Organic Chemistry in Space – X-ray Processing of a Realistic Ice Mantle

The absence of complicated species from the cold gas in protoplanetary disks, and the presence of abundant CO, HCO and H_2CO and negligible CH_3OH, is compatible with the simulated realistic ice with X-ray. The particularly small abundances of other COMs in the cold parts of the disk are formed in the ice bulk but not ejected into the gaseous phase.

Astronomical observations performed with airborne telescopes, equipped with an infrared spectrometer, show absorption bands of volatile species in the solid phase and a broad absorption due to silicates. These spectra correspond to (sub)micrometer silicate dust in interstellar and protoplanetary environments. Here the dust temperatures near 10 K allow the growth of an ice mantle on the dust grains, which is composed of simple species found to absorb in the infrared region, *i.e.*, water (H_2O) and smaller amounts of carbon monoxide (CO), carbon dioxide (CO_2), methanol (CH_3OH), methane (CH_4), ammonia (NH_3) and other molecules.

Laboratory simulations of multicomponent ice mantles performed at 10 K under ultra-high- vacuum conditions include irradiation with ultraviolet or X-ray photons. The irradiated ice samples are warmed to allow diffusion of the generated radicals and other reactive species. After sublimation of volatile components, an organic residue remains at room temperature. Such a residue contains a plethora of organic molecules of astrobiological interest; among them are amino acids, nucleobases, sugars, carboxylic acids *etc*. It is generally thought that such agglomeration of icy dust grains leads to formation of cometesimals and planetesimals. Indeed, some meteorites contain similar organic species. Cometary missions such as Stardust and Rosetta detected glycine, acetamide and several other prebiotic species in comets that are readily formed in experiments on ice irradiation. Cometary and asteroid impacts on the early Earth delivered water and such organic species that likely contributed to the origin of life.

Protoplanetary discs

The formation of such complicated organic substances would have added value if it occurred in the gas surrounding a young solar-type star, implying that their synthesis would be coeval with the formation of planets in a protoplanetary system. Star formation is a violent and chaotic event in which a gas flows in and is ejected outwards at speeds up to hundreds of km per second. This effect occurs because the gravitational infall is locally opposed by thermal, turbulent and magnetic pressures, by dynamical outflows, and, as the parent cloud is rotating, by effects of angular momentum. As a consequence of all such competing processes, the contracting cloud forms a swirling disc. Circumstellar discs are an inevitable consequence of the conservation of angular momentum during the formation of a star through gravitational collapse. Initially, discs rapidly funnel material onto the star but, as the surrounding molecular core is consumed or otherwise disperses, the rate of accretion decreases; only a small proportion of the original material persists in the disc. That these discs can be considered protoplanetary is apparent not only in the geometry of the Solar System but also in the large rate of detection of exoplanets. Observing discs around solar-type stars, we might catch a glimpse of the chemical evolution preceding the onset of life on our planet. Young solar-type stars emit X-rays at a level 3–4 orders of magnitude greater than the present-day Sun. For a 100-Myr-old star the X-ray flux is larger than the vacuum- and extreme-ultraviolet emission; their ratio remains within a factor two for stars as old as 1 Gyr. X-rays, being much more penetrating than ultraviolet radiation, might illuminate cold regions of a disc and, therefore, are a major agent in processing circumstellar material.

The molecular content of protoplanetary discs

The physical conditions in a protoplanetary disc vary greatly, with hot and dense regions of gas and dust near the star and much colder material at greater distances from it. In protoplanetary discs, the inner edge of the region at which the temperature falls below the condensation temperature of a volatile substance is referred to as the snow line (for that species). Each volatile has a distinct location of snow line, water ice being nearest the host star, farther on CO_2 and then CO. As a consequence, the ices within a disc are organized in a bi-layered structure of segregated polar (water-rich) and apolar (water-poor) components. The initial water-rich layer is thought to form early in the disc through hydrogenation of atomic oxygen. The bulk of solid CH_4 and NH_3 is likely also formed at this stage, through hydrogenation of carbon and nitrogen. As the disc gradually cools, free-flying molecules are removed from the gas, of which the main component (after volatile H_2 not sticking to dust) is carbon monoxide. The formation of a layer of CO ice provides a feedstock for the formation of icy methanol through hydrogenation of CO. The birth of methanol marks the first generation of complicated species.

