circumstellar envelopes so far (over 140, not including isotopologues bearing rare isotopes) a significant subsample has been detected in the diffuse interstellar medium, ranging from H_2 and HD (e.g. Rachford et al. 2002) to chemically rather complex species such as C_3 (Oka et al. 2003), and *c*- C_3H_2 (Lucas and Liszt 2000). As we shall discuss more extensively below, probing diffuse ISM molecules has proven to be an efficient method for studying the first steps of interstellar chemistry, and its interrelation with the interstellar medium dynamics and evolution.

In the diffuse ISM, molecules are ascribed to the so-called ‘‘Cold Neutral Medium (CNM)’’, because the narrow molecular linewidths (up to a few kms^{-1}) are comparable to the velocity dispersion of the CNM. The gas characteristics of the CNM cover a broad range, from a few tens to one hundred Kelvins for the kinetic temperature and from several tens to a few thousands particles per cm^3 for the density. The average thermal pressure is $\sim 3 \times 10^3 \text{ Kcm}^{-3}$, with large excursions above the median, up to 10^5 Kcm^{-3} (Jenkins & Tripp 2001). Excitation of polar molecules (e.g. hydrides) in collisions with H_2 and other neutrals is generally not efficient in those conditions, while the level populations of non polar species (e.g. C_2) are close to thermalization.

This Herschel programme is dedicated to the detection and study of key molecules, which are not accessible from the ground at FIR/submillimeter wavelengths, but which bear essential information on the physical and chemical processes ruling the ISM, and on the growth of molecular complexity. Complementary investigations are proposed in other HIFI guaranteed time key programmes, most notably HEXOS and ‘‘The Warm and Dense ISM’’.

1.2 The astrochemical importance of hydride molecules

Hydrides play a central role in interstellar chemistry, as significant reservoirs of heavy elements. Hydrides are at the root of the reaction chains theorized to form gas phase molecules – and hence are the most sensitive tests of these theories. **Observations of interstellar hydrides are therefore critical in advancing our understanding of astrochemistry.** Unfortunately, the large opacity of Earth’s atmosphere at far infrared and submillimeter wavelengths has severely limited the ability of ground-based observatories to probe hydrides containing just a single heavy element atom. Thus the properties of hydrides, with ground state rotational transitions at submillimeter wavelengths, are less well known than those of non-hydrides – with larger reduced masses – that radiate in the millimeter region.

In diffuse clouds, hydrides can be probed by means of optical or ultraviolet absorption line spectroscopy of background stars – indeed, the hydrides CH and CH^+ were among the first three molecules detected at optical wavelengths in the early 1940’s (e.g. Swings & Rosenfeld 1937, Douglas & Herzberg 1941). However, submillimeter and far-IR observations of rotational transitions have many critical advantages over optical/UV observations of electronic transitions: (1) submillimeter/far-IR absorption line observations can be carried along sightlines of larger visual extinction, allowing the chemistry of translucent and dense clouds to be probed; (2) many hydrides have electronic transitions at UV wavelengths that are inaccessible with current instrumentation and/or subject to confusion with H_2 Lyman and Werner bands; (3) submillimeter/far-IR transitions can be observed both in absorption and emission, providing a more complete sampling of the molecular clouds under investigation; (4) optical/UV observations are limited by spectral resolution – except for optical observations of the brightest background sources – and thus fail to fully elucidate the velocity structure of the absorbing molecules (Fig 1), hence the coupling of the gas dynamics with chemistry. The

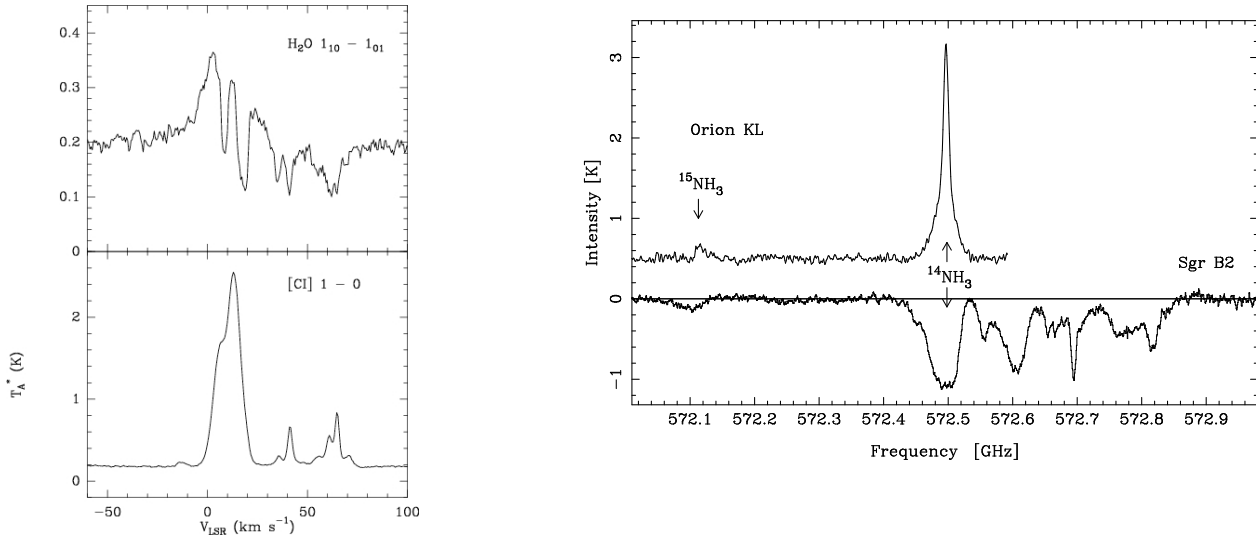


Figure 1: Left : SWAS spectra obtained towards the star forming region W49 by Plume et al. (2004), the ground state water line at 557 GHz is shown at the top and the fine structure line of carbon at 492 GHz at the bottom. Diffuse and translucent clouds along the line of sight show up as absorption features in the H_2O spectrum and as emission lines in the $[\text{CI}]$ spectrum. Right : Spectra of $^{14}\text{NH}_3$ and $^{15}\text{NH}_3$ obtained by ODIN towards Orion and SgrB2 (Hjalmarson et al. 2006). While the lines appear in emission in the nearby source Orion, the spectrum towards the distant, bright continuum source SgrB2 shows many absorption features, from the SgrB2 source and from diffuse clouds along the line of sight. The SgrB2 sight-line will be studied as part of the HEXOS programme, while other similar sight-lines will be sampled by PRISMAS.

great capabilities of heterodyne spectroscopy in the submillimeter have been demonstrated by the SWAS and ODIN satellites (Fig 1), and by the detection of the ground state line of $^{13}\text{CH}^+$ at 831 GHz (Falgarone et al. 2005).

In this Herschel key programme, **we will carry out a comprehensive study of some 24 hydride molecules towards 8 bright submillimeter continuum sources, leaving an important Herschel legacy to astrochemistry and interstellar medium science.** The target molecules comprise key hydrides and deuterides of the elements, C, N, O, F and Cl, and include both neutral species and molecular ions. The proposed observations will simultaneously provide both absorption-line spectroscopy of intervening clouds along the sightline to the target sources, together with emission-line spectroscopy of hydrides located within the sources themselves. Differential Galactic rotation will allow the various emission and absorption components to be disentangled kinematically.

In Appendix C, we discuss¹ how the proposed programme will advance our astrochemical understanding of molecules bearing each of the elements C, N, O, F and Cl. While specific puzzles will be discussed there, **two general scientific questions emerge repeatedly:**

- **What is the role of high temperature reactions in the formation of interstellar molecules, and how are such reactions driven?** As we shall discuss below, the relative abundances of several species argue independently for the importance of chemical reactions with significant energy barriers. Such species therefore yield an important probe of heating mechanisms, driven for instance by the dissipation of supersonic turbulence (shock waves and other dissipative processes). These signatures of turbulence dissipation are of general relevance to our understanding of the ISM evolution and the process of star formation.

The range of CH^+ column densities measured in the visible and now in the submillimeter (Fig. 3), is inconsistent with steady-state low-temperature chemistry because the main CH^+ formation process is the endothermic reaction between C^+ and H_2 , which is inoperant at diffuse cloud temperatures. The formation of other hydrides (OH , NH^+) is also governed by endothermic reactions, with smaller energy requirements.

¹The detailed discussion in Appendix C can be omitted by readers who wish to read a short description of the proposed key programme.

The regions where CH^+ is formed must be transiently overheated relative to the bulk of the ISM, whose gas physical conditions are well determined with other molecules such as C_2 or CN . Combined observations of CH^+ , OH , CH and the N-hydrides will provide a unique data base for investigating warm chemistry in the cold diffuse medium.

- **How do grain surface reactions affect the abundances of gas-phase molecules?** The likely importance of gas-grain chemistry has been recognized increasingly in recent years (e.g. Herbst 2005). The question is of great and general astrophysical significance, because gas-grain processes control the composition of icy grain mantles in molecular clouds. Hydrogenation reactions are extremely efficient on dust grains, leading to the formation of water, ammonia and methane among other species. Various processes can alter the grain mantle composition (for instance UV or CR radiation) and let a fraction of the ices be released into the gas phase and further processed. However, the abundance pattern of chemically related species mainly produced by gas phase or solid phase processes are different. By probing the N-hydride ($\text{NH}^+/\text{NH}/\text{NH}_2/\text{NH}_3$) and O-hydride ($\text{OH}^+/\text{OH}/\text{H}_2\text{O}/\text{H}_3\text{O}^+$) families, we will be able to disentangle the role of gas phase and solid phase processes in initiating the chemistry. UV and Cosmic-ray processing of ice mantles contribute in building the carbonaceous material of dust grains. The large abundances of carbon and hydrocarbon chains may be related to the release of solid matter to the gas phase as explained below.

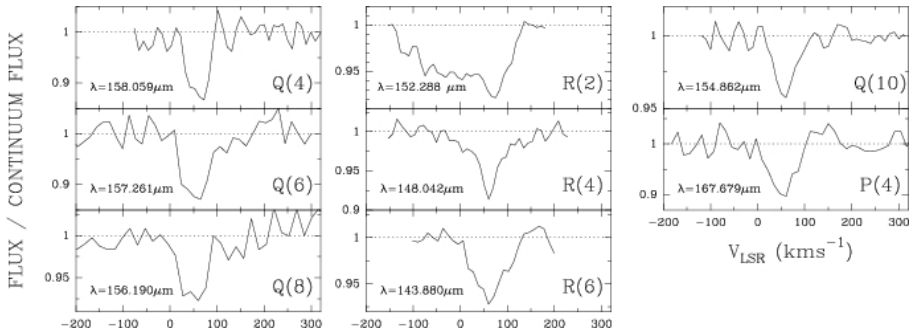


Figure 2: Detection of the C_3 FIR lines with the ISO-LWS spectrometer (Cernicharo et al. 2000).

1.3 Carbon chains and rings

Small carbon containing molecules, with a total of about 1 to 3 carbon atoms, are important due to several interesting properties: they show an ubiquitous interstellar spatial distribution, they likely participate in the formation of long carbon chain molecules, and they are involved in photo-fragmentation processes of larger species such as PAHs. Of particular interest is the sputtering process of the carbonaceous nanoparticles, forming a likely source for the high abundance of carbon in its various forms detected in the interstellar medium (Herbst 2005, Pety et al. 2005). It is widely believed, as has been suggested by Douglas in 1977, that carbon chain or ring species might be the candidates for the long sought-after assignments of the Diffuse Interstellar Bands (Herbig 1975 and 1995).

