Illuminating the Cosmic Laboratory with Vacuum Ultraviolet Light

Exploring the origin and evolution of interstellar and circumstellar molecules enhances our understanding of the Universe.

In the vast expanse of the cosmos, scientists are continuously uncovering secrets that bridge the gap between stars and the building blocks of life. Among these pursuits, three recent studies used the vacuum ultraviolet (VUV) beamlines of the Taiwan Light Source (TLS) to illuminate intriguing connections between interstellar chemistry, materials science, and the potential origins of life. These stories unfold like chapters in a grand cosmic narrative, each offering a glimpse into the intricate dance of molecules and light in the universe.

The first story begins with ethanolamine, a simple molecule with profound implications. Known as a precursor to amino acids, ethanolamine has the potential to unveil how the building blocks of life might have formed in the harsh environments of space. A joint research group led by Bhalamurugan Sivaraman from Physical Research Laboratory of India, delved into its mysteries by recreating astrochemical conditions in the laboratory. Using advanced spectroscopy, they probed the spectral fingerprints of this molecule, capturing the behavior of ethanolamine ice as it is warmed from frigid interstellar temperatures.1 Infrared and VUV spectroscopy provided critical insights, revealing how the molecule interacts with ultraviolet photons and sublimates as it transitions to higher temperatures. The end station connected to TLS 03A1 employed ultrahigh vacuum chambers to mimic interstellar conditions, with ethanolamine deposited on cryogenically cooled substrates. These setups allowed for precise control of temperature and environment, ensuring that the behavior of the molecule could be observed without interference. Coupled with computational models, this work pieced together plausible pathways for the molecule's formation on cosmic dust grains, providing a roadmap for future discoveries of prebiotic chemistry in the cosmos.

Next, their focus shifted to 1-propanol, a fatty alcohol that holds the potential to shed light on the origins of proto-cell membranes. The tale of 1-propanol is one of resilience, as experiments revealed its unusual stability in the icy realms of the interstellar medium. Despite warming beyond its melting point, this molecule defied expectations, remaining amorphous and adhering to simulated dust grain surfaces.² Mid-infrared spectroscopy was again employed to trace the molecular vibrations of 1-propanol across a range of temperatures, while VUV spectroscopy captured its absorption characteristics in the 115–220 nm range, as shown in **Fig.1**. Using a cryostat system with

LiF windows and controlled heating rates, researchers meticulously documented the phase transitions and sublimation behavior of 1-propanol. The VUV spectra of 1-propanol were recorded well beyond its melting point of 147 K, demonstrating that the solid-state sample remained amorphous throughout the warming process, from 10 K to 175 K, until sublimation. This represents the first observation of a molecule persisting on a cold substrate beyond its melting point in a UHV chamber. In contrast, 2-propanol, a positional isomer of 1-propanol, exhibits entirely different behavior: it crystallizes at approximately 120 K and sublimates at 150–155 K, prior to reaching its melting point. Mid-infrared spectroscopy was again employed to trace the molecular vibrations of 1-propanol across a range of temperatures, while vacuum ultraviolet spectroscopy captured its absorption characteristics in the 115-220 nm range. Complementing these experiments, molecular dynamics simulations unravelled the microscopic interactions between the alcohol molecules, offering a new perspective on the complexity of icy mantles in space. This surprising discovery challenges conventional ideas about the phase behavior of interstellar ices and expands our understanding of the molecular diversity in space.

Meanwhile, a different kind of light emerged from the depths of the Red Rectangle Nebula—a mysterious blue luminescence (BL). This glow had puzzled scientists for decades, with its origins tied to the enigmatic interplay of polycyclic aromatic hydrocarbons. BL is characterized by

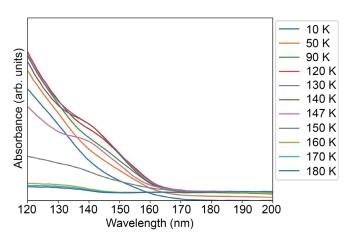


Fig. 1: VUV spectra of 1-propanol ice recorded after deposition at 10 K. The deposited ice was then warmed to higher temperatures and spectra recorded at specific temperatures until sublimation. [Reproduced from Ref. 2]

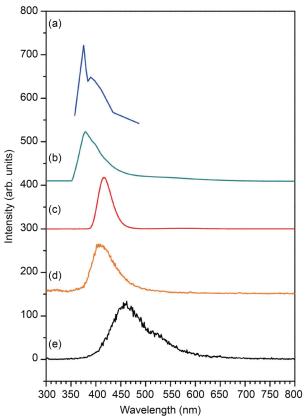


Fig. 2: (a) Blue luminescence recorded in the Red Rectangle Nebula,⁴ and PL spectra measured at 10 K upon excitation with 121.6 nm for (b) photochemically N₂-covered graphene, (c) photochemically O₂-covered graphene, (d) commercial N-doped graphene flakes, and (e) commercial graphene oxide flakes. [Reproduced from Ref. 3]

an asymmetrical spectral band peaking around 375-378 nm in the ultraviolet and visible regions. Its discovery in astrophysical environments such as the Red Rectangle Nebula links it to aromatic compounds and quantum effects in interstellar dust. In a breakthrough study,3 Y.-J. Wu (NSRRC) and his collaborators turned to graphene, a material as versatile as it is remarkable. By doping graphene with nitrogen atoms and exposing it to VUV light, they recreated conditions that echoed the astrophysical environments where BL thrives. The experimental setup involved single-layer graphene films, covered by a few layers of N₂ or O₂ solids and mounted on MgF₂ substrates, which were then cooled to 10 K and exposed to intense VUV light at 121.6 nm at TLS 21A2. Photoluminescence spectroscopy revealed a peak at 378 nm, closely matching the BL spectra recorded in the Red Rectangle Nebula, as shown in Fig. 2. Further analysis using Raman spectroscopy and X-ray photoelectron spectroscopy identified the structural defects and pyrrolic-N and pyridinic-N groups in the graphene lattice responsible for the luminescence. These defects disrupt the carbon network's symmetry, introducing localized electronic states that emit the characteristic blue light when excited. This study established N-doped graphene as a potential carrier of BL observed in astrophysical environments.

Together, these studies weave a rich tapestry of discovery, connecting laboratory experimentation with the mysteries of the universe. They remind us that the smallest molecules, whether in icy grains or luminous nebulae, hold the power to unlock profound insights into our cosmic origins. As scientists continue to explore these molecular frontiers, the stories of ethanolamine, 1-propanol, and N-doped graphene serve as beacons, guiding us toward a deeper understanding of the molecular universe and our place within it. (Reported by Yu-Jong Wu)

This report features the work of Bhalamurugan Sivaraman and his collaborators published in Astrophys. J. 975, 181 (2024) and MNRAS 530, 1027 (2024), and the work of Yu-Jong Wu and his collaborators published in Astrophys. J. 977, 230 (2024).

TLS 03A1 High-flux VUV Beamline TLS 21A2 VUV Photochemistry

- Photoabsorption, Photoluminescence
- Astrochemistry, Molecular Science

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