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Ices on Titan: Laboratory Measurements That Complement the Huygens Probe

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Ices on Titan: Laboratory Measurements that Complement the Huygens Probe

Jeanne M. Robinson*, Bryan F. Henson, Laura Foster, and Kevin R. Wilson (University of California-Berkeley)

Abstract

This is the final report of a three-year, Laboratory-Directed Research and Development (LDRD) project at the Los Alamos National Laboratory (LANL). The composition of the cold bodies in the outer solar system may hold some of the key molecular clues concerning the composition of the prestellar molecular cloud that gave rise to the solar system. We studied the physical chemistry and heterogeneous (gas/surface) reactivity of extraterrestrial ice analogs of the surfaces of Saturn's moon Titan. This program coupled our surface spectroscopic techniques with physical adsorption measurements. We addressed several of the pressing questions regarding Titan such as: Is storage of hydrocarbons in Titan's water ice crust feasible? Do heterogeneous processes influence the atmospheric chemical composition of Titan? Are phase transitions to be expected? These data can be incorporated into photochemical models with the goal of improved modeling of the chemical composition and meteorology of Titan's atmosphere. Titan will be probed by the Cassini-Huygens Mission. Our results on Titan ice analogs can be used to help interpret the mission data.

Background and Research Objectives

The study of planetary formation in the outer solar system by the investigation of extraterrestrial atmospheres began with the discovery of methane on Saturn's moon Titan [1]. Although complex models of atmospheric chemistry have been formulated for Titan [2,3], resulting from the information on chemical composition obtained during the Voyager 1 flyby in 1980, several important questions relevant to planetary formation remain unresolved. Given the presumed location of Titan during condensation, ammonia is expected to be the dominant nitrogen containing species, but molecular nitrogen is observed as the largest component. The origin of Titan's present atmosphere is thus an outstanding issue. It is speculated that ammonia may be locked up as a hydrate ice in the crust [4] or that molecular nitrogen was produced by shock induced heating of the primordial NH_3 [1]. Another proposed explanation is that Titan's atmosphere was formed from the volatiles in comets that collided with Titan, as is now believed to be the case for Earth.

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The meteorology of methane photolysis is thought to be the most important process in the long-term evolution of chemical composition of Titan [1,3]. A liquid hydrocarbon ocean was first proposed as the source and sink of methane in Titan's atmosphere [5], but recent evidence suggests that the surface is composed of a porous water ice crust [6] with smaller areas which may be ethane/methane lakes. The processes by which the porous ice surface influences the atmospheric methane cycle, including heterogeneous reactions, trapping of volatiles, and surface photolysis, are not understood. The atmosphere of Titan may also contain low-lying clouds composed of frozen or liquid methane. These clouds are thought to be sinks for molecular nitrogen. The role of these molecular ices in the evolution of Titan's atmosphere has been neglected in photochemical models [3,4,7].

Our thrust has been to study the physical chemistry and heterogeneous (gas/surface) reactivity of ice analogs for Titan. The Voyager flybys focussed on the atmosphere of Titan. Many questions remain about its surface composition and morphology and the nature of gas-surface interactions which motivate our proposed studies. Measurements of the physical adsorption of gases and the chemical reactivity of extraterrestrial ices analogs that simulate Titan's crust and clouds would be quite valuable in understanding its evolution. In the course of work devoted to the impact of ice catalyzed heterogeneous chemistry on terrestrial global change, we have developed a powerful new tool, nonlinear optical surface spectroscopy, to characterize thin, porous ices grown in the laboratory and to monitor the chemical composition of simple binary mixtures at the ice surface [8-11]. This program coupled our demonstrated surface spectroscopic techniques with mass spectrometric and classical physical adsorption measurements [9] to provide heretofore unavailable data about the role(s) of the ice surfaces on Titan in time for the Cassini-Huygens Mission.

