National Aeronautics and Space Administration

Using isotope mass spectrometry to study Titan's hydrocarbon cycle

Principal Investigator: Amy E. Hofmann (322)

Co-Is: Robert Hodyss (322), Michael Malaska (322), John Eiler (Caltech)

Program: Topic Area

Background:

Titan and Earth both have persistent bodies of liquid on their surfaces, dense atmospheres, and seasonal weather patterns. On Earth, the separation of isotopologues among snow, ice, and liquid water has been used to identify and characterize the processes that govern Earth's hydrologic cycle. Comparable data on the expected isotopic fractionations associated with specific physical processes on Titan (i.e., as determined via experiments) can aid our understanding of Titan's hydrocarbon cycle.

Crash-Course in Isotope Geochemistry

- Isotopologues = molecules that differ only in their isotopic composition (e.g., CH_4, CH_3D)
- "Vapor Pressure Isotope Effects" (VPIEs):
  - Isotopologues have different vapor pressures and thus are partitioned to different extents between coexisting vapor and condensed phases.
  - At equilibrium, the evaporation / condensation or the deposition / sublimation cycle imparts a distinct isotopic signature on each phase.

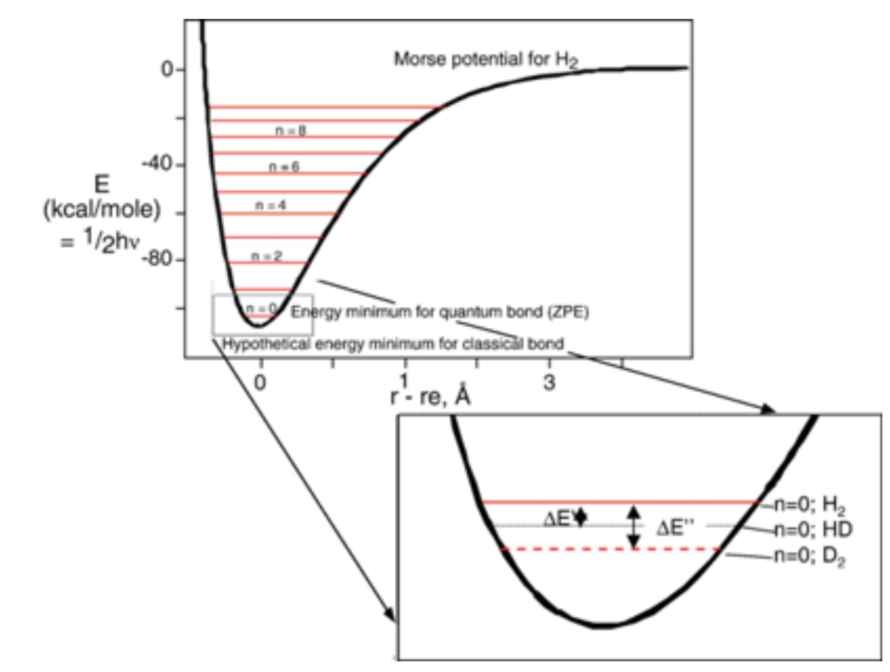

Figure 1. Cartoon illustrating zero-point energies for isotopologues of H_2.
http://www.carbonateresearch.com/sites/default/files/Fig1.png

Project Objectives (FY19 & FY20):

1. Quantitatively determine, in single-component systems of methane (CH_4), ethane (C_2H_6), and propane (C_3H_8), the isotopic fractionation between coexisting vapor- and condensed-phase molecules of that species following evaporation (or, in the case of ice/vapor systems, sublimation) of a condensate.
2. Using the results from Objective 1, predict what the isotopic signatures of such materials in Titan's atmosphere, in its lakes, and on its surface should be if evaporation / sublimation governs the near-surface distribution of these components.
3. Demonstrate the ability of an in-development-for-flight instrument—JPL's QIT-MS—to accurately resolve compound-specific carbon ($^{13}C/^{12}C$) and hydrogen (D/H) isotopic signatures in the experimental products and reactants.