Many carbon containing molecules, including carbon-hydrides, carry a permanent electric dipole moment and thus have been observed by their rotational spectra from ground. In contrast, pure carbon molecules lack a permanent dipole moment and can only be observed by ro-vibrational transitions in the Terahertz frequency region, or by electronic transitions in the UV/visible domain. Due to the opacity of the earth's atmosphere none of the pure carbon chain ro-vibrational transition (from C_3 to C_{11}) can be observed from ground. HIFI and PACS onboard Herschel are the only instruments with sufficient sensitivity and spectral resolution for a systematic study of carbon chain molecules in space. Until the present, the R(2) transition of C_3 is the sole line detected in full rotationally resolved resolution (Van Orden et al. 1995). Multiple lines of C_3 at lower spectral resolution have been detected with the ISO satellite towards Sgr B2 and IRC+10216 (Cernicharo et al. 2000, Fig 2). C_3 is also seen in diffuse and translucent interstellar clouds (Maier et al. 2001, Galazutdinov et al. 2002, Oka et al. 2003). **Detection of C_3 in various sources with larger column densities than accessible by visible spectroscopy is thus a main target for this proposal.** Several C_3 transitions at 1.8 – 1.9 THz are covered with the HIFI instrument.

For all heavier carbon chain molecules, none of the lowest bending mode transitions have been clearly

Table 1: Lowest energy bending modes of Carbon Chain Molecules (Botschwina (2006 & priv. comm.))

Molecule	C ₃	C ₄	C ₅	C ₆	C ₇	C ₈	C ₉	C ₁₀	C ₁₁	C ₁₂	C ₁₃
Frequency [GHz]	1901	5129	3373	2980	2098	1814	1367	1193	944	854	690
Dipole [D]	0.43	0.32	0.32	0.34	0.34	0.35	0.36	0.37	0.38		0.40

identified, either by laboratory or radio-astronomical detection. Laboratory studies on combination bands, coupled with advanced ab-initio calculations have led to predictions for the lowest bending modes for C₄ to C₁₃. Table 1 lists the frequencies of the lowest energy bending modes of pure carbon chains (P. Botschwina (2006) and priv. comm). Transitions of species ranging from C₄ to C₉ lie in the spectral range of the PACS instrument while the transitions of species from C₈ to C₁₃ are accessible to HIFI. Actually, far IR spectral features, detected in low resolution with ISO, have been tentatively assigned to C₄, C₅, and/or C₆ (Cernicharo et al. 2002, Goicoechea et al. 2004). The spectral resolution of PACS is sufficient to resolve ro-vibrational lines of small carbon clusters and to clearly confirm these earlier assignments. The search for precise transition frequencies under laboratory conditions continues at the Cologne laboratories.

The search for pure carbon clusters with Herschel is connected to the observations of small carbon-hydrides, since they are closely chemically related. The comparison of carbon cluster and C-hydrides abundances is an excellent test of the chemical paths to molecular complexity in the ISM, probing both gas phase and solid phase processes. While the inventory of species with two and three C-atoms seems to be fairly complete, our knowledge of species with more carbon atoms is still fragmentary. Further support for the presence of still unknown carbon chains is provided by the excellent correlation between CCH, c-C₃H₂ and C₄H (Liszt & Lucas 2000, Teyssier et al. 2004, Pety et al. 2005), and by the recent detection of C₆H⁻ in the dark cloud TMC-1 (McCarthy et al. 2006). It is very likely that many molecules with four or more carbon atoms remain to be identified in various regions of the interstellar medium.

It is our goal to make use of the excellent Herschel spectroscopic capabilities for making an inventory of the carbon clusters in the diffuse ISM, along the same lines of sight as the hydride species. HIFI will be used to probe C₃, while PACS scans will be used to fully survey the far infrared domain including medium size carbon clusters. Once we obtain accurate frequencies from laboratory spectroscopy, we propose to perform deep integrations with HIFI on selected frequencies towards the two best sources identified from the C₃ and PACS observations. W31C and W49N have been selected for the submission of the proposal, but we may revise this choice depending on the Herschel observations.

1.4 Why Herschel is essential

Herschel is uniquely suited for providing new information on two important classes of interstellar species - hydrides and carbon clusters. In particular, the HIFI and PACS instruments offer the necessary high sensitivity and spectral resolution over wavelengths that were previously inaccessible. With its broad wavelength coverage, HIFI can access key hydrides participating in interstellar chemistry with high sensitivity and high spectral resolution, in a frequency domain of poor atmospheric transmission. The list includes the carbon hydrides CH and CH⁺, the nitrogen hydrides NH, NH₂, NH₃, NH⁺, the oxygen hydrides H₂O, H₃O⁺ and OH⁺, the halides HF and HCl, with their most abundant isotopologues including the deuterated species.

Experience with ISO (Goicoechea et al. 2004), SWAS(Plume et al. 2004) and ODIN (Sandqvist et al. 2003) has shown that **absorption line studies remain the most sensitive and reliable method for measuring the column densities of interstellar species**. This is especially true for hydrides, because they are almost always subthermally-populated at interstellar densities, and therefore show emission line strengths that are proportional both to the poorly-known gas density and to the temperature dependent collisional rate coefficients. Furthermore, theoretical calculations suggest that the latter are often very different for excitation by ortho- and para-H₂, so the hydride abundances derived from emission line observations depend upon what is assumed for the H₂ ortho-to-para ratio; radiative transfer effects can also be problematic because of the large optical depths. Absorption line observations largely circumvent most of these difficulties.

HIFI is ideally suited for such studies, since it gives access to the ground state rotational

lines of those hydrides, and – most importantly – provides high (and critically needed) spectral resolution. The sensitivity is such that we shall be able to probe the abundance of interstellar hydrides over a large range of physical conditions, which overlaps the domain probed by electronic transitions for CH and CH⁺. As shown in Figure 3, typical CH and CH⁺ column densities for diffuse clouds lie in the range 10¹² to 10¹⁴ cm⁻². Such column densities will give rise to strong absorption features in the Herschel frequency domain, with opacities of order unity for a column density of 10¹³ cm⁻² and a linewidth of 1 kms⁻¹.

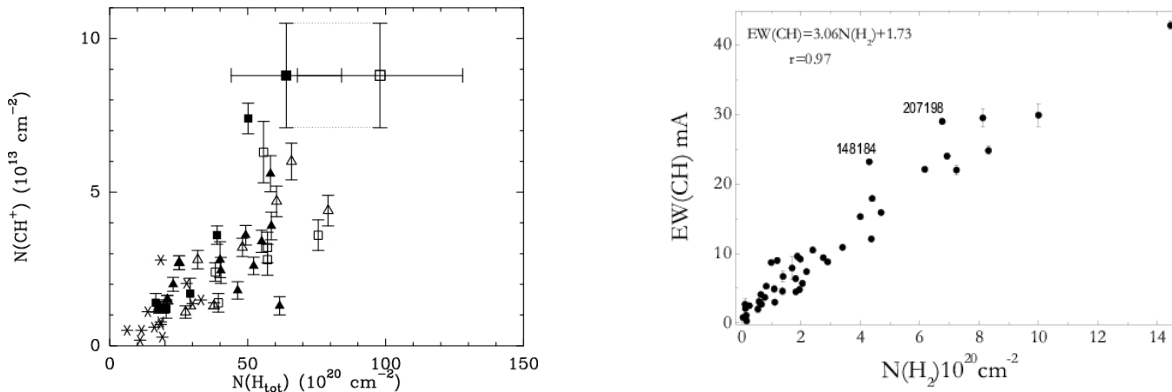


Figure 3: Left : The CH⁺ column density as a function of the total hydrogen column density N(H)+2N(H₂). The stars show the data of Crane et al. (1995) and the triangles those of Gredel (1997). The squares bracket the values deduced from submillimeter observations of ¹³CH⁺(1-0) (Falgarone et al. 2005). Right : CH equivalent width (mÅ) as a function of the H₂ column density (Galazutdinov et al. 2007). CH column densities range from $\sim 10^{12}\text{cm}^{-2}$ to $\sim 10^{14}\text{cm}^{-2}$.

1.5 Summary of proposed observations

We propose to search for absorption lines using bright submillimeter continuum sources as background sources, as this strategy maximizes the sensitivity to small column densities of absorbing material. Our observations will also probe emission from the same species that are intrinsic to the target sources themselves. We have selected a list of ~ 30 lines and 8 bright FIR/submm continuum sources for this survey. To completely cover the FIR/submm domain, we propose to perform a full PACS scan of all sources.

The selection criteria for the sources are the existence of a strong far infrared continuum and the presence of interstellar clouds along the line of sight, as evidenced by existing data (on HI, HCO⁺, H₂O, OH and other species, from ISO, SWAS and ODIN as well as ground based telescopes). The sample is described in Table 2. The line list, whose scientific rationale is explained above, is given in Table 3 with integration times listed in Tables 5, 6 & 7 for HIFI and Table 8 and 9 for PACS. Overall the allocated 128 hours (see Table 4) will be spend as follows : 86 hours on hydrides, 20 hours on PACS scans and 22 hours on HIFI observations of carbon clusters.

2 Science exploitation

The consortium gathers experts from different fields, from radio, FIR, IR and optical observations, to laboratory spectroscopy, and astrochemistry modeling. We propose to answer the science questions presented above by specifically studying key aspects of the hydride and carbon chemistry first :

- H₂O and the oxygen chemistry in the diffuse interstellar medium
- CH⁺ as a tracer of warm chemistry in the ISM
- C₃ as a tracer of the physical conditions of the ISM, and as a precursor of heavier carbon clusters
- Deuterium hydrides as probes of chemistry
- HF as a tracer of molecular hydrogen

- The role of surface reactions in the formation of interstellar molecules
- The size distribution of carbon clusters in the ISM

We will also take the opportunity of having gathered deep integrations over a broad spectral range for searching for new spectral features, in the HIFI and PACS data. The main targets will be large carbon molecules (carbon clusters, PAHs, ...) guided by laboratory work and theoretical predictions of consortium members. But we expect to also detect new spectral features revealing the presence of new chemical species in the ISM.

The initial analysis of the Herschel data will take place within the framework of the “hot” science questions, but we anticipate that the full exploitation of the data set will take place after its initial publication and dissemination via the public archive. Indeed, all data (from Herschel and ancillary ground based observations) will be made publicly available to be used for further and deeper analysis. Because Herschel will, for the first time, open the far infrared domain to high resolution spectroscopy, most of the spectral features we aim at, will be observed for the first time. New spectral features are likely to be present at well.

Therefore, the discovery potential of the data is not likely to be limited to the first analysis. It is likely that our data will be used for testing advanced radiative transfer models of the molecular line excitation, in conjunction with sophisticated chemical models of the diffuse interstellar medium. The development of such models is going on, as a preparatory effort, but the models will need to be first checked against Herschel data to reach maturity. We expect that the Herschel data will trigger new advances in modeling.

