

Carbon Chemistry in Photodissociation Regions

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Abstract. We present recent results on the carbon chemistry in photodissociation regions. We show that carbon chains and rings (CCH, $c\text{-C}_3\text{H}_2$ and C_4H) are tightly spatially correlated with each other, and with the mid-infrared emission due to PAHs (7 and 15 μm), mapped by ISOCAM. Neither the spatial distribution, nor the abundances of these species can be fit by state-of-the-art PDR models, which calls for another production mechanism. We discuss model predictions for carbon clusters and simple hydrocarbons. We show how selected abundance ratios can be used as a diagnostic of the physical conditions. We stress the need for more theoretical and laboratory work on fundamental processes relevant for the interstellar medium, which should be taken into account in the astrochemical models, but whose rates are not known accurately enough.

Keywords. astrochemistry — ISM: clouds — ISM: evolution — ISM: molecules — ISM: structure

1. Introduction

As carbon is one of the most abundant elements in the interstellar medium, which can bind to other elements in many ways, most of the interstellar and circumstellar molecules contain at least one carbon atom. Table 1 lists the detected interstellar and circumstellar species through September 2005. Carbon species account for 75% of the 144 detected molecules, and include the most complex and heaviest molecules detected.

Carbon chemistry is also important for understanding the structure and evolution of the interstellar medium (ISM). Carbon monoxide is the most abundant molecule after molecular hydrogen and a widely used tracer of molecular regions, as H_2 lines are usually weak and not easily accessible. Carbon chemistry affects the gas cooling processes as C^+ and C fine-structure line emission, together with CO and H_2O rotational line emission,

Table 1. Interstellar and Circumstellar Molecules

Molecular Hydrogen and Related Ions						
<u>H₂</u>	<u>HD</u>	H ₃ ⁺	H ₂ D ⁺	D ₂ H ⁺		
Carbon Chains and Rings						
<u>CH</u>	CH ⁺	C ₂	CH ₂	<u>CCH</u>	C ₃	CH ₃
C ₂ H ₂	<i>l</i> -C ₃ H	<i>c</i> -C ₃ H	CH ₄	C ₄ ?	<i>c</i> -C ₃ H ₂	<i>l</i> -C ₃ H ₂
C ₄ H	C₂H₄	C₅	C ₅ H	<i>l</i> -H ₂ C ₄	HC₄H	<u>CH₃CCH</u>
C ₆ H	C ₆ H ₂	HC₆H	C₇H	CH ₃ C ₄ H	C ₈ H	<u>C₆H₆</u>
Species with O, or H and C						
<u>OH</u>	<u>H₂O</u>	O ₂ ?	<u>CO</u>	CO ⁺	<u>HCO⁺</u>	HOC ⁺
<u>HCO</u>	<u>C₂O</u>	CO ₂	H ₃ O ⁺	HOCO ⁺	<u>H₂CO</u>	C ₃ O
HCOOH	CH ₂ CO	H ₂ COH ⁺	<u>CH₃OH</u>	CH ₂ CHO	<u>HC₂CHO</u>	C ₅ O
CH ₃ CHO	<i>c</i> -C ₂ H ₄ O	CH ₃ OCHO	<u>CH₂OHCHO</u>			
CH ₃ COOH	CH ₂ CHOH	(CH ₃) ₂ O	CH ₃ CH ₂ OH	CH ₂ CHCHO	CH ₃ CH ₂ -	HOCH ₂ -
(CH ₃) ₂ CO	CO(CH ₂ OH) ₂				-CHO	-CH ₂ OH
Species with N, or H and C						
N ₂	NH	<u>CN</u>	NH ₂	<u>HCN</u>	<u>HNC</u>	<u>N₂H⁺</u>
<u>NH₃</u>	HCNH ⁺	H ₂ CN	HCCN	C ₃ N	CH ₂ CN	CH ₂ NH
<u>HC₃N</u>	HC ₂ NC	NH ₂ CN	C ₃ NH	HC₄N	<u>CH₃CN</u>	CH ₃ CN
<u>HC₃NH⁺</u>	C ₅ N	CH ₃ NH ₂	C ₂ H ₃ CN	HC ₅ N	<u>CH₃C₃N</u>	C ₂ H ₅ CN
HC ₇ N	CH ₃ C ₅ N?	HC ₉ N	HC ₁₁ N			
Species with N, O or H and C						
NO	HNO	N ₂ O	<u>HNCO</u>	NH ₂ CHO		
Species with S, Si and Other Elements						
SH	<u>CS</u>	<u>SO</u>	SO⁺	NS	SiH	SiC
SiN	<u>SiO</u>	SiS	HCl	NaCl	AlCl	KCl
HF	AlF	CP	PN	H ₂ S	C ₂ S	SO ₂
<u>QCS</u>	HCS ⁺	<i>c</i> - SiC₂	SiCN	NaCN	MgCN	MgNC
H ₂ CS	HNCS	C ₃ S	c-SiC₃	SiH₄	SiC₄	CH ₃ SH
C ₅ S	FeO	AlNC	SiNC	CF ⁺		