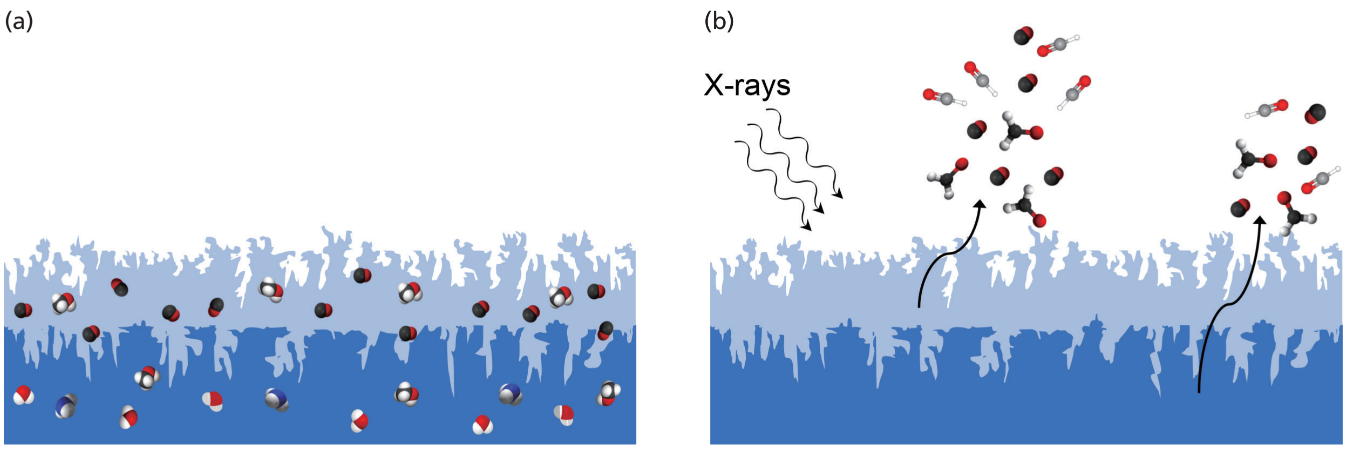

Fig. 1: Sketch of the bilayer ice experiment. (a) The bottom H_2O:CH_4:NH_3 mixture covered by a layer of CO:CH_3OH. (b) X-ray irradiation of the ice induces a rapid destruction of CH_3OH, leading to the formation of new species rather than its photodesorption. During the irradiation, a negligible desorption of CH_3OH was detected, whereas CO and products such as HCO, H_2CO and CO_2 show the most intense desorption signals. Desorption from the bottom layer species was also detected. [Reproduced from Ref. 1]

The cold gas in protoplanetary discs seems to be devoid of complicated organic species (known as COMs in the astronomy jargon). Whereas CO, CO_2, HCO and H_2CO are typically abundant molecules in the cold zones of the disc, methanol or acetonitrile are found in only a few regions, and more complicated organic species are not observed. This effect is to some extent unexpected, as chemical and physical conditions in discs appear not so drastically different from those in other interstellar regions, in striking contrast with the analysis of meteorites and comets that are instead rich in complicated organic species.

Laboratory experiments using the right ingredients

The work, published in PNAS, extended a step further than previous experiments. Instead of mixing common volatile species in the ice sample, an analogue of ice mantles was prepared that took into account the more realistic ice configuration composed of two layers. Indeed, hydrogenation of O, C and N on the bare dust surface produced a first layer of H_2O, CH_4, NH_3 and other reduced species. On top thereof, a second layer of species was formed in the gaseous phase and required lower temperatures to stick onto the dust, dominated by CO and CH_3OH, the latter presumably formed by hydrogenation of CO in the ice. The source of radiation, soft X-rays, was provided by **TLS 08B1** in NSRRC. These X-rays irradiating two layers in experiments led to either desorption of the ice molecules during irradiation or the destruction of molecules (**Fig. 1**). As a result of this breakage, more COMs were formed.

Comparison with the observed molecular distribution

Particular attention was paid to the desorption of molecules during the irradiation, as this condition allows comparison with recent observations of protoplanetary disks using the Atacama Large Millimeter Array, ALMA. The absence or small abundance of complicated species from the cold gas in protoplanetary disks, and the presence of abundant CO, HCO and H_2CO and negligible CH_3OH, is compatible with this laboratory simulations of X-ray processing of realistic ice. Moreover, these experiments offer an explanation of the particularly small abundances of other COMs in the cold parts of the disk, as they are formed in the ice bulk but not ejected into the gaseous phase. This finding is supported by the rich chemical inventory identified in the disc around V883 Ori, a system in which a suddenly increased luminosity of the central star quickly expanded the snow lines into the disc, creating a "sublimation front".

As the chemical implications of X-ray-rich environments are, so far, relatively unexplored, much more work remains to be done, and NSRRC will generate a fundamental and precious contribution. (Reported by Yu-Jung Chen and his collaborators, National Central University)

*This report features the work of Yu-Jung Chen, Angela Ciaravella and their collaborators, published in PNAS **117**, 16149 (2020).*

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- XPS, XAS
- Materials Science, Chemistry, Surface, Astro-Physics

Reference

1. A. Ciaravella, G. M. Munoz Caro, A. Jimenez-Escobar, C. Cecchi-Pestellini, L.-C. Hsiao, C.-H. Huang, Y.-J. Chen, Proc. Natl. Acad. Sci. USA **117**, 16149 (2020).