Condensed Phase Adsorption and Reactivity: Extraterrestrial Ices, Isotopic Enrichment

Michelle Brann, Steven Hansknecht, Mark Muir, and Steven J. Sibener

The James Franck Institute and Department of Chemistry, The University of Chicago

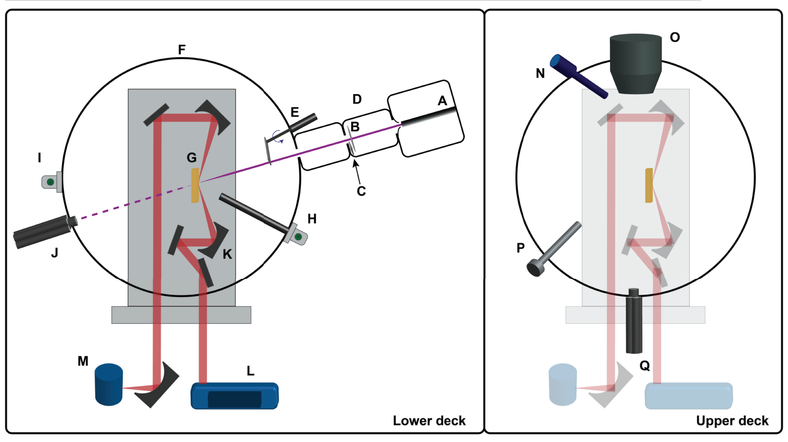
Correspondence: michellerbrann@gmail.com

Introduction

This poster details our recent work investigating acetone on top of astrophysical D_2O ices (high-density, non-porous amorphous (np-ASW) and crystalline (CI) films as well as porous amorphous (p-ASW) films with various pore morphologies). We also examine sticking probability differences between methane isotopologues. For both studies, changes on the surface were monitored in real time with time-resolved *in situ* reflection−absorption infrared spectroscopy (RAIRS) and mass spectrometry techniques. Our work demonstrates that isotopically-dependent gas-surface collisional energy transfer can influence molecular sticking and condensation allowing for an enrichment of the heavier methane isotope. We also determine that more hydrogen bonds occur between acetone and the p-ASW film structure compared to between acetone and the np-ASW or CI films. In general, our results offer a clearer picture of the mechanisms that can occur when small organic hydrocarbons interact with various icy interfaces; a quantitative understanding of these interactions is essential to understand chemical processing or production of novel molecules occurring on the surface of icy dust particles.

Experimental

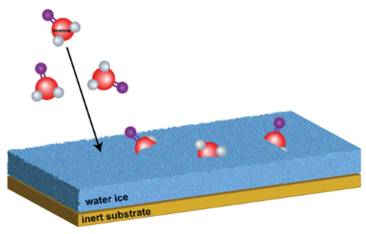
RAIRS Chamber – Time-Resolved Studies



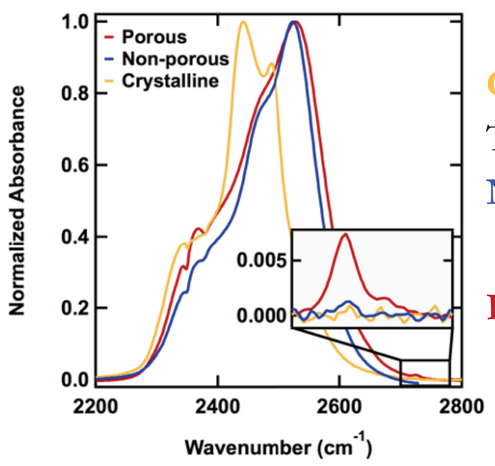
Schematic of the UHV main chamber. The lower layer (left) is used for RAIRS and molecular beam exposure. The upper level (right) is used for XPS, sputtering, and mass spectrometry.