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

and neutral oxygen fine structure line emission are the main gas coolants over a wide range of gas densities and temperatures (see, e.g., Kaufman *et al.* 1999; Wolfire *et al.* 2003). Finally, carbonaceous grains and PAHs contain a large fraction of the total carbon. These small solid particles and macro-molecules control the gas heating rate through the photoelectric effect, since the photoelectric efficiency is largest for small particles. Although grains are thought to be formed in circumstellar envelopes, their properties evolve as they travel through the interstellar medium. Various observational pieces of evidence for grain processing have been found (see, e.g., Jones 2005; Dartois *et al.* 2005). In addition to evolution of the grain material itself, dust grains can either grow, or fragment, in the interstellar medium, depending on their surroundings. Sputtering and fragmentation of carbonaceous grains is likely to release fresh carbon back into the ISM.

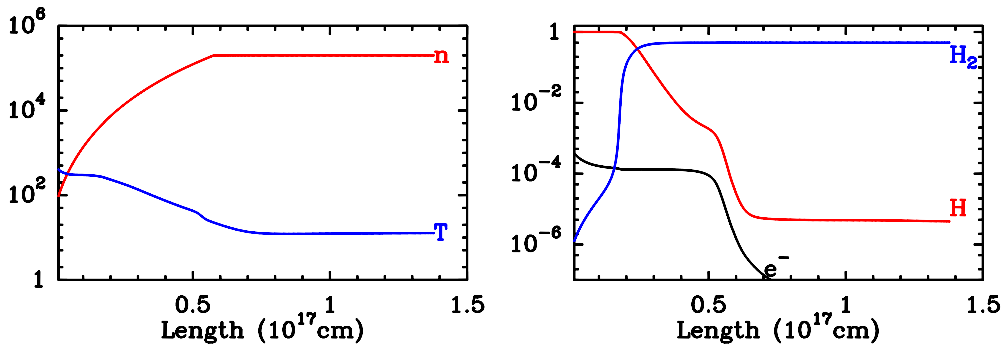


Figure 1. *Left:* Gas density and temperature for the Horsehead nebula model as a function of distance from the illuminated edge in cm. *Right:* Abundances of neutral (H) and molecular (H_2) hydrogen, and electron abundance (e^-). The FUV radiation field is 100 in Draine's unit.

Photodissociation regions (PDRs) are defined as the warm interfaces, where the gas is molecular but its heating is dominated by FUV photons (<13.6 eV). Such an environment can be found in reflection nebulae—where a massive star illuminates a nearby molecular cloud—but also at the surface of protostellar disks, in circumstellar envelopes and in (proto)planetary nebulae. Because of the enhanced heating, and the efficient cooling due to the moderate gas density, PDRs produce intense continuum and line radiation over a wide range of wavelengths. The intense cooling lines from PDRs are easily detected in external galaxies, and the most distant galaxies become accessible with state-of-the-art instruments (e.g., the detection of the $[\text{C II}]$ $158 \mu\text{m}$ line by Maiolino *et al.* 2005). Therefore PDRs are attractive sources, where the physical and chemical processes relevant for the ISM evolution can be studied in detail, and state-of-the-art models compared with accurate observations.