We also expect that follow up work will be necessary with Herschel itself, and/or with other instruments. Finally, as described above, the same studies of the interstellar medium which is performed locally in the Milky Way, will be made possible in distant galaxies with ALMA. Once established and tested in the Milky Way, the new diagnostic capabilities of the ISM offered by the spectral lines we aim at, e.g. HF and CH as tracers of molecular hydrogen, or CH⁺ as a tracer for warm chemistry, will be used for a deeper understanding of the ISM at high redshift.

3 Relation to past or future observations

Our consortium is already engaged in preparatory observations of the selected sources, using major international facilities (IRAM, CSO, VLA, ESO, etc.) together with extensive use of the ISO archive. These ancillary data we are collecting will reinforce the value of the Herschel observations by providing an homogeneous database from which a chemical inventory of the diffuse and translucent ISM will be built.

As described above, absorption line spectroscopy has been used for probing the interstellar medium since the 1940’s. New instruments always have contributed new and exciting results to interstellar medium science. The most recent discoveries by ISO, SWAS and ODIN, have questioned our understanding of oxygen chemistry (Neufeld et al. 2002), and have led to the detection of new interstellar lines, and to new interstellar species (Polehampton et al. 2007). Only the new frequency regimes and the sensitivity step provided by Herschel will allow us to continue this “success story”. The opportunity offered by Herschel should not be missed for the following reasons:

- Although very few hydride lines can be observed from the ground in the submillimeter region, most of them will be possibly accessible with SOFIA in the future, except for the water and CH⁺ lines which are unique to HIFI. However, HIFI is more sensitive than SOFIA because of the larger telescope size, and the lack of telluric features, which could overlap with the pattern of interstellar absorption features under investigation.
- Many of the absorption lines that are detectable only with Herschel in the local Universe become accessible to ground-based observatories at moderate to high-redshift. Thus, hydride absorption lines in quasar spectra are a potential probe of molecular gas at high-z; in the submillimeter spectral region, the high sensitivity of ALMA will generally be required. **Herschel observations of hydride absorption in the local Universe will provide an important benchmark for the future observations at high redshift that will become possible with ALMA** – particularly in the case of hydrogen fluoride, discussed in Appendix C below.

4 Technical implementation

4.1 Observing strategy and time requirements

We have selected 8 background sources (see Table 2), which have strong far infrared continuum emission, and intervening interstellar clouds along the line of sight, as evidenced by existing data (on HI, HCO⁺, H₂O, OH, H₃⁺, and other species, from ISO, SWAS and ODIN as well as ground based telescopes). The number of sources has been set so as to obtain more than 20 independent measurements from the numerous velocity components already known along those lines of sight. Because the sources are located at different galactocentric distances, this sample enables us to cover a wide variety of physical conditions in the interstellar medium, and to probe radial gradients of gas properties in the Galaxy which may result from the known Galactic gradients in elemental abundances or isotopic ratios. For instance, deuterated species are expected to be sensitive to the elemental D/H ratio.

Table 2: Absorption line sources

Name	R.A. (J2000)	Dec (J2000)	F _{100μm} ^a (Jy)	F _{350μm} ^b (Jy)	D ^c (kpc)	Priority
Sgr A (+ 50 km/s cloud)*	17 45 51.7	-28 59 08.7	23300	370	8.6	2
G005.88-0.39 (W28A)	18 00 30.4	-24 04 00	26800	950	3.8	2
G10.62-0.39 (W31C)	18 10 28.7	-19 55 50	21400	1110	4.8	1
W33A*	18 14 39.4	-17 52 00	6310	350	4.0	3
G34.3+0.1	18 53 18.7	01 14 58	32500	1125	3.8	1
W49N	19 10 13.2	09 06 12	36200	~ 2000	11.5	1
W51	19 23 43.9	14 30 30.5	26800	~ 1500	7.0	1
DR21(OH)*	20 39 00.7	42 22 46.7	~ 10000	800	1.0	1

^a IRAS, ^b Sandell (1994, 2000), van der Tak et al. (2000), Goldsmith et al. (1990), Mueller et al. (2002), Dowell et al. (1999), ^c Source distance,

* H₃⁺ observations near the same line of sight

4.1.1 HIFI Observations of hydride lines

The selected lines are listed in Tables 3. The same set of lines will be observed towards the Sgr B2 line of sight, as a part of the HEXOS key programme, where additional 15 hours are allocated for these observations. To illustrate the sensitivity of the proposed observations, opacities of ground state transitions, calculated for a column density of 10¹³ cm⁻² and a line width of 1 km s⁻¹ in the absence of collisional excitation (i.e. with $T_{ex} = 2.73$ K) are given. Even for absorption lines, the derivation of column densities is dependent upon the excitation conditions. While the assumption of a low excitation temperature is valid for most diffuse clouds, it can lead to severe errors in the derived column density if the line is formed in very dense or radiatively-pumped gas. To circumvent such errors, we propose to search for absorption from excited levels for selected species that are expected to produce the strongest features: H₂O, H₃O⁺, CH⁺, CH, and NH₃.

From published ground-based and space data, we expect continuum intensities of hundreds of Jy in the HIFI domain. Table 2 lists fluxes at 350 μ m. With a telescope sensitivity of 450 Jy/K, these fluxes correspond to continuum level (SSB) from 0.8 to 4 K at 350 μ m. We will observe in double beam switching mode as the continuum sources are moderately extended compared to the Herschel beam. Using HSPOT v2.0, we have computed observing times for all sources and lines, using a uniform velocity resolution goal of 0.5 kms⁻¹, and a conservative upper limit of 1 kms⁻¹. The observing times are listed in Table 5 for the template source W31C. The S/N ratio on the continuum is 50 – 80 for a velocity resolution of 1 kms⁻¹. Therefore, we will be able to detect signals as weak as $\tau = 0.1$ at the 5 σ level, reaching a similar sensitivity as visible spectroscopy of CH or CH⁺. We propose to observe in the "frequency clustering mode" with 3 LO tunings per target frequency. According to the HIFI project, this adds 90s overhead time per LO tuning, which are not implemented into HSPOT yet. We have also selected 7 frequencies for accurate determination

Table 3: Proposed line frequencies. Higher priority lines are listed on the left side, lower priority on the right side

Molecular transition	E_l (K)	Frequency (GHz)	τ^a	Molecular transition	E_l (K)	Frequency (GHz)	τ^a
o-H ₂ ¹⁸ O 1 _{1,0} – 1 _{0,1}	0	547.676	1.80	HDO 1 _{1,1} – 0 _{0,0}	0	893.639 ^b	3.54
o-H ₂ O 1 _{1,0} – 1 _{0,1}	0	556.936	1.80	D ₂ O 1 _{1,1} – 0 _{0,0}	0	607.350 ^b	4.03
p-H ₂ O 2 _{1,1} – 2 _{0,2}	89	752.033		D ₂ O 2 _{1,1} – 1 _{0,1}	0	897.947 ^b	1.89
p-H ₂ O 2 _{0,2} – 1 _{1,1}	53	987.927		ND ³ Σ ⁻ 1, 1/2 – 0, 1/2	0	522.077 ^c	
p-H ₂ ¹⁸ O 1 _{1,1} – 0 _{0,0}	0	1101.698	4.00	NH ₂ D 1 _{1,0} – 0 _{0,0}	0	494.454 ^b	0.62
p-H ₂ O 1 _{1,1} – 0 _{0,0}	0	1113.343	4.00	H ³⁷ Cl 1 – 0	0	624.978 ^b	0.72
o-H ₂ ¹⁸ O 2 _{1,2} – 1 _{0,1}	0	1655.868	1.80	H ³⁵ Cl 1 – 0	0	625.919 ^b	0.72
o-H ₂ O 2 _{1,2} – 1 _{0,1}	0	1669.905	1.78	DF 1 – 0	0	651.099 ^b	3.88
OH ⁺ ³ Σ ⁻ 1, 2, 5/2 – 0, 1, 3/2	0	971.804	3.2	H ³⁵ Cl ⁺ ² Π _{3/2} 5/2 – 3/2	0	1444.595 ^c	
o-H ₃ O ⁺ 0 ₀ ⁻ – 1 ₀ ⁺	7	984.697	0.3				
p-H ₃ O ⁺ 1 ₁ ⁻ – 1 ₁ ⁺	0	1655.814	1.10	U175.068		1712.4	
H ₂ O ⁺ 1 _{1,1} – 0 _{0,0}	0	1115.150 ^c					
H ₂ O ⁺ 1 _{1,0} – 1 _{0,1}	0	607.224 ^b					
H ₂ O ⁺ 1 _{1,0} – 1 _{0,1}	0	631.773 ^b					
¹³ CH ⁺ 1 – 0	0	830.131	1.17				
CH ⁺ 1 – 0	0	835.079	1.17				
CH ⁺ 2 – 1	40	1670.16					
CH ² Π _{3/2} 1, 2 – ² Π _{1/2} 1, 1	0	532.724	0.26				
CH ² Π _{3/2} 1, 2 – 1/2 1, 1	0	536.761	0.27				
CH ² Π _{5/2} 2, 3 – 3/2 1, 2	26	1656.961	0.08				
CH ² Π _{5/2} 2, 3 – 3/2 1, 2	26	1661.107	0.08				
¹³ CH ² Π _{3/2} 1, 2 – 1/2 1, 1	0	532.104	0.26				
¹³ CH ² Π _{3/2} 1, 2 – 1/2 1, 1	0	536.113	0.27				
¹³ CH ² Π _{5/2} 2, 3 – 3/2 1, 2	26	1647.239	0.08				
¹³ CH ² Π _{5/2} 2, 3 – 3/2 1, 2	26	1661.107	0.08				
o-CH ₂ 1 _{1,1} – 2 _{1,2}	65	945.839 ^c					
NH ³ Σ ⁻ 1, 1/2 – 0, 1/2	0	974.479 ^c	0.63				
NH ⁺ ² Π _{1/2} 3/2 – 1/2	0	1012.561 ^c					
o-NH ₂ 1 _{1,1} – 0 _{0,0}	0	952.578 ^c	0.57				
NH ₃ 1 ₀ – 0 ₀	0	572.498	2.46				
NH ₃ 2 ₀ – 1 ₀	23	1214.859					
NH ₃ 2 ₁ – 1 ₁	28	1215.245					
HF 1 – 0	0	1232.476	3.91				
p-D ₂ H ⁺ 1 ₁₀ – 1 ₀₁	0	691.660 ^b					
C ₃ ν 2 P(10)	66	1654.082	bonus				
C ₃ ν 2 P(4) 12		1787.896					
C ₃ ν 2 Q(2)	4	1890.558					
C ₃ ν 2 Q(4)	12	1896.706					
C ₃ ν 2 Q(6)	26	1906.338					

^a Optical depth for a linewidth of 1 km s⁻¹ and column density of 10¹³ cm⁻²

^b Line detectable from the ground under excellent atmospheric conditions (but severe absorption limits the precision of flux measurements) .

^c Complex hyperfine structure pattern

of the continuum flux, using the continuum stabilisation mode (see Table 6). We will spend the same observing time on all sources. The time required for this investigation of hydrides is **86.27 hours**.

4.1.2 HIFI observations of carbon chains

We propose to observe 4 ro-vibrational lines of C_3 , and to perform deep integration with HIFI at selected transitions of the heavier carbon chains C_{10} , C_{11} and C_{13} , when the frequencies will be known from the on-going laboratory spectroscopy in Cologne. The corresponding integration times for W31C are given in Table 7. We propose to perform C_3 observations toward the full sample and to restrict the search for heavier carbon clusters to the two most promising sources, based on the C_3 results. The time required for this investigation of carbon clusters is **21.37 hours**.