FY19 Results:

Completed Experiments

- Vapor pressure curves were determined at 2° intervals over temperature ranges encompassing Titan surface and near-surface temperatures for six hydrocarbon species: CH_4, C_2H_6, C_3H_8, C_2H_2, C_2H_4, C_4H_{10}. See **Figure 3**.
- Methodologies for CH_4, C_2H_6, and C_3H_8 VPIE experiments were established, including diagnostic experiments to evaluate and eliminate potential causes of non-VPIE-induced isotopic fractionations:
  1. ***TRANSFER***: Gas aliquots were allowed to transfer (a) between volumes of different sizes at room T, (b) between volumes at different T, and (c) across greater volumes (at room T) over different lengths of time in order to establish the time required for complete vapor transfer (necessary in order to avoid pumping away slow-diffusing [i.e., heavy] species).
  2. ***TIME SERIES***: Run at intervals from 5 minutes to 8 hours, each at multiple T, to establish time required to reach isotopic equilibrium.
  3. ***THERMAL GRADIENT***: Isotopic compositions of gas dispersed throughout the volume of the line (at room T) and within the trap (at various cryogenic T, but always in the absence of a condensate) were compared.
  4. ***PHASE RATIOS***: Isotopic compositions of products employing different ratios of condensate to vapor (e.g., 9:1, 8:1, 7:1) were evaluated to determine how much condensate is required in ice/vapor and liquid/vapor systems to achieve isotopic equilibrium.

Figure 2. 'Breakseals': Pyrex tubes into which experimental reactants and products are frozen for storage prior to analysis. Tubes are cracked in an evacuated, custom-designed Swagelok apparatus and gases are extracted using gas-tight syringes for injection into the GC-pyrolysis isotope ratio mass spectrometer for isotopic analysis. Experiments presented at left are awaiting analysis. Pen for scale.