2. Carbon Chemistry in the Horsehead Nebula

2.1. Observations

Unsaturated carbon chains and rings are rather abundant molecules in the ISM, and are even more abundant in carbon rich circumstellar envelopes around evolved stars, although these species are extremely reactive in the laboratory. In circumstellar envelopes (most notably the carbon rich star IRC+10216) and in dark clouds, the abundance ratios of these species follow a well-defined pattern with a slow decrease of the abundance as the molecule size increases (Guélin *et al.* 1977; Teyssier *et al.* 2004). Until recently, no such systematic studies had been performed for PDRs. Using the IRAM-30m telescope Fuente *et al.* (2003) observed reactive ions in PDRs and measured high abundances of HOC^+ and CO^+ . They also observed $c\text{-C}_3\text{H}_2$ lines in the same sources and concluded that the observed abundance is larger than PDR model predictions. Teyssier *et al.* (2004) studied the distribution and abundance of selected carbon chains and rings (CCH, the cyclic and linear isomers of C_3H and C_3H_2 , and C_4H) in three PDRs (ρ Ophiuchi, IC 63 and the Horsehead nebula). They concluded that the abundance and spatial distribution of these species are not well fitted by PDR models. However, these observations reached a moderate spatial resolution ($\sim 20''$), which did not allow the authors to resolve the steep abundance gradients predicted by the PDR models.

The Horsehead nebula was selected for a follow-up study at higher spatial resolution, using the IRAM Plateau de Bure interferometer. The Horsehead nebula is particularly