4.1.3 PACS Observations

The HIFI spectroscopic observations ($\lambda > 157 \mu\text{m}$) described above will be complemented with additional far-IR ($\lambda \simeq 57$ to $210 \mu\text{m}$) PACS scans. The PACS wavelength domain contains the spectral signatures of key ionic, atomic and molecular species that will support HIFI observations and help to better constrain the physical conditions and chemical content of the selected line-of-sights. Working as an integral field multibeam spectrometer, PACS provides a field of view of $47'' \times 47''$ by simultaneous observations of 5×5 pixels (i.e., an angular resolution of $9.4''$ per pixel). Therefore, each requested PACS full line survey consist of 25 multibeam surveys. These PACS small maps will allow to infer the true (small scale) spatial distribution of some of the most important species for this project (H_2O , CH , C_3 , HF ,...) detected in HIFI single-beam observations. We will make use of the information on the line profile from our HIFI and ground-based data to analyse the PACS data where the lines will be spectrally unresolved. We propose to perform full scans in the fast SED-mode, with three repetitions and to observe the extended source SgrA in the pointing-and-dithering mode for a total of **20.29 hours** (10 hours of mission scientist time from J. Cernicharo and P. Encrenaz, and 10.29 hours from the HIFI consortium). The detailed time estimates for PACS are given in Table 8 and 9.

4.2 Special requirements and constraints

Because of the limited chopping throw of 3 arcminutes, the Galactic Center observations may will require scheduling constraints in order to select a chopping direction. The selected sources have however been chosen as having a compact continuum core.

4.3 Impact of different instrument sensitivity

The consortium has agreed on different priorities for the selected sources as listed in Table 2, and for the selected lines. The highest priority sources will be selected for the observations in case of reduced sensitivity of PACS or HIFI. Furthermore, as we target spectral lines distributed over all HIFI bands, the programme will not be severely affected by the loss of a particular HIFI sub-band. In order to keep the survey as complete as foreseen, we plan to descope first by reducing the number of sources to be observed, and second the number of lines. We wish to keep the discovery potential of this programme open by giving the high priority to the new interstellar species which have not been observed/detected before in the ISM.

Furthermore, we propose to schedule the observations in such a way as to perform the highest priority observations first. This will allow us to check the Herschel performances. In case the performances are not optimal, we propose to spend more time on the high priority observations, and to withdraw the lower priority observations, as high S/N data are required for reaching our science goals ($S/N > 40$).

5 Description of data processing plan and archival data products and tools that will be produced

5.1 Data processing

We have chosen the same observing modes for all HIFI observations, as we wish to have a homogeneous survey. Data reduction of the HIFI observations will be performed using the HIFI reduction software, and other, publicly available, spectroscopic softwares. Team members have extensive experience with ground based millimeter and submillimeter telescopes (IRAM, CSO). Some have been involved with previous satellite data as well (ISO, Spitzer, SWAS and ODIN). We plan to perform the HIFI observations with different LO tunings in the “frequency clustering mode” which requires minimum overhead time, so as to be able to separate the signals from the two sidebands of the SIS mixers. Our team has been associated with the efforts of the HIFI sideband deconvolution team (P. Hennebelle, K. Menten, J. Stutzki, M. Perault), and we will work in close connection with the HEXOS team to exchange information on the HIFI results and data processing methods.

Data reduction of PACS full line surveys will be performed using the PACS data reduction software, with the help from A. Contursi from the PACS/ICC. The team has extensive experience in far-IR line surveys based upon ISO spectral scans with the LWS instrument (*e.g.* Goicoechea et al. 2004). In addition, the DAMIR/Madrid group has funding for a software engineer (3 years) to help in the PACS data analysis and software development.

Line identification will make use of the available on-line catalogs (JPL and CDMS), and additionally will use the personal catalog maintained by J. Cernicharo (DAMIR/Madrid). Team members from the JPL (J. Pearson) and CDMS (T. Giesen) groups have access to molecular spectroscopy laboratories, which could provide support to line assignment, and new frequency measurements in advance for publication.

The data processing will be performed using the same data reduction routines for all observations, with fine tuning for specific frequency domains. The scripts used for data reduction will be publicly available, once fully tested.

5.2 Science exploitation and advanced data analysis

The science exploitation will progress in several steps. After the Herschel data are properly calibrated and corrected from instrumental artifacts, we will start by identifying the emission and absorption spectral features. Experts in molecular spectroscopy (J. Pearson, T. Giesen, E. Herbst, J. Cernicharo, ...) will help in checking that the automatic identification done using line catalog, is reliable. The next step will be the derivation of column densities under simple assumptions. The absorption features are produced by intervening clouds along the line of sight, which have low to medium density and temperature. Hence the molecular line carriers are predicted to have low excitation temperatures. Therefore, we will use the assumption of a low excitation temperature, and Boltzmann populations to derive column densities for all species seen in absorption.

The level population of carbon clusters is governed by collisions and pumping. We will make use of specific excitation models for such species developed by independent teams (J. Krelowski & R. Kolos, J. Black, J. Cernicharo) for predicting the individual C₃ line strengths, and the expected band profiles for the heavier clusters, and compare with the observations. Even if individual lines are not resolved, it is expected that a clear identification is possible by comparing the band position and profile with detailed modeling (see Cernicharo et al (2002) for C₄ spectra using ISO-LWS).

The emission lines are produced in the hot cores associated with the star forming region in the background. We will use specific software tools (*e.g.* CASSIS, and XCLASS) to analyse these emission spectra in collaboration with the HEXOS team.

In a following step, we will compare various models to the Herschel observations. We will use stationary PDR models fitted to the conditions of the diffuse interstellar medium (*eg* Neufeld et al 2005 for the fluorine chemistry), but we will also make use of models combining chemistry and MHD for investigating the hot chemistry (*e.g.* Falgarone et al. 2006, Lesaffre et al. 2007). The carbon chemistry will be investigated by comparing several chemical networks, including the production of carbon clusters from carbonaceous grains.

5.3 Archive and data products

We have prepared a web accessible data base, which will contain all information about our programme. Herschel data, together with preparatory work from ground based observations, will be made available through this tool (<http://www.lra.ens.fr/hifi-abs>). The data base will also provide documentation on how the data were observed and how they were processed. The data base is currently password protected, but we will allow public access when the data are ready to be distributed.

We will provide calibrated spectra, including the available level of expertise for correcting for instrumental effects (e.g. baseline artifacts). The observing mode we have chosen will allow us to perform side band separation for most of the spectral features (emission or absorption) we will detect. This analysis step will be performed in collaboration with the HEXOS team in charge of the complete line survey towards SgrB2. Within the spectra, we will provide spectroscopic identification for the absorption lines which are part of our programme (based on line catalogs or on new laboratory spectroscopy), and we will do our best to identify the emission lines from the background sources as well as unexpected absorption features. Team members from the HEXOS programme (D. Lis, T. Bell) will take the lead in the analysis of the emission line spectra from the hot cores, using the information from the complete line surveys towards SgrB2 sources.

While calibrated spectra will be our main data product, we propose to provide tables listing line positions (frequency, velocity, line widths) and line integrated intensities for the foreground absorption features, as well as for the detected emission features from the hot cores. From the continuum stabilisation measurements, we will also provide continuum fluxes of the programme sources at selected frequencies over the Herschel frequency range.

The PACS spectral scan will be analysed using dedicated software from the PACS team. We will also provide the same data products, plus continuum maps across obtained with the PACS array. We also propose to provide line maps resulting from the PACS observations of the strongest spectral features within the PACS wavelength range which are important for diffuse ISM chemistry : HD, OH, CH, and H₂O ground state lines at 112, 119, 150 and 179 μm respectively.

Several groups within the consortium are developing models of the diffuse interstellar gas chemistry. While the models will stay proprietary to each, we will make the results of model fits to the Herschel Observations accessible on our web site.

6 Management and Outreach plan

6.1 Organization and Management Plan

The team gathers experts in all fields, from laboratory spectroscopy, theoretical modeling and multi-wavelengths observations, as explained in the short CVs (see B). Experts of both the HIFI and PACS instruments are part of the team to ensure a timely reduction and publication of the Herschel data. The project has been divided into specific investigations and tasks, which will be coordinated as follows :

- H₂O, HF and related species (D. Neufeld, D. Lis)
- CH⁺, NH and related species (E. Falgarone, M. Gerin)
- C chains and related species (T. Giesen, J. Krelowski)
- PACS spectral scans (J. Goicoechea, A. Contursi)
- D species (C. Vastel, J. Black)
- Emission lines from background sources (D. Lis, T. Bell)
- DSB deconvolution (P. Hennebelle, J. Stutzki)

Complementary ground based observations are being obtained at radio (VLA, IRAM) and IR wavelength. The affiliate T. Geballe and the associate E. Dartois have agreed to help with the IR observations

Table 4: Preliminary time allocation for the PRISMAS project (hours)

	USA	France	Germany	Poland	Sweden	Canada	MS ^a	Total
Hydrides	36	30	0	5	10	5	0	86
C Cluster	0	0	17	5	0	0	0	22
PACS	0	5	5	0	0	0	10	20
Total	36	35	22	10	10	5	10	128

^a Mission Scientists (J. Cernicharo and P. Encrenaz)

while low frequency radio observations (VLA, ATNF, Green-bank or Effelsberg 100m) observations are organised by P. Goldsmith, D. Neufeld, K. Menten and C. Vastel. B. Mookerjea and D. Lis have retrieved previous continuum observations from JCMT (SCUBA) and CSO (SHARC). P. Hily-Blant, M. Gerin and E. Falgarone are taking care of preparatory IRAM observations.

Regular consortium teleconferences ($\sim 4/year$) and meetings (1 / year before launch, more often during the first year) will be organised for following the progresses on data reduction, scientific analysis and preparation of publications of the Herschel observations.

6.2 Consortium resources

The allocated time for this project is 128 hours, split as described in table 4.

Most of the listed consortium members have permanent research positions. They will devote a significant fraction of their research time (from $\sim 30\%$ to $\sim 100\%$) to the analysis and publication of the Herschel data. The consortium resources will be strengthened by the participation of new post-docs and students. Some of these younger scientists are already identified and therefore listed among the consortium members. More young scientists are expected to join the team in the coming years, as we expect new funding to be accessible after Herschel is successfully launched. Overall, we can estimate that the manpower resources for this programme amounts to at least 13 man.year for the each of the 3 years of the Herschel mission.

The data base will be managed with help from JF Rabasse, software engineer in LERMA/CNRS.

6.3 Outreach

The uniqueness of the Herschel data warrants publicity towards the public, and especially students from high school to undergraduate level. We will collaborate with ESA, our national funding agencies and research institutes for communicating them our best results in advance of publication, and help them for preparing reports and press releases. The public access to our consortium site will include pages accessible to the general public together with more specialized information for astronomers.