Importance to LANL's Science and Technology Base and National R&D Needs

The joint U.S.-European Cassini-Huygens Mission will provide a new opportunity for detailed observations of Saturn and Titan. The Huygens probe will descend to Titan's surface in 2004. The probe contains an extensive array of analytical equipment to measure the physical and chemical characteristics of Titan's atmosphere as well as a surface analytical package for measurements upon impact. Of particular importance to our laboratory measurements involving model Titan ice surfaces are measurements that can identify the composition and phase of these ices. The Huygens probe will perform visible and near IR measurements of the surface and low-lying clouds, remote acoustic and Raman sounder measurements of surface physical properties, and measurements of the chemical and physical properties at the surface as the probe decelerates.

Onboard the orbiter, remote measurements using imaging radar and near-IR spectrometers will monitor the structure and composition of the surface while ion and neutral mass spectrometers will sample gases in the upper atmosphere. LANL researchers in NIS are part of the mission team; in particular B. Barraclough is developing the mass spectrometers for the orbiter.

This work supports the strategies of the SSR Directorate in fostering outstanding basic science that relies on the integration of experiment with theory. Our related work on the heterogeneous chemistry of ice films [8-11] important to understanding terrestrial environmental problems has had important spinoffs relevant to the NW Directorate. We have shown that our nonlinear optical probe is a dynamic, nondestructive probe of the phase behavior of explosives integral to conventional and nuclear weapons [12]. Our newest spinoff is exploring the utility of this approach in monitoring drug polymorphs, which is expected to help decrease the cost and the time required in bringing a new pharmaceutical to the marketplace.

Scientific Approach and Accomplishments

The atmosphere on Titan is composed primarily of N_2 , CH_4 and Ar, with small amounts of ethane and unsaturated hydrocarbons. Methane is probably the main climatological fluid on Titan, its thermodynamic behavior playing a role analogous to water in our atmosphere. Figure 1 shows the activity of methane on Titan at the surface temperature of 94K is about 50-60%. Activity is defined as the vapor pressure, P , relative to the condensation pressure, P_0 . This figure of merit can be thought of as analogous to the relative humidity of water. It is noteworthy that the triple point of methane is 90.7 K at 1.6 bar, very close to the surface temperature. Lara *et al.* [7] have inferred the rate of methane photolysis by UV light on Titan is 2.13×10^{-13} g/cm²s from product H concentrations in the upper atmosphere. At this rate, the atmospheric reservoir of methane would be photolytically depleted every 50 million years i.e., 100 times over the ~5 billion year existence of the solar system. *The outstanding question is then, what is the methane reservoir on Titan that buffers this gas phase loss process?* A global methane ocean was initially proposed by Tyler et al [13] and Owen, 1982 [14] but found to be inconsistent with methane activity, the atmospheric thermal structure and albedo measurements. Lunine *et al.* [5,15] later proposed a mixed hydrocarbon ocean comprised of N_2 , ethane and methane but that was found to be inconsistent with axial eccentricity measurements, tidal considerations and albedo [16]. Other models of methane sources included volcanism [17], cometary impacts [16] and photochemical collapse of the atmosphere

[18], all of which have various drawbacks. Albedo measurements [6] suggest that an ice crust fractured by cometary impacts called a regolith may cover much of Titan. The 'hidden ocean' model proposed by Stevenson [19] theorized that methane could be stored in this porous ice regolith. This model is consistent with ice rheology, tidal constraints, mechanical property simulations and albedo measurements but still inconsistent with methane activity.