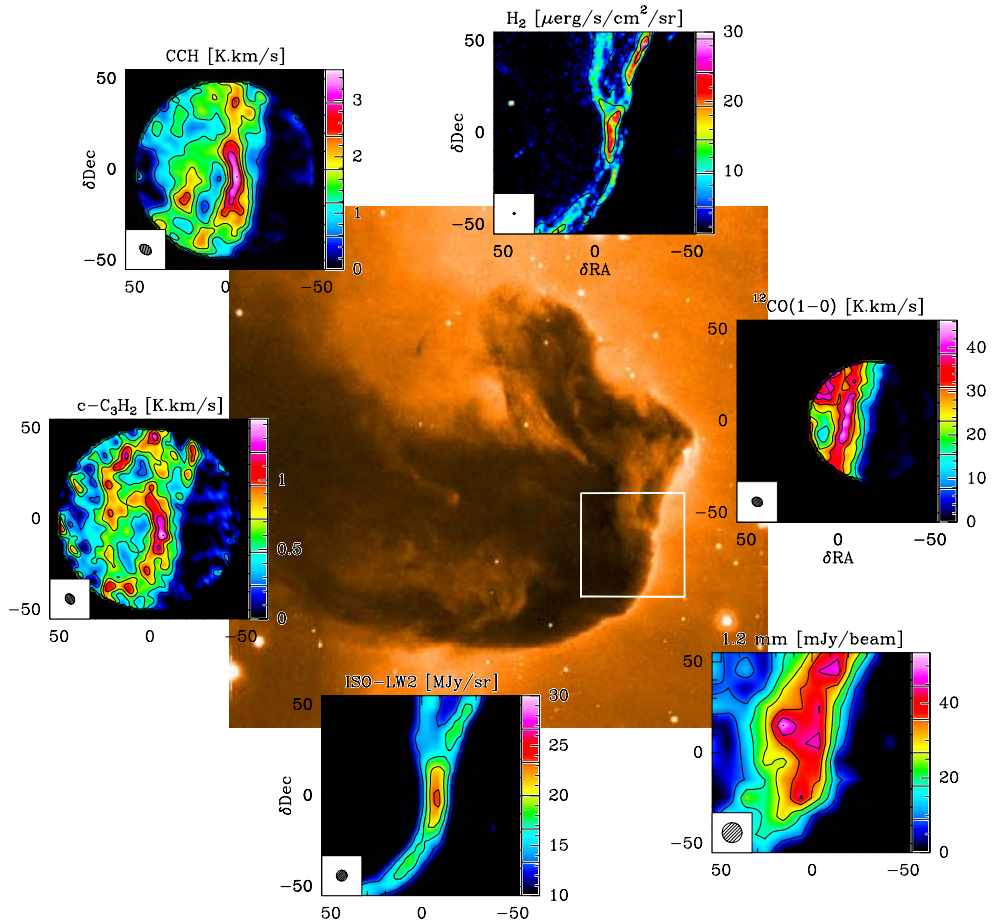


Figure 2. Summary of observations of the Horsehead nebula in LDN1630 from Pety *et al.* (2005) and Habart *et al.* (2005). The background image is taken from the ESO archive. The white square indicates the observed field of view of the IRAM Plateau de Bure interferometer. The CCH (*top left*), $c\text{-C}_3\text{H}_2$ (*left*), and $^{12}\text{CO}(1\text{-}0)$ (*right*) maps have been obtained with this facility. The PdBI data have been combined with short spacings from the IRAM-30m telescope to recover all spatial frequencies. The H_2 $v=1\text{-}0$ S(1) image (*top*) is from ESO-NTT, the 1.2 mm image (*bottom right*) from MAMBO on the IRAM-30m telescope, and the ISO-LW2 image (*bottom*) has been taken with ISOCAM (Abergel *et al.* 2003). Note the similarity of the CCH and $c\text{-C}_3\text{H}_2$ maps with the ISO-LW2 image, while the CO(1-0) and dust maps look different.

well suited as a template PDR, as it is viewed nearly edge-on (Habart *et al.* 2005 for a thorough discussion on the viewing geometry) and is nearby. At a distance of 400 pc, $1''$ corresponds to a linear size of 6.0×10^{15} cm, or 0.002 pc. The Horsehead nebula is illuminated by the O9.5 star σ Ori, ~ 3.5 pc away, resulting in a far UV radiation field $G_0 \sim 60$ times the mean interstellar radiation field, as determined by Draine (1978). As shown by Habart *et al.* (2005) and Pety *et al.* (2005), the gas density profile is well constrained by the infrared maps of the H_2 rovibrational emission, $v = 1\text{-}0$ S(1) at $2.1 \mu\text{m}$, and of the PAH emission near $7 \mu\text{m}$. The best-fit density profile rises steeply (in $\sim 10''$) from $n_{\text{H}} \sim 10^4 \text{ cm}^{-3}$ to $n_{\text{H}} \sim 10^5 \text{ cm}^{-3}$, the resulting model being almost isobaric (constant pressure). Figure 1 presents the adopted model.

A summary of the maps is shown in Figure 2. As discussed extensively by Pety *et al.* (2005), the spatial distribution of hydrocarbons is very similar to the PAH emission,

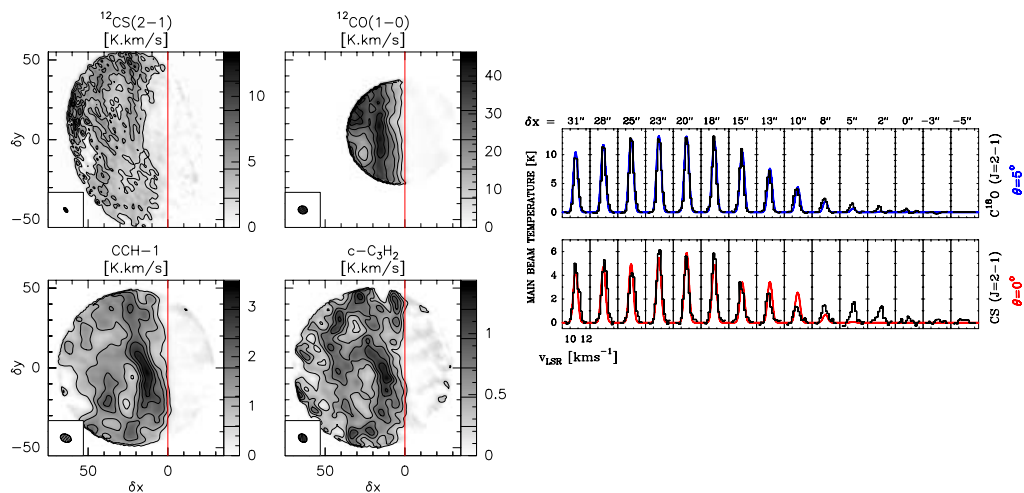


Figure 3. *Left:* PdBI Maps of the CS(2-1), CO(1-0), CCH(1-0) and $c\text{-C}_3\text{H}_2$ lines. The maps have been rotated by 14° in to ease the comparison with 1-D models. *Right:* Comparison of observed and modelled C^{18}O and CS spectra (from Goicoechea *et al.* 2005).