E. Falgarone will be the delegate of the consortium for outreach.

References

- Adams W.S., 1941, ApJ 93, 11.
- Bergin, E.,A., Ciardi, D.R., Lada, C.J., Alves, J., Lada, E.A. 2001, ApJ, 557, 209.
- Black J., 1998 Faraday Discussion 109, 257.
- Boonman A.M.S. et al., 2003, A&A 406, 937.
- Botschwina P., 2006, CPLett 421, 488-493.
- Botschwina P., 2007, Priv. communication.
- Cernicharo J., Goicoechea J. R, Caux E., 2000, ApJ 534, L199.
- Cernicharo, J., Goicoechea, J. R., Bénilan, Y., 2002, ApJ 580, L57.
- Cernicharo J., Goicoechea J. R, Pardo, J.R., Asensio-Ramos, A. 2006, ApJ, 642, 940.
- Comito C. et al., 2003, A&A 402, 635
- Crane et al., 1995, ApJ suppl. 99,107.
- Crawford, I. A., Williams, D. A., 1997, MNRAS 291, L53.
- Douglas A.E., Herzberg G., 1941, ApJ 94, 381
- Douglas A.E. Nature, 269, 130.
- Dowell C. D. et al., 1999, in *The Central Parsecs of the Galaxy*, ASP Conference Series, Vol. 186. p 453.
- Draine B.T., 1980, ApJ 241 1021.
- Falgarone et al., 1995, A&A 300, 870.
- Falgarone E., Phillips T.G., Pearson J., 2005, ApJ 603, L149.
- Falgarone E., Pineau des Forêts G., Hily-Blant P., Schilke P., 2006, A&A 452, 511.
- Flower D., Pineau des Forêts G., 1998, MNRAS 297, 1182.
- Flower D., Pineau des Forets, G., Walmsley, C. M. 2004, A&A, 427, 887.
- Galazutdinov G. et al. 2002, A&A, 395, 969.
- Galazutdinov G., Han I., Bondar A., Krelowski J., Cecchi-Petsellini C., Aiello S., and Musaev F.A., 2007, submitted to ApJ.
- Gerin, M., Fosse, D., Roueff, E. 2003 in *Chemistry as a Diagnostic of Star Formation, proceedings of a conference held August 21-23, 2002 at University of Waterloo, Waterloo, Ontario, Canada N2L 3G1. Edited by Charles L. Curry and Michel Fich. 2003*, p. 81.
- Giesen T. et al., 2001, ApJ 551, L181.
- Goicoechea, J.R. & Cernicharo J. 2002, ApJ 576, L77
- Goicoechea J.R., Rodriguez-Fernandez, N., Cernicharo, J. 2004a, ApJ, 600, 214.
- Goicoechea J.R., Cernicharo, J., Masso, H., Senent, M.L. 2004b, ApJ, 609, 225.
- Goldsmith P.F., Lis D.C., Hills, R., Lasenby J. 1990, ApJ 350, 186.
- Goldsmith P.F., et al. 2002, ApJ, 576, 814.
- Gredel R., 1997, A&A 320, 929.
- Herbig G.H., 1975, ApJ, 196, 129.
- Herbig G.H., 1995, ARA&A 33, 19.
- Herbst E., 2005, *Proceedings of "The dusty and molecular universe: a prelude to Herschel and ALMA"*, Ed. by A. Wilson. ESA SP-577, p. 205-210.
- Hjalmarson A et al., 2006, Adv. Space Research , submitted.
- Jenkins E.B. & Tripp T.M., 2001, ApJ suppl. 137, 297.
- Joulain et al. 1998, A&A 340, 241.
- Kaufman, M. et al. in *Astrochemistry Throughout the Universe: Recent Successes and Current Challenges, International Astronomical Union. Symposium no. 231, Asilomar, California, USA. Edited by Dariusz C. Lis, Geoffrey A. Blake & Eric Herbst. Cambridge University Press, 2005.*
- Larsson B., Liseau R., Pagani L. et al., 2007, A&A in press.
- Le Petit, F., Roueff, E., Le Bourlot, J. 2002, A&A, 390, 369.
- Lesaffre P., Hennebelle P., Gerin, M., 2007, A&A in press.
- Liseau, R., Fridlund, C. V.,M., Larsson, B. 2005, ApJ, 619, 959.
- Liszt H. & Lucas R., 2000, A&A 358, 1069.
- Lucas R. & Liszt H.S., 1996, A&A, 358.1069.

Maier, John P., Lakin, N.M., Walker, G.A. H., Bohlender, D.A. 2001, ApJ, 553, 267.
McCarthy, M. C., Gottlieb, C. A., Gupta, H., Thaddeus, P. 2006, ApJ, 652, L141.
Mckellar A., 1941, PASP 53, 233.
Mueller, K. E., Shirley, Y.L., Evans, N.J., II, Jacobson, H.R. 2002, ApJS, 143, 469.
Neufeld D. et al., 1997, ApJ 488, L141.
Neufeld D. et al., 2002, ApJ 580, 278.
Neufeld D, Wolfire, M.G., Schilke, P. 2005, ApJ, 628, 260.
Oka T. et al., 2003, ApJ 582, 823.
Pagani, L., et al. 2003, A&A, 402, L77.
Pan, K., Federman S. R., Welty, D. E., 2001, ApJ 558, L105.
Pety J., Teyssier, D., Fosse, D., Gerin, M., Roueff, E., Abergel, A., Habart, E., Cernicharo, J. 2005, A&A, 435, 885.
Plume R. et al., 2004, ApJ 605, 247.
Polehampton E.T. et al., 2007, MNRAS in press.
Rachford, B.L, et al. 2002, ApJ, 577, 22.
Roberts, H., Herbst, E., Millar, T. J. 2003, ApJ, 591, L41.
Roueff, E., Lis, D. C., van der Tak, F. F. S., Gerin, M., Goldsmith, P. F. 2005, A&A, 438, 585.
Salez M. et al., 1996, ApJ 467, 708
Sandell G., 1994, MNRAS 271, 75.
Sandell G., 2000, A&A 358, 242
Sandqvist A. et al., 2003, A&A 402, L63
Schilke P. et al. 1995, ApJ 441, 334
Swings P., Rosenfeld L., 1937, ApJ 86, 483.
Teyssier, D., Fosse, D., Gerin, M., Pety, J., Abergel, A., Roueff, E. 2004, A&A, 417, 135.
Van der Tak F.S. et al., 2000, ApJ 537, 283.
Van Dishoeck, E.F., Jansen, D.J, Phillips, T.G., 1993, A&A 279, 541
Van Orden, A., Cruzan, J.D., Provençal, R. A., Giesen, T. F., Saykally, R. J., Boreiko, R. T. & Betz, A. L. 1995, Airborne Astronomy Symp. on Galactic Ecosystem, ASP Conf. Ser. Vol. 73, 67.

A Observing time estimate

In the following tables, we give expected sensitivity and observing times of the proposed observations, performed with HSPOT 2.0. The observations are listed for one source W31C. The same settings and integration times will be used for all sources.

Table 5: HIFI settings per source (e.g. W31C). Estimations with HSPOT 2.0. S/N means continuum signal-to-noise ratio in a 1 km s^{-1} resolution element.

Species	Frequency (GHz)	Band	Flux (Jy)	T_{rms} (K)	S/N	HSPOT	Time (s)
NH ₂ D	494.455	Ia	370	0.017	48		724
ND	522.077	Ia	412	0.014	65		531
¹³ CH	532.104	Ia	428	0.014	68		531
CH	532.724	Ia	429	0.014	68	with ¹³ CH	
¹³ CH	536.113	Ia	435	0.014	69		531
CH	536.761	Ia	436	0.014	69	with ¹³ CH	
o-H ₂ ¹⁸ O	547.676	Ia	454	0.015	67		531
o-H ₂ O	556.936	Ia	469	0.015	70		531
NH ₃	572.498	Ib	496	0.017	65		531
H ₂ O ⁺	607.224	Ib	558	0.017	73		571
D ₂ O	607.350	Ib	558	0.017	73	with H ₂ O ⁺	
H ³⁷ Cl	624.978	Ib	591	0.017	77		571
HCl	625.919	Ib	593	0.019	69	with H ³⁷ Cl	
H ₂ O ⁺	631.773	Ib	604	0.017	79		571
DF	651.099	IIa	641	0.020	71		700
p-D ₂ H ⁺	691.660	IIa	724	0.024	67		700
p-H ₂ O	752.033	IIIb	856	0.029	66		700
¹³ CH ⁺	830.131	IIIa	1043	0.034	68		790
CH ⁺	835.079	IIIa	1055	0.034	69		745
HDO	893.639	IIIb	1208	0.036	75		724
D ₂ O	897.947	IIIb	1220	0.036	75		724
o-CH ₂	945.813	IIIb	1354	0.039	77		724
NH ₂	952.578	IIIb	1373	0.039	78		724
OH ⁺	971.804	IVa	1429	0.044	72		822
NH	974.479	IVa	1437	0.043	74		822
o-H ₃ O ⁺	984.697	IVa	1467	0.044	74		822
p-H ₂ O	987.927	IVa	1477	0.051	64		661
NH ⁺	1012.561	IVa	1551	0.046	75		748
p-H ₂ ¹⁸ O	1101.698	IVb	1837	0.062	66		564
p-H ₂ O	1113.343	IVb	1876	0.063	66		564
H ₂ O ⁺	1115.150	Va	1882	0.080	52		886
NH ₃	1214.859	Vb	2233	0.098	51	with NH ₃	
NH ₃	1215.245	Vb	2235	0.098	51		982
HF	1232.476	Vb	2298	0.105	49		949
H ³⁵ Cl ⁺	1444.700	VIa	3155	0.159	33		1498
o-D ₂ H ⁺	1476.606	VIa	3299	0.154	36		1498
p-H ₃ O ⁺	1655.814	VIIb	4149	0.144	48		1193
o-H ₂ ¹⁸ O	1655.868	VIIb	4149	0.144	48	with H ₃ O ⁺	
CH	1656.961	VIIb	4154	0.144	48		1193
CH	1661.107	VIIb	4175	0.145	48		1193
¹³ CH	1661.107	VIIb	4175	0.145	48	with CH	
CH ⁺	1669.160	VIIb	4221	0.149	47		1144
o-H ₂ O	1669.905	VIIb	4219	0.149	47	with CH ⁺	
U175.068	1712.400	VIIa	4437	0.170	43		965
C ₃	1787.896	VIIb	4837	0.150	54		1144
C ₃	1890.558	VIIb	5408	0.148	61		1144
C ₃	1896.707	VIIb	5443	0.148	61		1144
C ₃	1906.338	VIIb	5499	0.148	62		1144

sub-total: **9.23 hours**

+Frequency clustering overhead: 1.00 hours

contamination stability: 1.00 hours

Table 6: HIFI continuum optimization measurements per source (e.g. W31C). S/N means continuum signal-to-noise ratio in a 1 km s^{-1} resolution element.

Species	Frequency (GHz)	Band	Flux (Jy)	T_{rms} (K)	S/N	HSPOT Time (s)	
o-H ₂ O	556.936	Ia	469	0.035	30	385	
p-H ₂ O	752.033	IIb	856	0.080	24	385	
HDO	893.639	IIIb	1208	0.122	22	382	TOTAL: 1.82 hours
p-H ₂ O	1113.343	IVb	1876	0.180	23	382	
NH ₃	1215.245	Vb	2235	0.239	21	790	
o-H ₂ O	1669.905	VIb	4219	0.753	9	2295	
C ₃	1896.707	VIIb	5443	0.867	10	1938	

Table 7: C_n deep integrations HIFI settings (2×4 GHz). With HSPOT 2.0.