To address this question, we have considered the possible effect of heterogeneous (i.e. gas/ surface) processes involving the porous ice crust on Titan's methane inventory. A 2 km deep ice regolith offers $\sim 8 \times 10^{16} \text{ m}^3$ of surface area. A model by Kossacki and Lorenz [20] considered regolith densification as a storage mechanism. They simulated pore structure on the mm scale and calculated that a methane reservoir equivalent to several hundred meters ocean depth. However, a reservoir comprised of pore structure on this large scale does not affect the thermodynamics of the methane or methane/nitrogen/ethane solutions which are proposed to fill them. Thus the atmospheric activity of these species would be equivalent to that over a single large liquid body, the methane ocean, and serious inconsistencies with observation have been noted concerning methane activity and atmospheric thermal structure. What is thus required is a large liquid reservoir, in order to accommodate the mass of methane which must be accounted for, which has a vapor pressure consistent with observation. We propose an ice reservoir similar to that of Kossacki and Lorentz [20], an ice regolith permeated by a pore structure of sufficient total volume to accommodate the mass of methane. However, we propose a microporous structure, such that the thermodynamics of the sequestered liquid methane is modified via a capillary absorption mechanism to reflect the observed methane activity. We show that this proposal is consistent with the measured properties of ice films condensed at temperatures representative of those on Titan, and also consistent with our measurements of the capillary thermodynamics of liquid methane absorbed in these films.

In our studies [9] of vapor deposited ice films, we have found that the ice is extremely porous and that the pores are very small (20-150 Angstrom in diameter). We note that our ices are grown at a higher partial pressure of water and lower total pressure than exists on Titan. However, the temperature range over which we studied methane uptake easily covers the range relevant to Titan. Our approach is to consider how this microporosity may alter methane uptake on Titan. Figure 2 summarizes the literature data [21, 22] for methane uptake by ice films. Most of the experiments were performed at methane activity several orders of magnitude lower than surmised for Titan and at temperatures well below 94K. We have performed physical adsorption measurements of methane on well characterized porous ice films that simulate

Titan's crust from 85 K to over 100K at activities up to about 35%. The ices are grown by vapor deposition on a cold support in a vacuum chamber [9,11]. The surface area of the ices are known from our measurements of argon uptake on ices grown under the same conditions using controlled annealing protocols [9].

Figure 3 shows pressure isotherms for the uptake of argon and of methane on vapor deposited ice films. The argon data are for an amorphous ice as deposited near 85K whereas the methane data were obtained for a sample that were first annealed to form hexagonal ice (Ih). Both isotherms display classic Brunnauer-Emmett-Teller (BET) Type IV behavior [23], indicative of mesoporous solids with an open network accessible to the vapor. The initial uptake occurs by multilayer physical adsorption. Using BET theory to analyze the initial uptake data, we determined that the surface area density of unannealed ices is typically 230 m²/g with a variability of +/-20% whereas the surface area density of annealed ices is typically about three times smaller. At higher exposure (activity), the gas begins to condense in the pores of the ice by capillary absorption. The vapor pressure at which capillary absorption occurs is lower than the normal condensation pressure, P₀, because of the curvature of the pores. This vapor pressure depression is referred to as the Kelvin effect, as described by the Kelvin equation,

$$\ln P/P_0 = \ln(x) = -2\gamma V_m / (R r_m) 1/T \quad (1)$$

where γ is the surface tension of the adsorbate, V_m is the molar volume, R is the gas constant, r_m is the radius of the pore and T is the temperature. The methane isotherm in Figure 3 shows multilayer adsorption followed by capillary absorption at 87K. The fits to γV_m are shown in the figure and are independent of whether the sample is either amorphous or Ih ice.

Figure 4 shows that the form of the methane isotherms varies significantly with temperature. Of particular importance is the observation that the relative methane humidity at which capillary absorption begins is very sensitive to temperature. At temperatures below about 90-91K, the onset of capillary absorption following multilayer adsorption is readily apparent. Figure 5 shows how the Kelvin equation (Eq. 1) predicts the onset of capillary absorption versus temperature. It clearly shows that previous measurements [21, 22] at very low temperatures were not performed at large enough activity to observe this effect whereas at temperatures relevant to Titan's surface, capillary uptake occurs at extremely low methane activity. The data suggest that as the surface temperature on Titan fluctuates about 90-91 K, large quantities of methane are evaporated or condensed. This is a much larger effect than simple vapor pressure changes during physical adsorption or desorption.