and different from CO and other species. Both the spatial distribution and the molecule abundance could not be fitted by PDR models, even by trying different chemical networks or small modifications of the source geometry and density structure. Because the molecule destruction is dominated by photodissociation in the external layers where the carbon chains are most abundant, detecting species with high abundance implies that their formation is efficient. Pety *et al.* (2005) reached similar conclusions as Fuente *et al.* (2003) and Rizzo *et al.* (2003, 2005), namely that the PAHs responsible for the mid-infrared emission features play a role in the formation of small carbon chains and rings. The most likely explanation is that, when these particles are released from larger structures (Rapacioli *et al.* 2005; Jones 2005), a fraction of these PAHs fragment and feed the gas with small carbon clusters and molecules.

2.2. Carbon Molecules and Grains

Indeed, much observational evidence has now been presented on the evolution of carbonaceous material in the interstellar medium. For instance, Rapacioli *et al.* (2005) have isolated three characteristic spectra in the reflection nebula NGC 7023, which neatly trace the evolution of PAHs as a function of the distance to the illuminating star. Vijn *et al.* (2005) discuss the spatial distribution of the recently discovered blue luminescence and also conclude that the carriers are liberated in situ, from larger carbonaceous structures.

While PDR models take into account the role of PAHs in the ionization balance, the influence of PAHs on the carbon chemistry has not been studied yet, because of the lack of basic information. Le Page *et al.* (2001, 2003) discuss the processes governing the size distribution, ionization balance and hydrogen coverage of PAHs in the ISM. The destruction of PAHs is limited to photodissociation because they do not include possible reactions with species other than hydrogen. Data on reaction rates between oxygen, carbon or nitrogen and PAHs are critically needed to assess possible growth paths of carbon species in the ISM.

2.3. Further Comparison with Observations

While the above analysis is based on comparisons of molecular abundances, it is now possible to perform a more accurate comparison between models and observations,

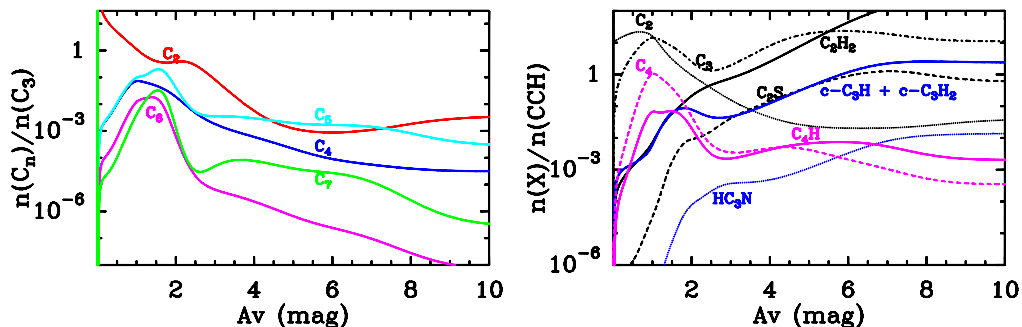


Figure 4. Prediction of the abundance ratio of carbon clusters (*right*) and other hydrocarbons (*left*) compared to C_3 and CCH respectively, for physical conditions of the Horsehead nebula.

using the full power of the high spectral resolution provided by millimeter observations. Figure 3 shows how well observed spectra can be fitted by combined PDR and Monte-Carlo radiative transfer models. A very small inclination along the line of sight (6°) can be identified when performing such detailed modelling work.