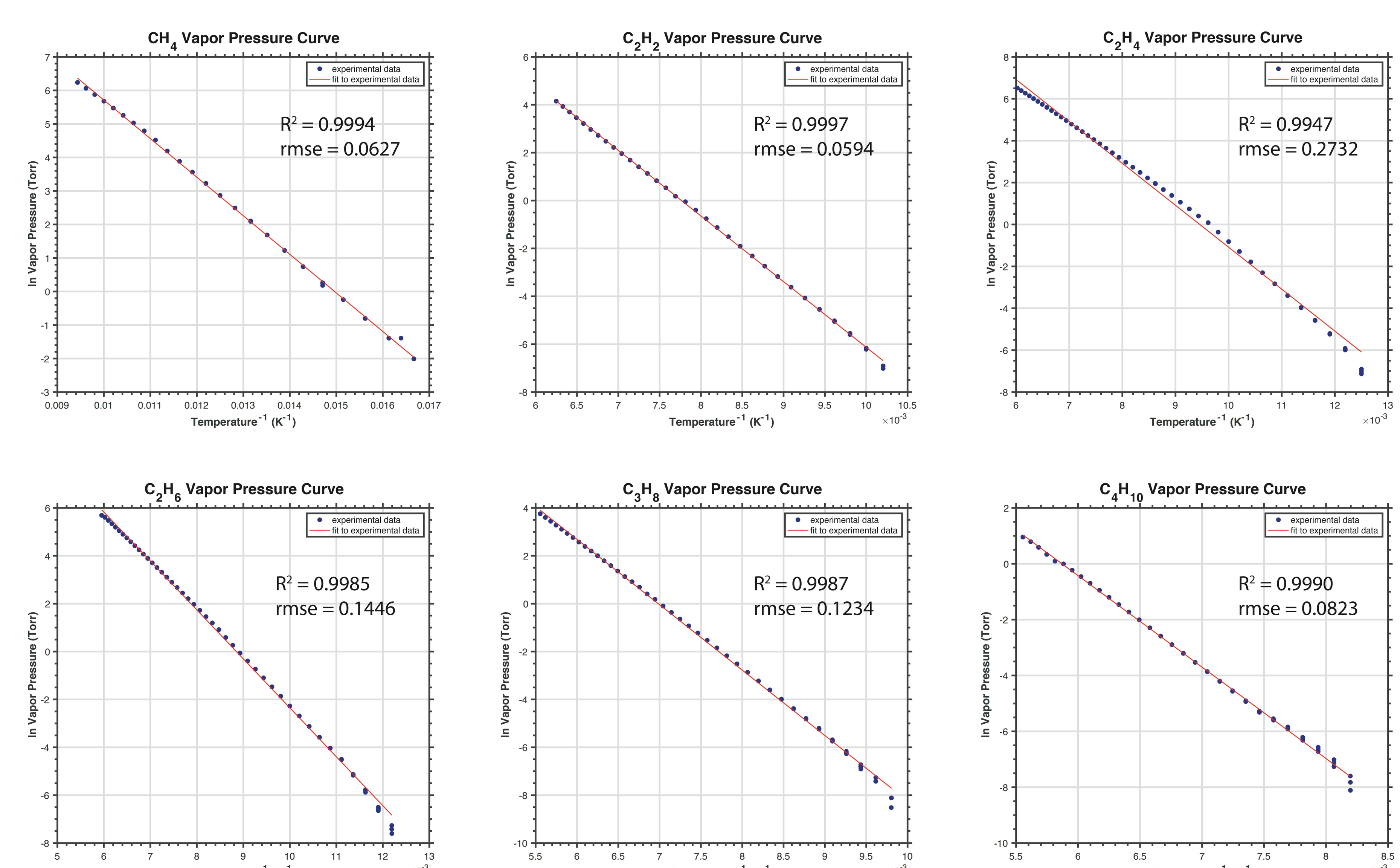

Figure 3. Vapor pressure curves determined for all three analytes (CH_4, C_2H_6, and C_3H_8) plus an additional three Titan-relevant hydrocarbons (C_2H_2, C_2H_4, and C_4H_{10}). Vapor pressures at each experimental temperature must be known in order to determine when the system has reached a stable state and the VPIE equilibration experiment can begin. Data (filled blue circles) were fit with a thermodynamically appropriate Clausius-Clapeyron relationship: $\ln P = A + B/T$ (shown as red lines). Some species (like C_2H_4) are better fit with the addition of a C/T^2 term (a common practice in published vapor pressure papers)—not shown here. Associated R^2 and root mean square error (rmse) statistics for each linear regression are given on the corresponding plot.

Significance of Results:

- In-situ isotopic measurements of Titan's near-surface organics can provide information about the geological, chemical, and potentially astrobiological processes that occur on Titan.
- Results from FY19 experiments provide the necessary diagnostic and methodological information required to move forward with VPIE equilibration experiments in FY20.

Benefits to NASA and JPL:

- Titan's hydrocarbon cycle is poorly understood, and in-situ isotopic measurements of the major components could, within the context of experimental investigations into fractionation mechanisms and the isotopic signatures they impart, reveal how Titan's atmosphere is coupled to its surface—a major step forward in Titan science.
- This work will allow us to validate instrument performance requirements to make such measurements on a feasible platform: JPL's QIT-MS.
- The ability to make accurate and precise in-situ stable isotope measurements with a mass spectrometer (MS) could give JPL PIs and Co-Is a more competitive edge on mission proposals in which isotope measurements are required for achieving mission science objectives.

National Aeronautics and Space Administration

Jet Propulsion Laboratory
California Institute of Technology
Pasadena, California

www.nasa.gov

For general experimental methods / setup, see:

Eiler JM, Kitchen N, Rahn TA (2000) "Experimental constraints on the stable-isotope systematics of CO_2 ice/vapor systems and relevance to the study of Mars". *Geochimica et Cosmochimica Acta* **64**: 733–746.

Eiler J, Cartigny P, Hofmann AE, Piasecki A (2013) "Non-canonical mass laws in equilibrium isotopic fractionations: Evidence from the vapor pressure isotope effect of SF_6". *Geochimica et Cosmochimica Acta* **107**: 205–219.

PI/Task Mgr. Contact Information:

E: amy.e.hofmann@jpl.nasa.gov

M: 626.864.3791

Poster No. RPC-097