Department of Chemistry, IIT Madras
Ph.D. Second Seminar

Clathrate hydrates in ultrahigh vacuum under cryogenic conditions

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Abstract

Clathrate hydrates (CHs) are solid crystalline inclusion compounds in which different guest molecules are trapped in H-bonded water-cages.[1] These trapped guest molecules are generally small such as CH_4, CO_2, N_2, H_2, THF, etc. These hydrates have drawn close attention of the scientific community due to their wide use as potential future source of energy, gas storage material, seawater desalination, separation of flue gases, etc.[1] CHs are naturally found in deep ocean layers, permafrost, and marine sediments on the outer continental shelves at ambient temperatures (<300 K) and moderately high pressures (~6 atm).[1] CHs are ubiquitous in earth, under high-pressure conditions but their existence in the interstellar medium (ISM) remains unknown. Formation of clathrate hydrates in interstellar conditions (low pressure and cryogenic conditions) can be an emerging direction to explore. We reported experimental observations of the formation of methane and carbon dioxide hydrates in an environment analogous to ISM.[2] Thermal treatment of solid methane and carbon dioxide-water mixture in ultrahigh vacuum (UHV) of the order of $\sim 10^{-10}$ mbar for extended periods, led to the formation of CHs at 30 and 10 K, respectively. This finding implies that CHs can exist in extreme low-pressure environments present in the ISM.[2] These hydrates can also accommodate two different guest molecules in different cages and termed as binary CHs. THF is known to be a stabilizing guest or promoter for the formation of binary CHs. Formation of THF hydrate was studied at $\sim 10^{-10}$ mbar and 120-130 K.[3] The associated kinetics and different thermodynamic parameters were also determined. This study can help in further exploring the formation and stabilization of binary CHs in UHV.[3] It is known that dissociation of CHs can lead to various morphologies or structures of ice. We observed the formation of cubic crystalline ice (Ice I_c) upon the dissociation of acetone hydrate, prepared in ultra-high vacuum at cryogenic conditions. High sensitivity surface science techniques such as reflection absorption infrared spectroscopy (RAIRS), temperature programmed desorption-mass spectrometry (TPD-MS), and reflection high-energy electron diffraction (RHEED) are used for these studies. Understanding different phenomena of ices (phase transition, diffusion, phase segregation, etc.) are very important in understanding the astrochemical processes that lead to star and planet formation, and may even help to understand the origin of life itself.

References:

(1) Sloan Jr, E. D.: Fundamental principles and applications of natural gas hydrates. *Nature* **2003**, *426*, 353-363.

(2) Ghosh, J.; Methikkalam, R. R. J.; Bhuin, R. G.; Ragupathy, G.; Choudhary, N.; Kumar, R.; Pradeep, T.: Clathrate hydrates in interstellar environment. *Proc. Natl. Acad. Sci. U.S.A.* **2019**, *116*, 1526-1531.

(3) Ghosh, J.; Bhuin, R. G.; Ragupathy, G.; Pradeep, T.: Spontaneous Formation of Tetrahydrofuran Hydrate in Ultrahigh Vacuum. *J. Phys. Chem. C* **2019**, *123*, 16300-16307.

Guide Head of the Department

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