Species	Frequency (GHz)	Band	Flux (Jy)	T_{rms} (K)	S/N	HSPOT Time (s)
C ₁₃	690-low	IIa	720	0.011	146	2558
C ₁₃	690-high	IIa	720	0.011	146	2558
C ₁₁	944-low	IIIb	1348	0.022	136	1912
C ₁₁	944-high	IIIb	1348	0.022	136	1912
C ₁₀	1193-low	Vb	2154	0.037	129	5340
C ₁₀	1193-high	Vb	2154	0.037	129	5340
sub-total:					5.45 hours	
+Frequency clustering overhead:					0.15 hours	
TOTAL:					5.60 hours	

Table 8: PACS line survey in SED mode per source (e.g. W31C). HSPOT 2.0.

Wavelength range (microns)	Wavelength sampling	Continuum rms (Jy)	5σ sensitivity (W m ⁻²)	HSPOT time (s)
BLUE 55-72	<i>Nyquist</i>	~1.37	~9.1e-17	3255
RED 72-210	<i>Nyquist</i>	~0.27	~2.5e-17	5853
TOTAL:			TOTAL:	2.53 hours

Table 9: PACS line survey in pointing+dither mode (SgrA) . HSPOT 2.0.

Wavelength range (microns)	Wavelength sampling	Continuum rms (Jy)	5σ sensitivity (W m ⁻²)	HSPOT time (s)
BLUE 55-72	<i>Nyquist</i>	~1.37	~9.1e-17	3337
RED 72-210	<i>Nyquist</i>	~0.27	~2.5e-17	5935
TOTAL:			TOTAL:	2.58 hours

B Curriculum Vitae

We provide below a short description of the projected roles of the consortium members. This list includes HIFI co-Is, together with associate and affiliate members which will contribute significantly to the programme. Associate members include T. Bell, E. Dartois, P. Hennebelle, P. Hily-Blant, J. Goicoechea, B. Mookerjee, M. Schmidt, while T. Geballe and K Menten are affiliate members, whose expertise in ground based IR and Radio observations will increase the scientific value of this programme. The list is still evolving. It is likely that new members will join the team, especially new students or post-docs.

Maryvonne Gerin (PhD 1988, Université Paris 7)

Senior scientist (directeur de recherche) at CNRS. ODIN and HIFI co-Investigator, coordinator of the PRISMAS key programme.

M. Gerin will manage the programme, assist in the data reduction and analysis of the C-,N- and D-hydride observations, and in the ancillary ground based observations.

John H. Black (PhD 1975, Harvard University)

Professor of Radio Astronomy, Chalmers University of Technology, Sweden. ODIN and HIFI co-I.

J. Black will assist in theoretical modelling of the molecular excitation and chemistry, and for Deuterium chemistry.

Tom A. Bell (PhD 2006, University College, London)

Postdoctoral Scholar, California Institute of technology. Programme associate.

T. Bell will assist in the coordination with the HEXOS program, and in the data reduction and analysis for the O-, F- and Cl-hydrides.

François Boulanger (PhD 1987, Université Paris 7)

Directeur de Recherche (CNRS) at the Institut d'Astrophysique Spatiale Université Paris Sud Orsay, France and HIFI co-I.

F. Boulanger will assist in the HIFI and PACS data analysis, working on dust continuum modelling and on the C- and N-hydride chemistry.

José Cernicharo (Ph.D. 1988 University Paris 7)

Research professor at the Consejo Superior de Investigaciones Científicas (CSIC). Herschel Mission scientist.

J. Cernicharo will help in the analysis of the PACS spectral scans, in coordination with the leaders of the chemistry sub-programmes. He will contribute to the line identification work, and to the line excitation modelling, using proprietary software tools.

Alessandra Contursi (PhD University "Pierre et Marie Curie " Paris VI 1998)

PACS calibration scientist at the Max Planck Institute für Extraterrestrische Physik, Garching, Germany. PRISMAS associate.

As a PACS calibration scientist, A. Contursi will help in the PACS data planning and analysis.

Emmanuel Dartois (Ph.D., Orsay, 1998)

CNRS staff scientist at the Institut for Space Astrophysics (IAS) in Orsay. PRISMAS associate

E. Dartois will work on the hydride emission and absorption analysis and contribute to the ground based IR spectroscopic observations. He will also aid with laboratory spectroscopy.

Pierre Encrenaz (PhD 1972)

Professor, University Pierre and Marie Curie and Paris Observatory

Member of the Cassini radar and radiometer team

Co-Investigator on the Miro instrument on Rosetta

Member of the French Academy of Sciences
ODIN co-I and Herschel Mission Scientist
P. Encrenaz will work with J. Cernicharo on the PACS spectral scans.

Edith Falgarone (PhD 1979, Université Paris 7)

Director of research at CNRS. ODIN and HIFI co-Investigator, involved in several GT projects.
E. Falgarone will lead the studies on non equilibrium chemistry, and the C- and N-hydride data reduction and analysis. She will participate in ancillary ground based observations.

Thomas R. Geballe (PhD in physics in 1974 under Prof. Charles Townes at U.C. Berkeley).

Staff astronomer of the GEMINI observatory, and PRISMAS affiliate
T. Geballe will participate in performing IR spectroscopic observations with ground based telescopes (e.g. UKIRT, VLT, Gemini).

Thomas Giesen, (PhD 1991, University of Cologne)

Assistant Professor, University of Cologne, HIFI co-Investigator.
T. Giesen will lead the studies of carbon clusters with HIFI. His expertise in laboratory spectroscopy will be most useful for HIFI line identifications, and for measuring the line frequencies of carbon clusters in the Cologne laboratories.

Javier R. Goicoechea (PhD, Universidad Autonoma de Madrid, Madrid, 2003)

Marie Curie postdoc at the Observatory of Paris, and PRISMAS Associate.
J. Goicoechea will lead the analysis of the PACS spectral scans, in coordination with the leaders of the chemistry sub-programmes and with the HEXOS team analysing PACS scans. He will contribute to the data modelling (line excitation and chemical abundances).

Paul Goldsmith, (PhD 1975, University of California, Berkeley)

Senior Research Scientist, Jet Propulsion Laboratory, California Institute of Technology. HIFI co-Investigator, involved in several GT projects.
P. Goldsmith is coordinator of the SgrB2 line of sight program in the HEXOS programme. He will coordinate the exchange of information between HEXOS and PRISMAS programme.

Cécile Gry (PhD 1983, Paris Observatory)

Senior astronomer at the Laboratoire d'Astrophysique de Marseille. Former ESA resident astronomer for the satellites IUE, ISO and ASTRO-F, member of the ISO-LWS consortium, associate member of the FUSE science team, co-I of the Grantecan instrument EMIR, HIFI astronomy co-I.
C. Gry will participate in the analysis of the PACS spectral scan, and in the study of the C- and N-hydride chemistry.

Patrick Hennebelle (Ph.D., Observatoire de Paris, 2000)

Staff astronomer at the Observatoire de Paris, HIFI associate.
P. Hennebelle is working in the dedicated spectral line deconvolution team. He will participate in the analysis and DSB deconvolution of the HIFI data. P. Hennebelle performs numerical simulations of the 2-phase interstellar medium including reduced chemical networks.

Eric Herbst (PhD 1973, Harvard University)

Distinguished University Professor, The Ohio State University
Department of Physics, Astronomy, and Chemistry
HIFI co-Investigator
E. Herbst will participate in the chemical modelling of the molecular abundances, using steady-state and time dependent chemical models, including the effects of non-thermal desorption of ice mantles. E. Herbst

will also contribute to the line identification.

P. Hily-Blant (PhD 2004, Université Paris Sud)

Post-doctoral fellow at Institut de Radioastronomie Millimétrique (IRAM). Coordinator for the CLASS software, and heterodyne array HERA data reduction. PRISMAS associate.

P. Hily-Blant will assist for the HIFI and ground based data analysis and interpretation, with special emphasis in the data calibration and reduction. P. Hily-Blant will also contribute to the warm chemistry modelling efforts.

Christine Joblin, (PhD 1992/Univ. Paris 7; Habilitation 2005/Univ. Toulouse 3)

Research scientist at CNRS, Centre d'Etude Spatiale des Rayonnements, Toulouse, France.

HIFI co-Investigator, PI of the SPECPRD program on Spitzer Space Telescope, PI of the PIRENEA laboratory set-up.

C. Joblin will participate in the modelling of the carbon cluster production mechanism, based on results on the PIRENEA laboratory set-up, operating at CESR (Toulouse).

Robert Kolos (PhD 1991, Polish academy of Science, Warsaw)

Associate Professor at the Institute of Physical Chemistry, Polish Academy of Sciences. HIFI co-Investigator.

R. Kolos will participate in the modelling of carbon cluster and C-hydride spectra and in the ISM chemical modelling.

Jacek Krelowski (PhD 1975, Nicolaus Copernicus University, Torun)

Full professor at Torun Center for Astronomy (Nicolaus Copernicus University). HIFI co-Investigator.

J. Krelowski will participate in the reduction and analysis of the carbon molecules data, the derivation of the physical conditions, and the comparison with diffuse cloud data acquired in the UV and visible wavelength ranges.

Dariusz C. Lis, (Ph.D. 1989/University of Massachusetts)

Senior Research Associate in Physics, California Institute of Technology. HIFI Co-Investigator, subprogramme coordinator in the HEXOS and HS3F key programmes.

D. Lis will lead the analysis of the emission lines from PRISMAS sources. He will also participate in the O-,F- and Cl-hydride sub-programme, and in the acquisition of complementary submillimeter line and continuum data from ground based telescopes.

Jesus Martìn-Pintado (PhD/1983 Universidad Complutense de Madrid)

Research Professor at Consejo Superior de Investigaciones Científicas (Spain). HIFI Co-Investigator, sub-program coordinator in the HIFI Extragalactic key program.

J. Martìn-Pintado will coordinate the exchange of information between PRISMAS and the HIFI Extragalactic key programs.

Karl Menten (Dr Rer. nat. 1987, Bonn University)

Director for Millimeter and Submillimeter Astronomy, Max Planck Institute für Radioastronomie, Bonn and Professor of experimental astrophysics, Bonn University. Principal Investigator, Atacama Pathfinder Experiment (APEX), HIFI-coI.

K. Menten will aid in the analysis and interpretation of the emission line spectra, and with complementary radio interferometric data (VLA, ATNF, PdBI).

Bhaswati Mookerjea (Ph.D. 2001 from Indian Institute of Science (IISc), Bangalore, India)

Research associate at Department of Astronomy, University of Maryland, College park. PRISMAS associate.

B. Mookerjea will assist in the HIFI data reduction and analysis, especially with the determination of the source continuum and comparison with ground based observations.

David Neufeld (Ph.D., Harvard, 1987)

Professor in the Department of Physics and Astronomy of the Johns Hopkins University. SWAS and HIFI co-Investigator.

D. Neufeld will lead the data reduction, analysis and interpretation of the O-, F- and Cl- hydride lines.

John C. Pearson, (PhD 1995/Duke University)

Member of technical staff, Jet Propulsion Laboratory, California Institute of Technology NASA HIFI Instrument Manager, HIFI co-Investigator.

