

Irradiation of methane-laden water ice films: Relevance to TNOs and Centaurs. E. H. Mitchell¹, U. Raut¹, and R.A. Baragiola¹, ¹Laboratory for Atomic and Surface Physics, 351 McCormick Rd, Thornton Hall B 113, University of Virginia, Charlottesville, VA 22904.

Introduction: Visible and near-infrared spectra of a number of the Transneptunian objects (TNOs, which include Pluto and Charon) and Centaurs have shown that their surface is composed of ices containing primarily H₂O, CH₄ and N₂ with smaller amounts of NH₃, CH₃OH, C₂H₆, CO, CO₂, and HCN. The relative amounts of different constituents vary among the TNOs observed so far; for instance, solid CO and N₂ have been observed on Triton and Pluto, and CO₂ has only been reported on Triton [1]. Spitzer's observations of TNOs in the far-infrared have also suggested the presence of silicates and complex carbonaceous materials [2]. The Ralph visible and infrared spectrometer onboard New Horizons, due to reach Pluto in July 2015, is expected to constrain the surface composition of Pluto and Charon.

The surfaces of TNOs are continually processed by energetic cosmic rays, solar wind and photons. Some known effects of such radiation processing are the production of exospheres via sputtering, and changes in the surface composition via radiolysis. To understand these effects, we have irradiated porous water ice films loaded with methane (two dominant species of TNOs) with 100 keV H⁺ ions at 40 - 50 K. Irradiations were performed in the presence of ambient methane. We report two main findings from these experiments: (i) ion-induced enhancement of CH₄ uptake by water ice and (ii) the formation of new species by radiation chemistry.

Experimental Procedures: The experiments were performed in an ultrahigh vacuum chamber with a base pressure of 10⁻⁹ Torr. Water ice films were vapor-deposited at 45° incidence onto the optically flat gold electrode of a quartz crystal microbalance (QCM) at 70 K. All films were deposited to a column density of 5000 ML H₂O (1 ML = 10¹⁵ molec. cm⁻²), measured by the QCM. The 45° angle deposition results in films with ~21% porosity, as per previous estimates [3].

Following water ice deposition at 70 K, the films were cooled to temperatures between 40 K and 50 K and exposed to ¹³CH₄ at ~7 (±1) × 10⁻⁷ Torr. The ice films were then irradiated at normal incidence with 100 keV protons from an ion accelerator with a magnetic mass filter. The ambient CH₄ pressure was maintained during irradiation for a more realistic simulation of radiation processing of icy satellites and TNOs with surface-bound exospheres.

The ion fluxes were varied between 2 and 200 × 10¹⁰ H⁺ cm⁻² s⁻¹. The chemical changes in the films

induced by ion irradiation were studied using infrared spectroscopy. Specular reflectance spectra of the films were collected at 35° incidence at 2 cm⁻¹ resolution. The spectra R were divided by the reflectance spectrum R_0 of the bare gold QCM substrate. The ratios were then converted to optical depth, $-\ln(R/R_0)$. The areas of infrared absorption bands were calculated from the optical depth spectra after subtracting polynomial baselines that matched the absorption continuum.

Isotopic labeling was used to differentiate the ¹³C-bearing species from the adventitious ¹²C-bearing species that can accumulate in the film from spurious sources.

Results and Discussion: *I. Ion-induced enhancement in ¹³CH₄ uptake:* The QCM showed adsorption of methane within the pores of the water ice film at 40-50 K, following admission of CH₄ gas into the chamber.

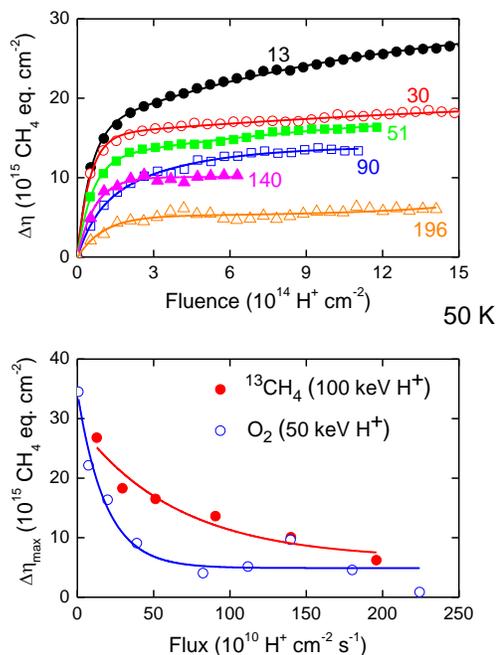


Fig. 1: Top panel: Net ion-induced equivalent CH₄ uptake ($\Delta\eta$) in 5000 ML H₂O porous ice films vs. fluence during 100 keV H⁺ irradiation at 50 K, following a pre-irradiation uptake of 78 ML from ~7 × 10⁻⁷ Torr CH₄ exposure. This pressure was maintained during irradiation. The curves are labelled with the flux, in 10¹⁰ H⁺ cm⁻² s⁻¹. Bottom panel: Flux dependence of the maximum ion-induced uptake. The methane uptake is compared to that of similar experiments with O₂ [3]. Lines are to guide the eye.