A - Molecular beam source
B – Chopper (beam modulation)
C - Flag for timing exposure
D - Differential pumping
E - Rotatable flag
F - UHV chamber
G - Au(111) sample
H - Directed doser
I - Leak valve
J - Inline QMS
K - RAIRS optics
L - FTIR spectrometer
M - MCT/A detector
N - X-ray source
O - Cylindrical mirror analyzer
P - Ion gun for sputtering
Q - Residual gas analyzer

Growing Various Astrophysical Ices Before Acetone Deposition

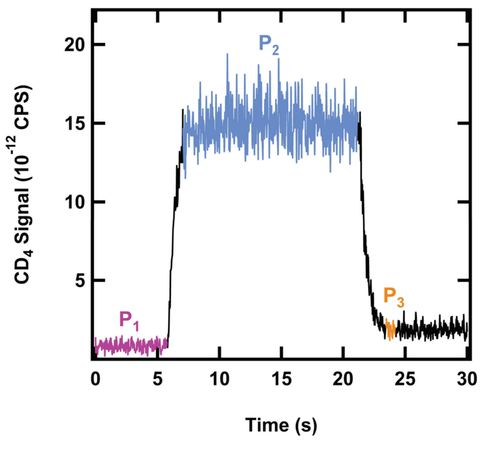


D_2O Deposition:
Directed Doser
Acetone Deposition:
Molecular Beam



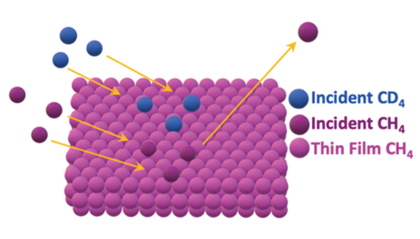
Crystalline (CI)
T_s > 140 K
Nonporous (np-ASW)
Ts < 140 K
Porous (p-ASW)
Ts < 30 K

King and Wells to Measure Methane Isotopologue Sticking Probability



P_1 = Background CH_4 signal
P_2 = Full CH_4 flux with flag blocking the crystal
P_3 = CH_4 adsorption with the flag removed

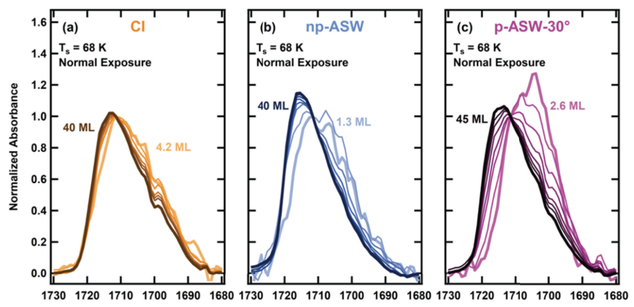
Sticking Probability: $S = \frac{(P_2 - P_3)}{(P_2 - P_1)}$



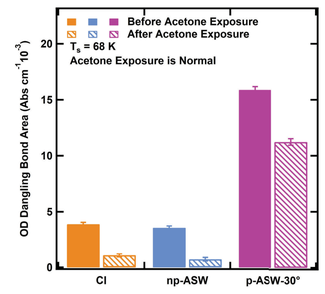
References

1. Brann, M. R.; Hansknecht, S. P.; Muir, M.; Sibener, S. J. Acetone–Water Interactions in Crystalline and Amorphous Ice Environments. *J. Phys. Chem. A* **2022**, *126*, 2729–2738.
2. Brann, M. R.; Hansknecht, S. P.; Ma, X.; Sibener, S. J. Differential Condensation of Methane Isotopologues Leading to Isotopic Enrichment under Non-Equilibrium Gas–Surface Collision Conditions. *J. Phys. Chem. A* **2021**, *125*, 9405–9413.