J. Pearson's expertise in molecular spectroscopy including line identification, molecular Hamiltonian modeling, calculation of line frequencies and intensities will be essential for line identification and derivation of spectroscopic parameters.

Michel Pérault (PhD 1987, Université Paris 7)

Director of research at CNRS, HIFI co-I, member of the HIFI calibration team.

M. Pérault will participate in the HIFI data analysis and calibration, removal of instrumental effects and side band deconvolution. He will contribute to the hydride analysis and interpretation.

Thomas G. Phillips (PhD 1964/ Oxford UK)

Altair Professor of Physics, California Institute of Technology and Director, Caltech Submillimeter Observatory, HIFI co-PI.

T. Phillips will participate in the hydride line analysis and interpretation.

René Plume (PhD, 1995/University of Texas at Austin)

Associate Professor, Department of Physics and Astronomy, University of Calgary. SWAS and HIFI co-Investigator, coordinator of Orion S line survey subproject.

R. Plume will participate in the O-hydride lines analysis and interpretation.

Morvan Salez (PhD 1992, University Paris VII).

Senior Research scientist at CNRS (LERMA, Observatoire de Paris and Laboratoire des Solides Irradiés, Ecole Polytechnique, France). Scientific Manager of the Herschel HIFI Band 1 and HIFI co-I.

M. Salez will participate in the O- and Cl-hydride data analysis and interpretation.

Mirosław Schmidt (PhD 1998 at N. Copernicus Astronomical Center, Warsaw)

Research associate at N. Copernicus Astronomical Center in Torun.

M. Schmidt will participate in the C-hydride and C-cluster analysis and interpretation including radiative transfer models of molecular lines.

Jürgen Stutzki, (PhD 1985, University of Cologne)

Full Professor of Physics at the Universität zu Köln. HIFI Co-principal investigator.

J. Stutzki will work on the carbon cluster data reduction and analysis. He will also participate in the side band deconvolution of the HIFI spectra.

David Teyssier (PhD 2002, University of Paris VII)

HIFI Instrument and Calibration Scientist at the European Space Astronomy Centre, Spain, since 2005, HIFI co-Investigator.

D. Teyssier will contribute to the HIFI data calibration and analysis. He will work on the C-Hydride chemistry.

Charlotte Vastel, (PhD 2001/Université Paul Sabatier, Toulouse, France)

Astronome Adjoint, Observatoire Midi-Pyrénées/CESR, France. HIFI co-I

C. Vastel will coordinate the search for deuterated species. Her expertise with the CASSIS software tool will be most valuable for the modelling and interpretation of the HIFI spectra.

C The chemistry of interstellar hydrides

C.1 Oxygen chemistry

The chemistry of oxygen-bearing molecules has been the subject of intensive investigation, particularly with the ISO, SWAS and ODIN satellite observatories, which have opened up the study of water vapor and molecular oxygen. Recent observations have posed several key puzzles:

- **Why is the water vapor abundance so small in cold, dense, quiescent molecular clouds?**

While large water vapor abundances have been detected in hot core and outflow regions (e.g. Boonman et al. 2003, Cernicharo et al. 2006), in good agreement with theoretical expectations, the cold cloud abundances fall at least one – and perhaps two – orders of magnitude below the predictions of standard astrochemical models (e.g. Bergin et al. 2001). The effects of ice mantle formation have been proposed as a possible explanation of the low water abundances measured in the gas-phase. Some water vapor is still expected to remain in the gas resulting from the evaporation of/ejection from mantles, and indeed observed by ISO, SWAS and ODIN towards cold sources. To account for the low water vapor abundances observed in cold, dense clouds, another destruction mechanism must be considered which will further decrease the gas phase water vapor abundance, or the release from grain mantles must be inhibited in the very dense and cold cores where very low water vapor abundances have been measured. The large abundance of atomic carbon in the same cores, which remains not fully understood, may contribute to solving the puzzle because atomic carbon efficiently cycles oxygen nuclei into CO as a result of its reactions with OH and O₂.

- **Why is the molecular oxygen abundance so small?** A tentative detection of molecular oxygen has been reported by Larsson et al. (2007) using the ODIN satellite, which is consistent with previous upper limits (Goldsmith et al. 2002, Pagani et al. 2003). Overall, the O₂ abundance is low in molecular gas, contrary to early models. Again, the freeze-out of oxygen nuclei into icy grain mantles is a possible solution to the puzzle.

- **In diffuse clouds, why is the OH/H₂O ratio variable?** In standard astrochemical models, where both molecules are formed by the dissociative recombination of H₃O⁺ and destroyed primarily by photodissociation, the OH/H₂O ratio is expected to show little variation. Observations of substantial variations from one sightline to another suggest the importance of additional formation mechanisms for OH and/or H₂O (Neufeld et al. 2002; Plume et al. 2004, Fig 1). These might include (1) formation via endothermic neutral-neutral chemistry, in a component of the gas where the temperature is enhanced by shocks or turbulence; or (2) formation via grain catalysis, in which oxygen atoms stick to grain surfaces, react with H to form OH and then H₂O and are then photo-desorbed by the interstellar UV radiation field (Kaufmann et al. 2005).

Herschel promises to provide **a critical and unique probe of water vapor in cold, absorbing clouds of various density and column densities lying along sightlines to submillimeter continuum sources.** Absorption features due to water lines are ubiquitous in the spectra of bright FIR and submillimeter continuum sources (e.g. Neufeld et al. 2002, Sandqvist et al. 2003), but thus far only the 557 GHz 1₁₀ – 1₀₁ line has been detected at high spectral resolution. SWAS and ODIN have detected optically-thick water absorption against several sources, so a promising target list is already in place. Unfortunately, the SWAS sensitivity was too poor to permit the detection of H₂¹⁸O along any sightline other than Sgr B2, so almost all water column density determinations are lower limits derived from optically-thick H₂¹⁶O lines. ODIN spectra of the H₂¹⁸O and H₂¹⁷O lines towards SgrB2 show that the different absorbing clouds along the line of sight have varying H₂O column densities (Hjalmarson et al. 2006). HIFI will have a big advantage both in sensitivity and spectral coverage because it will access both ortho- and para-H₂O. We will target the lowest transitions of both ortho- and para-H₂¹⁶O, the 557 GHz 1₁₀ – 1₀₁ and 1113 GHz 1₁₁ – 0₀₀ transitions respectively, as well as the analogous 548 GHz and 1102 GHz lines of H₂¹⁸O.

Another key advantage of Herschel/HIFI will be **the ability to study the molecular ions OH⁺ and H₃O⁺ in absorption along the same sightlines where water is observed.** These species are key intermediaries in the cosmic-ray driven ion-molecule chemistry leading to OH and H₂O. OH⁺ is produced by proton transfer from H₃⁺ to O, and subsequently undergoes hydrogen atom abstraction reactions with H₂ to form H₂O⁺ and then H₃O⁺, which ultimately undergoes dissociative recombination to form OH or

H₂O. Measurements of the OH⁺ and H₃O⁺ abundances will therefore probe directly the ion-molecule route to OH and H₂O formation, allowing the relative importance of cosmic-ray driven chemistry to be compared with those of high temperature chemistry and gas-grain chemistry.

Using PACS in its spectrometer mode, we shall be able to complete our investigation of oxygen chemistry with data on O (from the fine structure lines at 63 and 145 μm) and OH (ground state transitions at 119, 79 and 53 μm and excited lines at 163 and 98 μm , see Goicoechea and Cernicharo 2002 for OH spectra in the far infrared) at the same spatial resolution as the HIFI data.

In the warm, dense gas within the target sources themselves, multi-transition studies are needed to pin down the excitation conditions and provide more accurate measurements of the water vapor abundance. For instance, with a multi-transition study of water and its isotopes, combining emission and absorption lines, Comito et al. (2003) revisited the water abundance in the Sgr B2 cloud and inferred large variations of the gas phase water abundance through the Sgr B2 molecular core. To probe denser, radiatively-excited regions, we will also observe the $2_{02} - 1_{11}$ and $2_{11} - 2_{02}$ lines of both para-H₂¹⁶O and para-H₂¹⁸O.

C.2 Fluorine chemistry

The chemistry of interstellar fluorine is qualitatively different from that of any other element, because – unlike the atom of any other element found in diffuse or dense molecular clouds – atomic fluorine undergoes an exothermic reaction with molecular hydrogen. Neufeld, Wolfire & Schilke (2005) have recently presented a theoretical investigation of the chemistry of fluorine-bearing molecules in diffuse and dense interstellar gas clouds, combining recent estimates for the rates of relevant chemical reactions with a self-consistent model for the physical and chemical conditions within gas clouds that are exposed to the interstellar ultraviolet radiation field. Over a wide range of conditions attained within interstellar gas clouds, the product of that reaction – hydrogen fluoride – is predicted to be the dominant gas-phase reservoir of interstellar fluorine nuclei. **Fluorine is expected to be the heavy element which shows the greatest tendency toward molecule formation; in diffuse clouds of small extinction, the predicted HF abundance can even exceed that of CO**, even though the gas-phase fluorine abundance is four orders of magnitude smaller than that of carbon.

Model calculations predict HF column densities $\sim 10^{13} \text{ cm}^{-2}$ in dark clouds and column densities as large as 10^{11} cm^{-2} in diffuse interstellar gas clouds with total visual extinctions as small as 0.1 mag. Such diffuse clouds should show HF absorption lines detectable in high signal-to-noise HIFI spectra. To date, the only molecules detected in clouds of such small visual extinctions are H₂ and HD, observed in absorption toward hot background stars at UV wavelengths. **This raises the surprising possibility that spectroscopic observations of far-infrared continuum sources with Herschel/HIFI will reveal a component of foreground molecular gas that is observable exclusively by means of its HF absorption lines.**

Because of the unique simplicity of the interstellar fluorine chemistry, the abundance of HF can be used as a powerful probe of the freeze-out of atoms and molecules onto grains. For example, the ISO detection of HF $J = 2 - 1$ in absorption toward Sgr B2 (Neufeld et al. 1997) indicated an abundance 50 times smaller than the cosmic abundance of fluorine nuclei, thus providing compelling evidence for high levels of depletion in dense interstellar environments. By contrast, diffuse cloud observations of atomic fluorine with Copernicus implied depletion factors of at most three.

ISO observations were limited to the $J = 2 - 1$ line, which can be detected in absorption only in regions like Sgr B2 that are subject to strong radiative excitation. By contrast, HIFI observations of the HF $J = 1 - 0$ line will yield a more versatile probe of depletion that is usable in a wide variety of environments. By observing HF, we will be able to probe the gas phase abundance of fluorine across the Galaxy and to detect diffuse molecular clouds of very small column density.

Herschel observations of Galactic HF in the local Universe will provide an important benchmark for future observations at high redshift that will become possible with ALMA. HF absorption in quasar spectra is a potential probe of molecular gas at high- z , providing a possible bridge between the UV/optical observations capable of probing H₂ in low column density systems and the radio/millimeter-wavelength observations that probe intervening molecular clouds of high extinction and large molecular fraction; at redshifts beyond ~ 0.3 , HF is potentially detectable from ground-based submillimeter observatories in several atmospheric

transmission windows.