From these measurements, we calculate that sufficient quantities of methane could be stored in a 2 km thick regolith to buffer the photolytic loss. We find that 2.6×10^{23} g of methane could be stored via capillary absorption, which is a factor of five larger than that lost by photolytic depletion over the age of the solar system (4.7×10^{22} g). By comparison, monolayer uptake would store 7.8×10^{21} g, insufficient to buffer the photolytic loss. Considering that methane is also an important greenhouse gas, these data illustrate that the thermodynamics of capillary absorption provide a strong feedback mechanism between surface temperature and methane activity in the atmosphere of Titan. Thus taking into account the detailed nature of the heterogeneous interaction of methane with ice, we are able to explain how methane controls the climatology of Titan.

We have also characterized the dynamics of water vapor over Titan ice analogs [9]. Specifically, we have measured the water vapor pressure over ice films vapor condensed near 85 K during annealing up to 260K and subsequent cooling. Ice films grown under these conditions are known to form highly porous, amorphous ice. We have confirmed this in physical absorption measurements of surface area like those previously discussed. Figure 6 shows our mass spectrometric measurements of water vapor pressure over several ice samples during annealing to form cubic (Ic) and then hexagonal ice and subsequent cooling. The data clearly show that amorphous ice is metastable with respect to hexagonal ice. Hexagonal ice is formed irreversibly. For heating above ~ 200 K and subsequent cooling and rewarming, the polycrystalline ice is in equilibrium with the known vapor pressures of water based on the Clausius-Clapeyron relationship.

Figure 7 shows the desorption flux for water from these films calculated from the mass spectrometric pressure measurements in Figure 6. Although the ice regolith on Titan is quite cold (94K), it has been assumed to be hexagonal ice that has cooled. The solid lines in Figure 7 are linear fits to the data based on zero order kinetics with an Arrhenius temperature dependence. The dashed lines are calculations using parameters reported in the literature [24-26]. These measurements show that whether Titan's crust is amorphous or hexagonal ice leads to an uncertainty in the flux of 12 decades (the rectangle in Figure 7). We calculate that a 2 km ice regolith would restructure in 7×10^3 years if it were comprised of amorphous ice whereas cooled Ih ice would be 'inert' by comparison, restructuring in 10^{15} years.

To the extent that our laboratory grown ices mimic the regolith on Titan, we have shown that a model incorporating capillary uptake of methane in a microporous ice regolith may provide the elusive methane reservoir necessary to stabilize the observed climate of this body.

The thermodynamic form of the ice in the regolith, amorphous or crystalline, is not known and was shown to have a significant impact on the rate of restructuring the regolith. In 2007, the Huygens probe will provide us with direct measurements of Titan's surface for the first time. These are just two of the many questions that the probe will help answer.

Publications

B. F. Henson, K. R. Wilson, and J. M. Robinson, "The Characterization of Porous Water Ice Films by Physical Adsorption and Mass Spectrometry: Stratospheric and Astrophysical Implications," *J. Phys. Chem.* (to be submitted).

L. Foster, B. F. Henson, and J. M. Robinson, "Capillary Absorption Buffers Photolytic Loss of Methane on Titan," *Nature* (in preparation).

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Figure 1. Relationship between methane activity and temperature based on Clausius Clapeyron data. The data point shows the methane activity near 94K, the surface temperature on Titan.

Figure 2. Measurements of the uptake of methane on ice of various forms prior to this work. Data were reported by Chaix and coworkers [21,22]. No indication of capillary absorption is apparent at the temperatures and methane activities investigated.

Figure 3. The uptake of argon and of methane on porous ice. The initial behavior follows multilayer physical absorption. At higher relative humidity, x , capillary absorption into the pores is observed.

Figure 4. The measured uptake of methane in moles as a function of the relative humidity of methane, $x=P/P_0$. P is the measured vapor pressure of methane over the porous ice film and P_0 is the condensation pressure of methane. Multilayer adsorption into smaller pores is followed by capillary absorption into the larger pores.

Figure 5. The inverse temperature dependence of the relative humidity of methane at which capillary absorption begins. The line through the data obeys the form of the Kelvin equation. The data suggest that capillary absorption near Titan's surface temperature of 94 K occurs at a low relative methane humidity of $<5\%$, in agreement with the measurements in Figure 4.

