From Interstellar Ices to PAHs
A symposium to honor Lou Allamandola's Contributions to the Molecular Universe
Annapolis, MD, USA - September 13^{th} to September 17^{th}, 2015

INVITED TALK

The Role of Dust in Interstellar Chemistry

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Surface reactions are an important component of chemical simulations for diverse sources in the interstellar medium. Indeed, much of the synthetic, "bottom-up" chemistry that occurs in the interstellar medium takes place on the surfaces of dust particles, which can be either bare silicates or carbon, or the top of ice mantles, which grow in cold dense regions. Some chemistry can also take place within ice mantles. Unlike gas-phase processes, which can easily be treated by standard differential rate equations, surface chemistry must sometimes be treated by the use of stochastic methods, especially if small numbers of reactive species are present on individual grains (Charnley 2001).

Probably the most important reaction occurring on dust particles is the formation of molecular hydrogen, the dominant interstellar molecule, from two hydrogen atoms. A gas-phase process cannot occur efficiently at the low temperatures of interstellar clouds for a variety of reasons. Depending upon the physical conditions of the source, the formation of H_2 on surfaces can occur via a diffusive, Langmuir-Hinshelwood mechanism, or via an Eley-Rideal mechanism, in which a gas-phase reactant collides with a rather stationary adsorbate species (Herbst 2014). In addition, the binding of the hydrogen atoms can be weak, known as physisorption, or strong, known as chemisorption. In general, weak binding is necessary for diffusion at low temperatures, whereas strong binding is needed at high temperatures to keep the adsorbates on the grain long enough for them to react.

In addition to the formation of molecular hydrogen, surface chemistry accounts for a large number of heavy molecules in a variety of different environments, even if these molecules eventually end up in the gas phase, where they can be detected more easily. In addition to the Langmuir-Hinshelwood and Eley-Rideal mechanisms, other more complex mechanisms are also possible, including chain reactions and complex formation (Garrod & Pauly 2011; Herbst 2014; Ruaud et al. 2015). In cold dense cores, the dominant surface processes involve the diffusion of at least one weakly bound atom or diatomic molecule that has considerable mobility even at 10 K. Examples include the hydrogenation of water via the sequence of reactions

$$\mathrm{O} + \mathrm{H} \rightarrow \mathrm{OH}; \mathrm{OH} + \mathrm{H} \rightarrow \mathrm{H_2O}, \tag{1}$$

in which the H and O atoms adsorb from the gas and then diffuse towards each other. Following the formation of OH, a second hydrogen atom is adsorbed and converts OH into water. Other mechanisms for water formation exist. Another important sequence of surface reactions partially converts CO, formed mainly in the gas, into formaldehyde and methanol (Charnley et al. 1997):

$$\mathrm{CO + H \rightarrow HCO; HCO + H \rightarrow H_2CO; H_2CO + H \rightarrow H_2COH; H_2COH + H \rightarrow CH_3OH.} \quad (2)$$

Although non-thermal mechanisms to remove heavy molecules from the ice mantles exist; viz., photodesorption and reactive desorption, the ice mantles can grow to more than 100 monolayers per grain, which corresponds to a fractional abundance with respect to hydrogen ot 10^{-4}. The ice mantle is dominated by water, with smaller abundances of CO, CO_2, methanol, and a variety of trace but observable species detectable by infrared absorption of background continuum radiation.

Some cold cores are precursors to the formation of low-mass stars and planetary systems, undergoing a series of stages involved in collapse. Although the initial stage of collapse is isothermal, eventually the collapsing core begins to heat up and a protostar begins to form in the middle of the structure. The surrounding material can heat up to a few hundred Kelvin, and the molecular constituents of this warm gas, known as a hot corino, are different from those of the cold interstellar gas, with the main difference being high abundances of more terrestrial-like organic molecules and fewer exotic species. Although gas-phase syntheses of these terrestrial-like molecules are sometimes efficient, much of the synthesis is thought to occur on warming interstellar grains, when larger molecules begin to diffuse on the surface (Herbst & van Dishoeck 2009). Although most of these species are unreactive, agents such as VUV photons, protons, and electrons collide with the grain mantles and produce radicals from the more stable neutral species. The association of radicals proceeds in competition with other possible classes of reaction such as abstraction. For example, the radicals HCO and CH_3O can associate to form methyl formate ($HCOOCH_3$). When the temperature exceeds 100 K, the mantle begins to desorb, and the newly formed organic species now inhabit the gas phase, where they can be detected in rotational emission. Interestingly, a subsequent evolutionary stage, the so-called protoplanetary disk, is sufficiently cool in regions removed from the central young star that the organic molecules once more form mantles on cold grains. The term “complex interstellar molecules” has been applied to the organic molecules formed in hot corinos (and their high-mass cousins, the hot cores) although these species are nowhere near as complex as PAH’s and fullerenes. Nevertheless, they contain the elements H, C, N, and O, and so appear to be precursors for the molecules that grow into biological species and perhaps populate newly formed planets, which form out of dust particles in protoplanetary disks.

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