C.3 Carbon chemistry

The ability of carbon to form single-, double- or triple-bonds leads to a complex chemistry with a variety of chemical bonds and structures. Most of the carbon containing molecules detected so far have a linear carbon chain skeleton, prominent examples are the cyano polyynes (HC_nN , $n=1,3, 5,\dots,11$). In contrast to organic species found on earth many carbon containing molecules in space are poor in hydrogen. The degree of hydrogenation depends on the local physical conditions of the source and they can thus be used as sensitive probes of local chemical conditions. Based on chemical models hydrogen rich carbon molecules are expected to be found in dense warm regions, whereas highly unsaturated hydrocarbons are predominant in cold quiescent clouds. In some cases the abundance of pure carbon molecules, such as C_3 , C_4 , and C_5 , is expected to exceed the abundance of the related hydrocarbons C_3H , C_4H , C_5H and C_3H_2 , C_4H_2 , and C_5H_2 . It is thus essential for further modeling to determine the relative abundances of pure carbon molecules compared to their hydrogenated analogues.

The chemistry of the carbon hydrides has been studied extensively by means of ground-based optical absorption line spectroscopy of electronic transitions. In some exceptional cases, data with very high spectral resolution have been obtained, in which CN, CH and CH^+ present different line profiles: while the velocity structure of the CN electronic transitions is similar to that of the ground state rotational line of carbon monoxide seen in emission at 115 GHz, the CH^+ line is broader, and has a different velocity structure (Crane et al. 1995, Pan et al. 2001).

CH^+ , like other extremely reactive molecules (such as H_2^+ , CO^+ , OH^+ , H_2O^+), is particularly interesting as a diagnostic of interstellar processes, since it is destroyed rapidly (by collision with H, H_2 and other neutrals), and may keep a memory of its formation process in its velocity distribution and rotational excitation (Flower & Pineau des Forêts 1998, Black 1998). **The range of measured CH^+ column densities (from 10^{12} to 10^{14} cm^{-2} using observations in the visible and now in the submillimeter, Fig. 3), is clearly inconsistent with steady-state low-temperature chemistry** because the main CH^+ formation process is the endothermic reaction between C^+ and H_2 , which is very slow at diffuse cloud temperatures of a few $\times 10$ K. The likely reason for this failure is the still incomplete description of the structure and kinematics of the ISM in steady state chemical models, leading to an incomplete coverage of the relevant physical processes. Steady state models fail for at least two reasons: (1) the assumption of uniform physical conditions (density and temperature) is clearly not valid for CH^+ and other species formed in endothermic reactions or in reactions with activation barriers; and (2) the regions where CH^+ is formed must be very small, and probably transient, because the gas physical conditions along the same lines of sight (density $n_{\text{H}} \sim \text{few} \times 100 \text{ cm}^{-3}$, kinetic temperature $\sim \text{few} \times 10$ K) are fairly well determined with less reactive molecules such as C_2 , and the observed CH^+ column densities cannot be produced under those physical conditions.

Magneto-hydrodynamical shocks (i.e. C-type shocks; Draine 1980, Flower & Pineau de Forêts 1998) can explain the observed CH^+ abundances, but predict a velocity shift between neutral and ions ($\sim 2 \text{ km s}^{-1}$ in the comprehensive models of Flower & Pineau des Forêts 1998). An alternative hypothesis is that reactive species form in regions where bursts of turbulent dissipation locally heat the gas to temperatures as large as 10^3K (Joulain et al. 1998, Falgarone et al. 2006). An efficient CH^+ formation is then obtained within active regions, which become warm enough that the formation rate becomes significant. Other molecules are formed in the same environment, notably OH, HCO^+ and H_2O . In order to explain the efficient formation of CH^+ , while not over-predicting the OH abundance, models attempt to take proper account of the interstellar magnetic field and transient decoupling of ions and neutrals. As in the case C-type shocks, ion-neutral drift has the effect of enhancing the energy available in reactive collisions of C^+ and H_2 whilst leaving that in collisions of O and H_2 unchanged. Therefore, the formation rate for CH^+ is increased by a much larger factor than that for OH. In the Joulain et al. (1998) picture, all species would form with the same centroid velocity, as is observed in most sightlines. **Whether C-type shocks, turbulent dissipation in large velocity shear regions, or some other mechanism (e.g. turbulent diffusion, Lesaffre et al. 2007) is responsible for enhancing the CH^+ abundance in diffuse clouds, HIFI is ideally suited to**

detect CH^+ in this highly excited, small scale, component of the interstellar medium, because it will provide the key information on the abundance dependence with velocity.

Studying CH^+ formation is also important for understanding carbon chemistry in the diffuse medium, since CH^+ is an intermediary in the formation of many carbon-bearing interstellar molecules. CH^+ reacts with molecular hydrogen to form CH_2^+ , then CH_3^+ , and finally CH_5^+ . The recombination of CH_2^+ and CH_3^+ with electrons produce CH and CH_2 , but CH_3^+ participates in many ion-molecule reactions, leading ultimately to other molecules such as C_2 , C_2H_2 and to the carbon chains and cyanopolyynes (Terzavia and Herbst 1998). The carbon hydrides to be observed with HIFI – CH , CH_2 , and CH^+ – are therefore key species for understanding the first steps of carbon chemistry.

C.4 Nitrogen chemistry

Nitrogen chemistry is unique because of the importance of neutral-neutral reactions. In order to produce nitrogen hydrides, especially ammonia, in the gas phase, it is first necessary to synthesis molecular nitrogen, N_2 , which is produced by neutral-neutral reactions involving nitrogen atoms and other diatomics such as OH and NO . The low temperature rates of these processes are not really known. Once sufficient N_2 builds up, reaction with abundant He^+ ions leads to the production of the atomic nitrogen ion N^+ .

The formation of ammonia starts with the weakly endothermic reaction $\text{N}^+ + \text{H}_2 \rightarrow \text{NH}^+ + \text{H}$, which can be powered at low temperature by either fine-structure excitation of the nitrogen ion or by the ortho spin modification of H_2 , the lowest rotational state of which ($J = 1$) lies 170 K above the ground ($J = 0$) rotational state. The availability of either source of energy is uncertain. Subsequent hydrogen atom-transfer reactions with molecular hydrogen lead to NH_2^+ and NH_3^+ . The final reaction in the series, $\text{NH}_3^+ + \text{H}_2 \rightarrow \text{NH}_4^+ + \text{H}$, is known to be slow at room temperature and to decrease initially in rate as the temperature is reduced below 300 K. But, at temperatures near 100 K, the rate begins to increase and lower temperatures lead to an even higher rate. Since ammonia is formed by dissociative recombination of the NH_4^+ ion, its abundance may well be temperature dependent.

In summary, the nitrogen chemistry through ammonia is still somewhat uncertain and more observational data on nitrogen hydrides are clearly needed for a better understanding. The data on nitrogen hydrides are extremely scarce up to now with only a few reported detections (Crawford and Williams 1997, van Dishoeck et al. 1993 for NH_2 , Goicoechea et al. 2004 for $\text{NH}/\text{NH}_2/\text{NH}_3$ from ISO). Moreover, there is also the possibility that nitrogen hydrides can be produced on the surfaces of grains and desorbed into the gas via non-thermal desorption mechanisms such as photo-desorption. The detection of NH in diffuse clouds is often ascribed to a surface formation mechanism, but this assignment is very uncertain.

C.5 HCl

While the program proposed here focuses primarily on the hydrides of first-row elements, HIFI presents an opportunity to study the heavier hydride HCl .

HCl is expected to be an important major reservoir of gas-phase chlorine, and thus measurements of its abundance serve as a valuable probe of depletion – as in the case of HF . Under favorable atmospheric conditions, observations of $\text{HCl } J = 1 - 0$ are possible from ground-based observatories; to date, only two ground-based detections of HCl have been reported (Schilke et al. 1995, Salez et al. 1996). Severe atmospheric absorption always limits the precision of $\text{HCl } J = 1 - 0$ flux measurements from the ground, and the stability of a space-based heterodyne system will be important in doing quantitative science.

C.6 Deuterium fractionation and interstellar deuterides

The detection of deuterium isotopic fractionation in the interstellar medium is of great interest, because the **fractionation is a strong indicator of the physical conditions in any source where it is observed.** Once the chemistry proceeds to the point where the HD/H_2 abundance ratio reaches the elemental value of $\sim 10^{-5}$, ion-molecule reactions produce very large abundance ratios of deuterated to normal species for most heavy interstellar molecules with at least one hydrogen atom. This effect, known as fractionation, occurs in the gas phase via exchange reactions, the most important of which is $\text{H}_3^+ + \text{HD} \rightleftharpoons \text{H}_2\text{D}^+ + \text{H}_2$.

Analogous systems exist for the ions CH_3^+ and C_2H_2^+ . Because of zero-point vibrational energy differences and the Pauli Exclusion Principle, the left-to-right reaction for the $\text{H}_3^+ + \text{HD}$ system is exothermic by 230 K. Thus, in a cloud much colder than this, the backwards reaction becomes very slow. If there were no other destruction pathways for H_2D^+ , the predicted $\text{H}_2\text{D}^+/\text{H}_3^+$ abundance ratio would exceed unity at 10 K (Roberts, Herbst & Millar 2003; Walmsley, Flower & Pineau des Forets 2004). However, H_2D^+ is destroyed by reactions with electrons and heavy species such as CO.

The reactions of H_2D^+ with heavy species serve to spread the deuteration around and cause typical abundance ratios between singly deuterated isotopomers and normal species (e.g. $\text{DCO}^+/\text{HCO}^+$) in the range 0.01 – 0.10. For regions at particularly high densities (10^{6-7} cm^{-3}) and low temperatures, heavy species are significantly depleted onto grains within rather short periods (1000 yr) and then the $\text{H}_2\text{D}^+/\text{H}_3^+$ abundance ratio can indeed exceed 1. Moreover, subsequent exothermic reactions with HD produce D_2H^+ – detected by Vastel et al. 2004 with a $p - \text{D}_2\text{H}^+ / o - \text{H}_2\text{D}^+$ ratio ~ 1 as predicted (Roberts et al. 2003, Flower, Pineau des Forêts & Walmsley 2004) – and even D_3^+ . Reactions between the deuterated ions and heavy species still in the gas lead to multiply-deuterated heavy neutrals such as D_2CO and ND_3 (Roueff et al. 2005). When comparing the degree of deuterium fractionation of H_3^+ isotopologues with models, care must be taken of the molecule symmetry properties which depend in a complex way on the H_2 ortho/para ratio (Flower et al. 2004). Unfortunately only one symmetry state of each H_2D^+ and D_2H^+ are accessible from the ground, in windows with rather poor atmospheric transmission. Given the importance of these species for the propagation of D fractionation in all interstellar molecules, accurate determination of their abundances is a must. In addition, dissociative recombination reactions with deuterated ions produce atomic deuterium, which, upon sticking to the surfaces of interstellar grains, is able to deuterate species such as CO into deuterated isotopologues of formaldehyde and methanol. Such deuterated isotopologues remain in the solid phase unless some event, such as star formation, causes surface temperatures to rise and accelerates evaporation.

Although deuterated species typically possess rotational transitions at lower frequencies than the normal isotopomers, several important transitions (ground state lines) are found at frequencies uniquely accessible to HIFI. Some deuterated molecules of interest for HIFI include HDO, D_2O , ND, NH_2D , DF, and D_2H^+ .