Chemistry in UV-irradiated interstellar clouds

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Far-UV photons (FUV, $E < 13.6$ eV) from massive stars regulate, or at least influence, the dynamics, heating, ionization, and chemistry of most of the neutral ISM (HI and H$_2$ clouds). Investigating the interaction between FUV radiation and interstellar matter (molecules, atoms, and grains) thus plays a central role in Astrochemistry. Indeed, it contributes to a better understanding of a broad range of environments in which similar physical and chemical processes operate (diffuse clouds, the interface between HII regions around massive stars and their parental dense cloud, planetary nebulae, starburst galaxies, etc.) all generically known as “photodissociation regions” (PDRs).

The chemistry of PDRs depends on the propagation and attenuation of stellar FUV photons into the cloud. Different physical processes and chemical reactions control the molecular composition as a function of cloud depth. Traditionally considered to be too harsh environments to host a rich chemistry, modern-day observations using multi-wavelength techniques and broad-band spectrometers do show a distinctive (photo)chemistry. Specific “PDR molecules” are the molecular ions CF$^+$, CO$^+$, HOC$^+$, CH$^+$, SH$^+$, OH$^+$ or H$_2$Cl$^+$ ions (some of them extremely reactive). Their formation routes often represent the first steps of interstellar chemistry. The list of molecules detected in prototypical PDRs such as the Horsehead Nebula or the Orion Bar steadily increases. It ranges from well-known radicals (e.g., C$_2$H, CN, OH, HCO), heavier ions (such as $^1$C$_3$H$^+$) involved in the formation of small hydrocarbons (e.g., C$_3$H$_2$ and C$_3$H), isotopologues and isotopomers (e.g., $^{13}$CCH, C$^{13}$CH, DCN and HNC), to PAHs and complex organic molecules (COMs, e.g., CH$_3$CN, HCOOH, CH$_2$CO, etc.). Explaining the presence of COMs in PDRs is particularly challenging, and opens new avenues for grain surface and ice-mantle desorption studies.

The emission from the above species not only reflects subtle excitation and chemical processes (photoreactions, state-to-state reactions with FUV-pumped vibrationally excited H$_2$, fractionation reactions, photo-erosion of grains, etc.), also they trace the steep variations in the gas properties (physical and FUV-illumination conditions, ionization fraction, etc.) as a function of cloud depth. In this contribution I will review our on-going modelling and observational efforts (with ALMA, Herschel and the IRAM 30m telescope) to characterize the chemistry of PDRs.