The uptake, resulting from the net effect of adsorption and thermal desorption, increased linearly with time and asymptotically approached an equilibrium value at which the adsorption and desorption rates were equal. Once the methane uptake equilibrated (to 384 ML at 40; 78 ML at 50 K), the films were irradiated with varying fluxes of 100 keV H^+ . Irradiation caused an increase in methane uptake, consistent with previous measurements with O_2 and Ar [3]. The films were irradiated until a second, higher equilibrium in methane uptake was achieved. We show this second increase at 50 K as a function of ion fluence in the top panel of Figure 1. In the bottom panel, the maximum of the irradiation-induced uptake, $\Delta\eta_{\max}$, is plotted as a function of ion flux and compared to previous results using O_2 [3]. The ion-induced enhancement in CH_4 uptake decreases with increasing irradiation flux.

We postulate two possible causes for the irradiation-enhanced increase in CH_4 uptake: (i) the conversion of low- into high-energy binding sites for adsorption competing with pore collapse [3] and (ii) radiolytic dissociation of methane and water molecules, together with the subsequent recombination of radicals to form newer, less volatile species that bind to the ice more effectively than methane. The enhancement is largest at lower fluxes because additional gas can adsorb in the new sites with higher binding before pore collapse.

II. Radiation chemistry in methane-water ice: The amount of methane adsorbed into pores of the ice film at 40 K decreased during irradiation, as shown by the exponential decrease with ion fluence of the area of the CH_4 absorption band at $7.7 \mu m$ (1294 cm^{-1}) (Top panel, Fig. 2). At high fluences, the band area of methane is at 8% of the initial value, suggesting processes that re-form methane from radiation products. Methane and water molecules are dissociated into radicals such as C, CH_x , OH, O and H as a result of energy deposited by the ions. These radicals react to form other ^{13}C -, H-, and O-containing species, including $^{13}CO_2$, ^{13}CO , $^{13}CH_3OH$, and H_2 . The fluence dependence of the main infrared band areas of these species are shown in the bottom panel of Fig. 2. Other species such as HCO, H_2CO_3 , CH_3CHO , C_2H_5OH , C_3H_8 , C_2H_6 and C_3O_2 have also been identified and details will be presented elsewhere.

Astrophysical Implications: These experiments suggest a new mechanism for gas trapping on the surfaces of TNOs with exospheres, such as Pluto [4], which are subject to low fluxes of energetic solar wind and cosmic rays. Further, we show that the radiation-induced chemistry of methane-water ice leads to formation of H_2 , CO, CO_2 , CH_3OH , and other complex

carbon-bearing species, most of which are released during heating to ~ 170 K, where the ice film desorbs. In addition, we observe a non-volatile residue of complex carbonaceous species formed by irradiation that remains on the QCM even after it is taken to room temperature. This deposit may help explain reddening observed in the spectra of TNOs. Our results, particularly the identification of new species, should be helpful in the interpretation of spectral data to be obtained by New Horizons beginning in 2015.

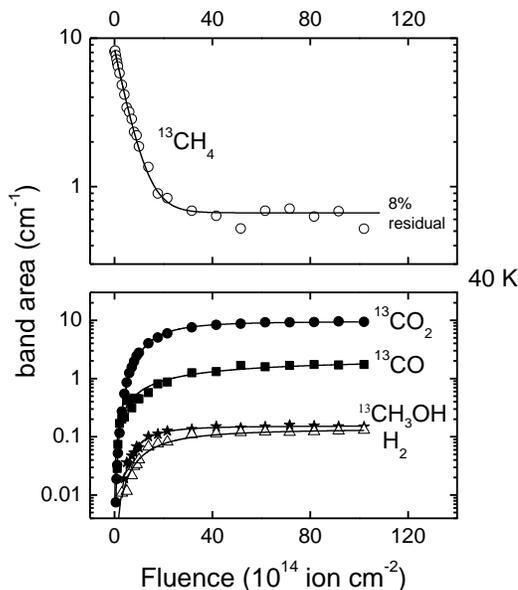


Fig. 2. Fluence dependence of band areas of $^{13}CH_4$ (1294 cm^{-1}), $^{13}CO_2$ (2275 cm^{-1}), ^{13}CO (2088 cm^{-1}), H_2 (4140 cm^{-1}), and $^{13}CH_3OH$ (997 cm^{-1}) during 100 keV H^+ irradiation of a 5000 ML H_2O porous ice film containing 384 ML of $^{13}CH_4$ at 40 K. The solid black line through $^{13}CH_4$ data points is an exponential fit. Other lines are guides to the eye.

Reference: [1] de Bergh C. et. al. (2013) The Ices on Transneptunian Objects and Centaurs, *The Science of the Solar System Ices Ed. Gudipati and Castillo-Rogez*, 107. [2] Emery J. P. et. al. (2007) *Astron Astrophys* 466, 395–32, A74. [3] Shi J. et. al. (2009) *Phys Rev B* 79, 235422. [4] Stern S.A. (1992) *Annu Rev Astron Astrophys*, 285, 233.