Figure 6. Measurements of the vapor pressure of water over vapor deposited ice films as a function of temperature using mass spectrometry. The films were condensed at 85K, slowly annealed to 260K, then cooled and rewarmd. Three replicate measurements are shown.

Figure 7. Water desorption flux as a function of inverse temperature for vapor deposited ice films during annealing and recooling. The flux is calculated from the measured vapor pressure over the ice determined by mass spectroscopy shown in Figure 6. Desorption measurements reported in Ref. 24-26 are also shown.

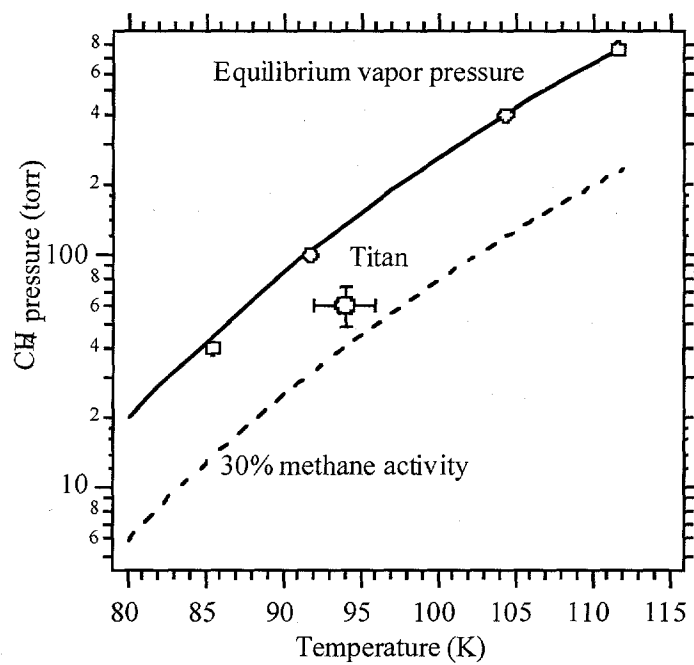


Figure 1

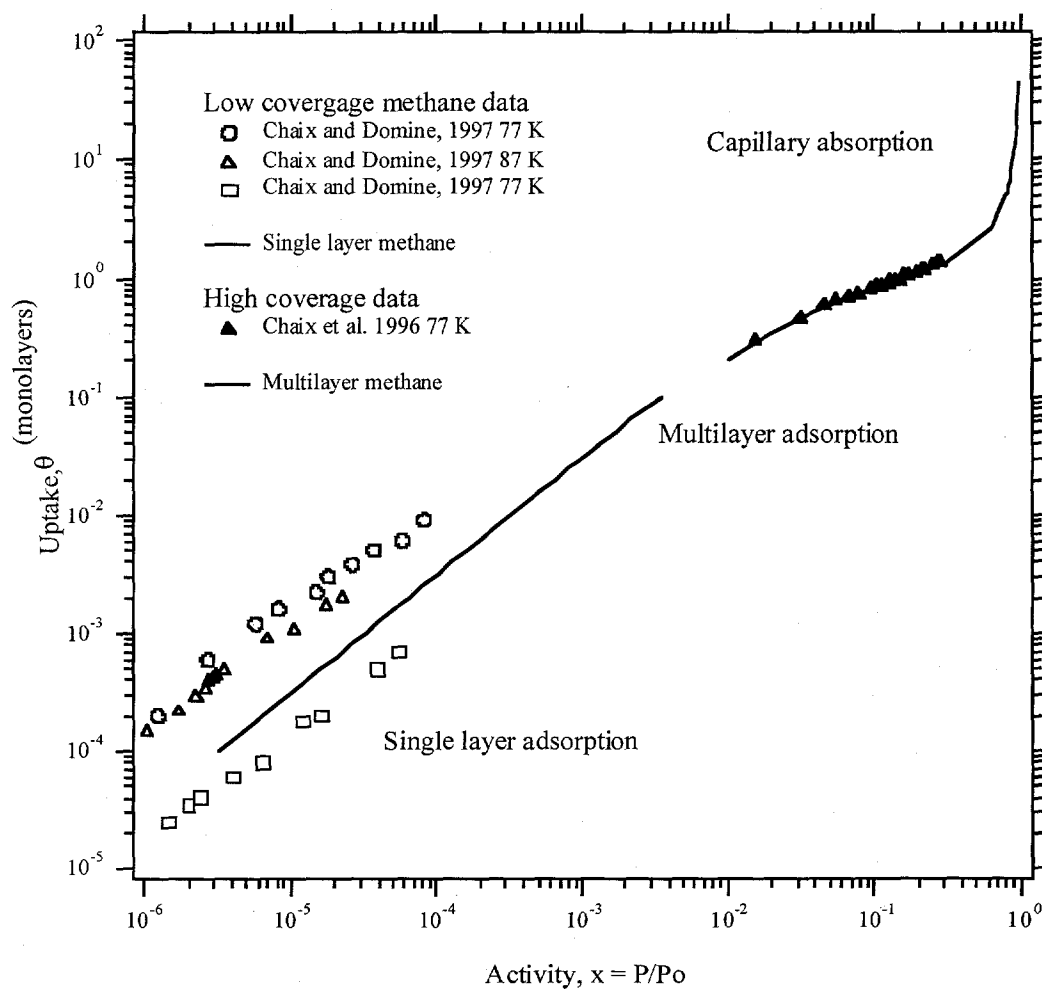


Figure 2

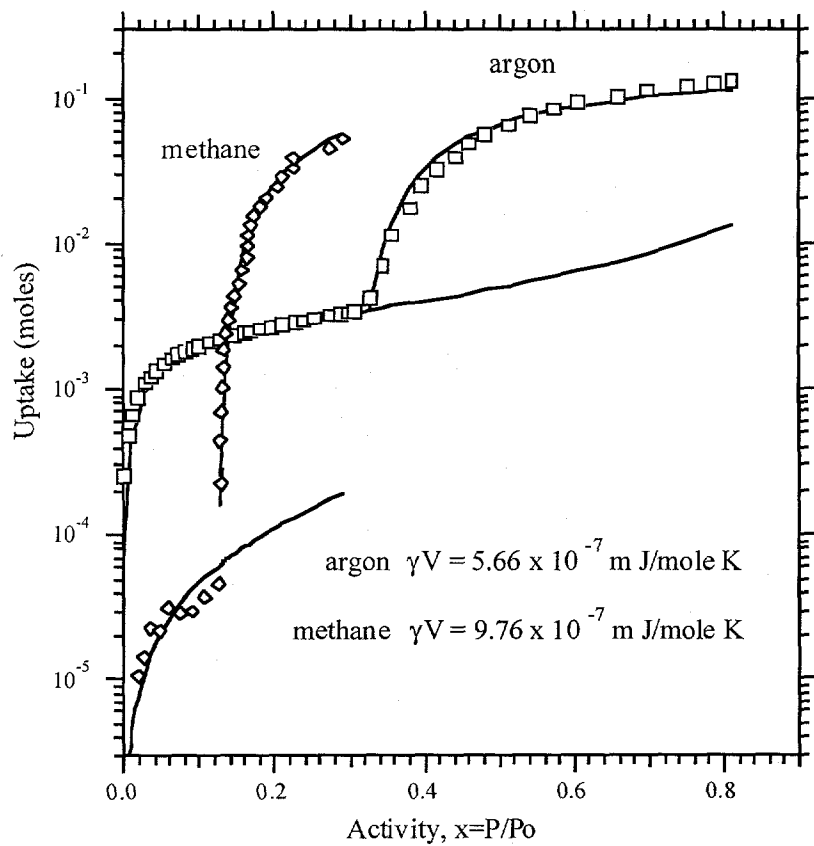