2.4. Carbon Budget

As shown in Fig. 4, C_2 is predicted to be abundant at low A_V , while C_3 and heavier carbon clusters are predicted to be most abundant at moderate extinctions, $A_V \sim 1$ – 3 mag. Saturated species, such as acetylene, C_2H_2 , participate in the carbon budget at higher A_V 's. Though the carbon chemistry is still not well understood, these conclusions are qualitatively in agreement with the observational data. Carbon clusters (C_2 , C_3 and maybe even C_4) have been widely observed in the ISM (Oka *et al.* 2003; Cernicharo *et al.* 2002), with a tight correlation between C_2 and C_3 abundances. The low abundance of both HC_3N and CH_3CCH in the Horsehead nebula PDR (Teyssier *et al.* 2004) is also consistent with model predictions.

3. Carbon Chemistry as a Tracer of Gas Properties

Chemical models show that interstellar molecular abundances are sensitive to the gas physical conditions, such as the density, temperature, but also the electron abundance. This important parameter for the gas physics cannot be measured directly, as the main carriers of the charges cannot be observed. However, a few molecular abundance ratios have been shown to scale with the electron abundance. In dense and shielded regions, the degree of deuterium fractionation of molecular ions (HCO^+ , N_2H^+ , etc.) can be used to measure the electron abundance (Guélin *et al.* 1982; Caselli *et al.* 1999). Fossé *et al.* (2001) have showed that the $[c-C_3H_2]/[l-C_3H_2]$ abundance ratio is sensitive to the electron abundance in the dark cloud TMC-1. Teyssier *et al.* (2005) have presented observational evidence for a similar behaviour in the Horsehead PDR. Figure 5 presents model predictions of abundance ratios as a function of the electron density. While $[HCN]/[HNC]$ is not sensitive to the electron abundance, the ratio of C_3H_2 and C_3H isomers can indeed be used to estimate the fractional ionization. As suggested by Sternberg (2005, this volume), $[CN]/[HCN]$ can also be used for probing the electron abundance. $[CN]/[HCN]$ gradients have been observed in the Orion Bar and NGC 7023 by A. Fuente and co-workers (e.g., Fuente *et al.* 1993), though the spatial resolution provided by a single dish telescope was

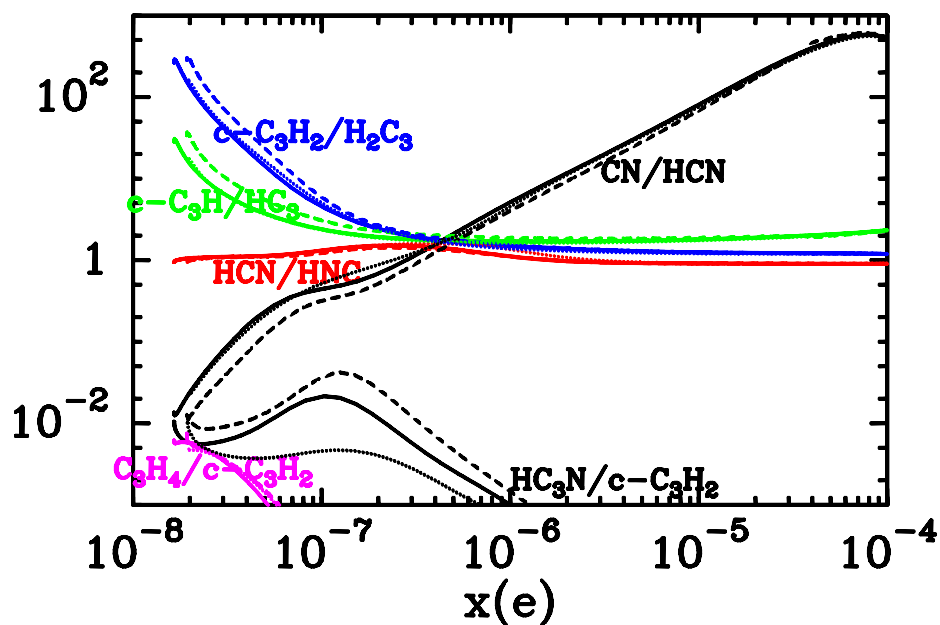


Figure 5. Molecular abundance ratios as a function of electron density for conditions suited to the Horsehead nebula. The radiation field is $G_0 = 100$. The full line corresponds to a varying gas density, with a complete thermal balance. The dashed line corresponds to a model using the same density profile, but with a minimum temperature set to 30 K, as used by Goicoechea *et al.* (2005) to fit the CS and $C^{18}O$ data. The dotted line corresponds to a model with a constant gas density of $n_H = 10^5 \text{ cm}^{-3}$. High electron abundances are found in the warm outer layers, while the low values correspond to the dense, well shielded regions (see Fig. 1).