Acetone Interaction with CI, np-ASW, and p-ASW Ice Films

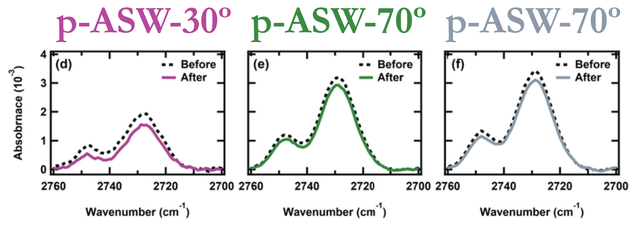


p-ASW: 14 cm^{-1} shift to ~1703 cm^{-1} from the bulk value of 1717 cm^{-1}, **indicative of hydrogen bonding to the carbonyl oxygen.**

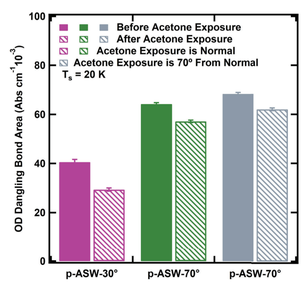


Increased hydrogen bonding occurs between acetone and p-ASW films compared to acetone and np-ASW or CI films.

Acetone Interaction with p-ASW Films: Increased Porosity



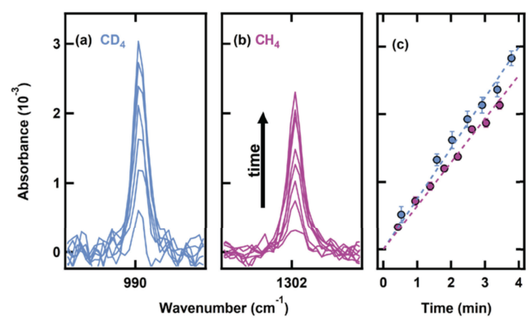
Reduction in the amount of hydrogen bonding for more porous films.
Same number of hydrogen bonds between acetone and p-ASW-70° **regardless** of incident acetone angle.



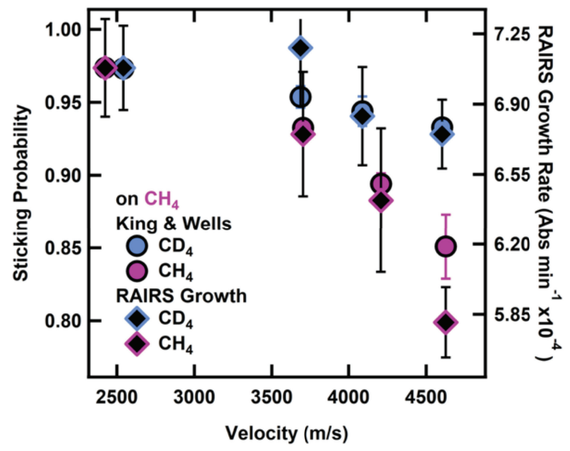
Results from a lack of access to sites within the pores: acetone covering the ices surface prevents additional acetone molecules from accessing the pore structure.

Methane Isotopes: How do Condensation and Projectile Mass Differences Impact Adsorption?

On Condensed CH_4

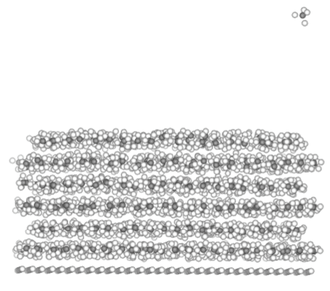


Initial growth of CH_4/CD_4 calculated from the RAIRS intensity of the ν_4 bending mode



There is a higher sticking coefficient for CD_4 → More CD_4 ends up on the surface

Building a Theoretical Model to Understand Interactions Between the Surface and Incident Molecule



This is the first calculated methane surface, and MD trajectories **support differential condensation of CH_4 and CD_4 on CH_4.** Full analysis of these MD studies will provide necessary insight into lattice vibrations and how energy is efficiently dissipated to trap the methane isotopologues .

VENUS Molecular Dynamics Code: Hu, X.; Hase, W. L.; Pirraglia, T. *J. Comput. Chem.* 1991, 12, 1014−1024

Acknowledgments

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