Figure 3

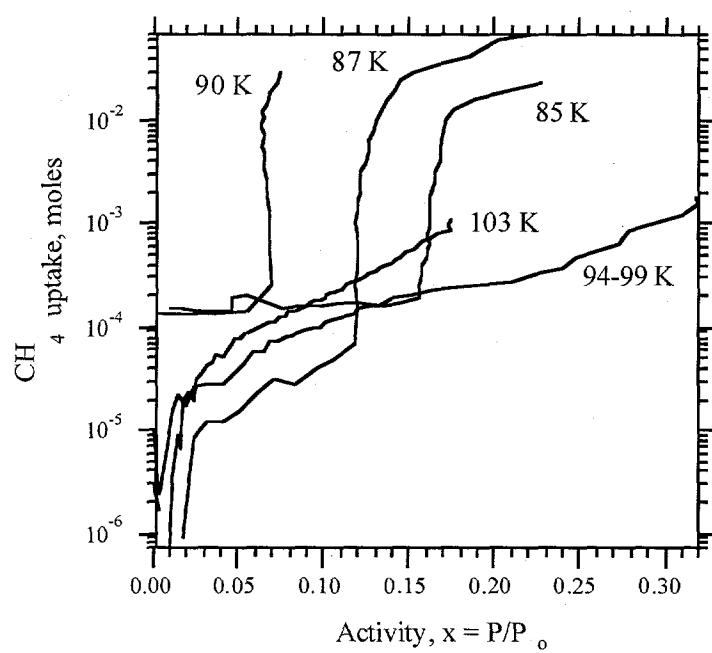


Figure 4

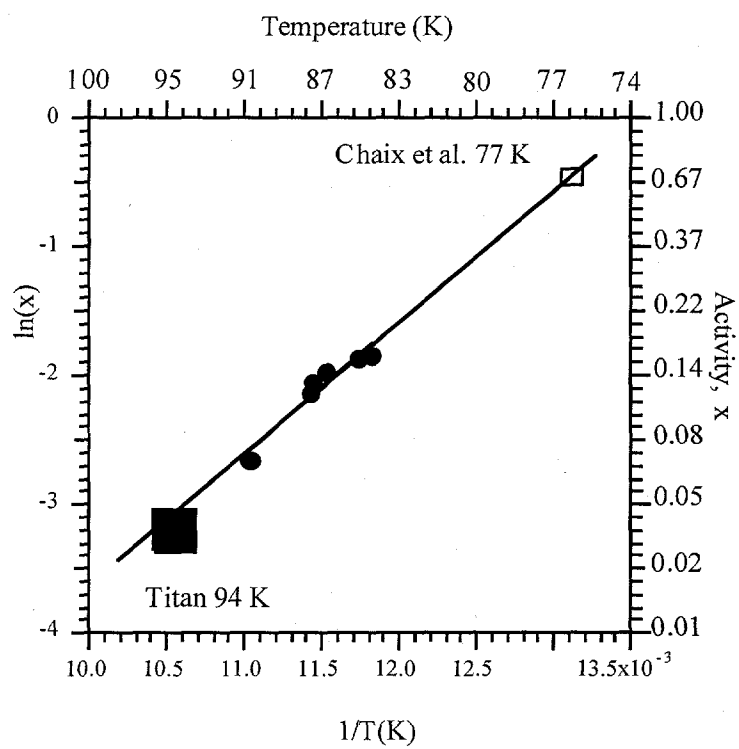


Figure 5

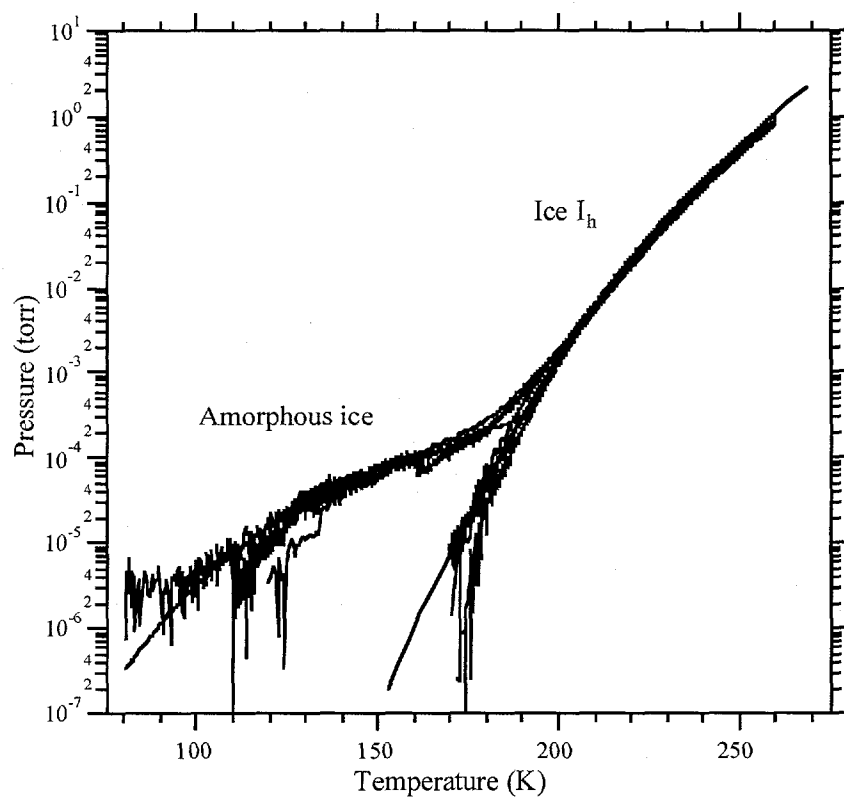


Figure 6

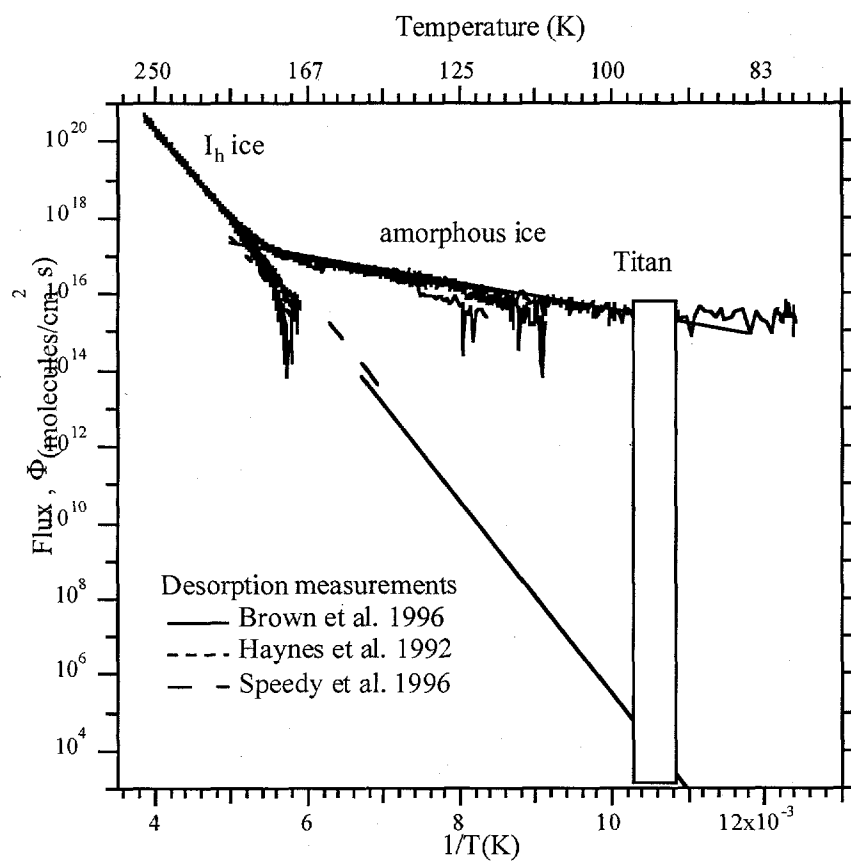


Figure 7