not quite sufficient. Higher spatial resolution maps, which can now be obtained with millimeter interferometers, can be used to constrain the models accurately.

4. Conclusions

With the current generation of instruments, and even more with the upcoming generation, excellent data can be obtained, which will allow us to probe interstellar chemistry accurately. State-of-the-art chemical models can now be combined with sophisticated radiative transfer codes to obtain accurate predictions of the line and continuum emission, which can be compared with the observed data. This method requires a simple source geometry (an inaccurate geometry can lead to important differences in line predictions and invalid conclusions). PDRs will remain template sources where physical processes, which operate on a wide range of physical conditions, can be studied with the greatest detail. Carbon chains and rings, and carbon clusters, are promising probes of the interstellar chemistry as they can be used for studying the ionization balance, the relationship between dust grains, macromolecules and gas phase species, as well as the formation routes of complex molecules.

However, PDR models still need improvement. In the coming years, advances are expected on the following aspects:

- Many parameters which are used in current models suffer from large uncertainties. Chemical reaction rates, such as those governing the sulfur chemistry for instance, are not known to the required accuracy over the temperature range relevant for interstellar chemistry.

- Although PDR models solve self-consistently for the gas chemistry and thermal balance, the predicted temperatures are too low at moderate extinction. This old problem has important consequences, as the predicted intensities of millimeter rotational lines are strongly dependent on the assumed gas kinetic temperature. Hence molecular abundances deduced from those lines can be affected by an error in the gas temperature determination.

- Observations of both gas-phase and solid-phase species point to the necessity of including a tight coupling of the dust and gas phase chemistry in the models. This requires, however, the knowledge of reaction rates for reactions involving abundant ions and atoms and PAHs, for instance. Laboratory studies are underway, as shown by posters presented at this conference (Betts *et al.* 2005; Joblin *et al.* 2005).

- Most PDR models solve the gas chemical abundances at steady state, in order to be able to correctly treat the FUV radiative transfer and H₂ photodissociation and ro-vibrational excitation. However, this hypothesis is not completely valid, as PDR are usually bordered by an H II region (associated with the illuminating star), which could be in expansion. Further developments could include a combined treatment of the ionized, neutral and molecular gas, as presented by R. Ferland and co-workers for the CLOUDY model (Ferland *et al.* 2005). Work aiming at understanding the temporal evolution of a PDR (see e.g; Morata & Herbst 2005) should also be pursued. Finally dynamical models, such as those presented by Hosokawa & Inutsuka (2005), provide a complementary view of the evolution of the gas density structure.

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Discussion

PAPADOPOULOS: It has been 20 years since the first PDR models were published. Since then the “sandwich” distribution of $C^+/C I/CO$ at the edges, $A_v \sim 1 - 3$, of clouds has failed to show up anywhere in the sky. So why should we believe/trust any other predicted distribution of species coming out of such models?

GERIN: First, the model fares well for other species: CO, $C^{18}O$, CS for instance. An accurate fit needs to consider the cloud geometry: the predictions for an infinite edge-on slab need to be tailored for a finite slab of gas, including two surfaces along the line of sight which contribute some of the emission for C and ^{12}CO . A careful understanding of the source geometry and structure is mandatory before assessing model success and failures. Of course, the question of the atomic carbon abundance and spatial distribution is probably not totally understood yet.

GUÉLIN: What about desorption from dust grains in PDRs?

GERIN: Desorption from dust grains could be considered, but it is most relevant for species which are abundant in the mantles (H_2O , CH_3OH , H_2CO , etc.), and not so much for the hydrocarbons, which we study.



Photo: E. van Dishoeck