

# Gas Hydrate Experimental Capabilities at the Los Alamos Neutron Scattering Center (LANSCE)

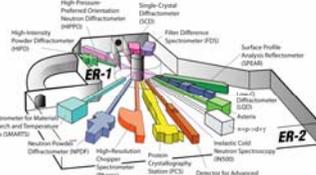
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## Introduction

The Los Alamos Neutron Scattering Center (LANSCE) is a pulsed spallation neutron source (80 kW proton beam) which produces white neutron beams for time-of-flight neutron scattering.



## Gas hydrates

Gas hydrates (clathrates) are elevated-pressure ( $P$ ) and low-temperature ( $T$ ) solid phases in which gas molecule guests are physically incorporated into hydrogen-bonded cage-like water frameworks.

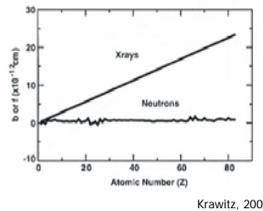
Natural methane clathrates have been found worldwide in permafrost and in ocean floor sediments, as well as in the outer solar system (the Moon, comets, Mars, satellites of the Giant gas planets).



Methane clathrates reservoirs contain 5 to 10 times the currently known reserves of natural gas.

For my PhD thesis I am investigating synthesized (both in-situ and ex-situ) gas hydrates (methane, ethane, propane, CO<sub>2</sub> and H<sub>2</sub>) using neutron diffraction and other relevant techniques at varying  $P$  and  $T$  conditions to determine crystal structure variations, formation and decomposition kinetics, and guest-host interactions.

## Why neutrons?



Low atomic number elements (e.g., C, O, H) are poor x-ray scatterers, but good neutron scatterers.

Isotopic substitutions (such as hydrogen/deuterium) allow one to highlight portions of a system (e.g., host or guest).

Neutrons interact with nuclei rather than electrons and yield precise structural information on atomic positions, interatomic distances, and atomic thermal vibrations under a variety of experimental conditions.

Neutrons, unlike x-rays, can penetrate with little attenuation through bulky sample environment equipment (e.g., a pressure cell).

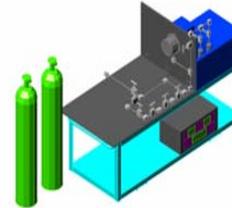
## Ex-situ synthesis of clathrates

Several complications arise during gas hydrate experiments; namely repeatability of the synthesis, time of reaction, texture, stoichiometry control, and amount of sample produced.

We have overcome these hurdles by building an ex-situ synthesis apparatus at LANSCE.



We can make large samples of gas hydrates with uniform grain size in the laboratory. This reduces the amount of neutron beam time used for synthesis and provides better control over sample quality.



## Neutron experiments at LANSCE

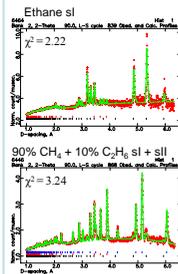
There are three principal instruments used for gas hydrate experiments at LANSCE- HIPPO, HIPD, and PHAROS.

## Diffraction experiments on HIPPO and HIPD

HIPPO and HIPD have a wide range of ancillary equipment that can study gas hydrates (gas pressure cells, closed-cycle refrigerators, ...)



## CH<sub>4</sub>+C<sub>2</sub>H<sub>6</sub> mixed hydrates



Methane and ethane two major components of natural gases & even a few weight % of the 2<sup>nd</sup> gas changes the crystal structure.

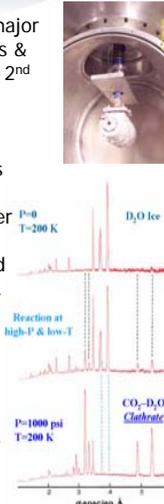
By pre-synthesizing various compositions + neutron diffraction we hope to further the understanding of the stability ranges of the sI and sII clathrates in this system.

## CO<sub>2</sub> hydrates



Kinetic studies on CO<sub>2</sub> hydrate and methanol were carried out on HIPD with a novel high pressure cell design for in situ synthesis and neutron scattering.

It was determined that methanol can act as a kinetic promoter for the formation of gas hydrates.



Bobev & Tait, 2004

## Inelastic Neutron Scattering on PHAROS

Neutron inelastic scattering has made contributions to the study of ice clathrates, to probe the potentials that describe the guest-host interactions that drive structure and dynamics.

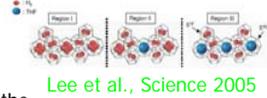
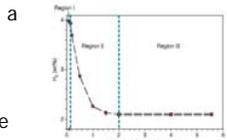
## THF + D<sub>2</sub> clathrates

Storage of hydrogen in molecular form within a clathrate framework has been one of the suggested methods for storing hydrogen fuel safely.

Tetrahydrofuran (THF)-containing gas hydrate has been proposed as a storage material.



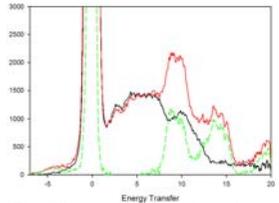
Neutron inelastic scattering measurements on hydrogen adsorbed in d-THF/D<sub>2</sub>O ice clathrate were carried out on the PHAROS spectrometer at LANSCE with a specially designed high pressure cell.



Lee et al., Science 2005

Experiments at 8K yielded two excitations at neutron energy gains of approximately 14 and 4.7 meV as compared with the H<sub>2</sub> free rotor separation of 14.7 meV.

There is also an excitation at a neutron energy loss of 9.3 meV, which must be a center of mass mode as it is not present in neutron energy gain.



The difference spectrum (green) between the H<sub>2</sub>-loaded (red) and the unloaded (black) D<sub>2</sub>O + d-THF hydrate

Further experiments and modeling are in progress to come to a detailed understanding of the adsorption sites of H<sub>2</sub> in THF/D<sub>2</sub>O ice clathrate.

## Summary

Studying the structure of clathrate hydrates under varying pressure and temperature a) will help explain the role played by natural gas hydrates in global warming; b) will further the understanding of the formation of large bodies in the outer solar system, such as Titan - Saturn's largest moon, and c) will lead to better techniques for natural clathrates extraction from the ocean floor to increase the global energy supply.

## Acknowledgements

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