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Ion irradiation of TNO surface analogue ice mixtures: the chemistry

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Abstract. Vis–NIR spectra of some Centaurs and Trans-Neptunian Objects (TNOs) indicate surfaces rich in H_2O, N_2, CO_2, CH_4 e CH_3OH. Cosmic ion irradiation is one of the processes driving the evolution of TNO surfaces. A main role is played by the chemistry induced by colliding ions; many molecular bonds are broken along the ion track, and this may lead to the formation of byproduct molecules. Starting from laboratory experiments, it is possible to infer the presence of molecules still undetected on TNOs. For instance, carbonic acid (H_2CO_3) is produced after irradiation of H_2O:CO_2 icy mixtures, while irradiation of H_2O:N_2 icy mixtures causes the production of N_2O, NO, and NO_2. From H_2O:CH_4:N_2 mixtures, many species are formed, such as CO, CO_2, HCN, HNCO, N_2O, and molecules including CN bonds. Moreover, ion irradiation may modify the relative intensity of NIR features, as in the case of solid methanol, whose 2.34 μm band decreases in intensity with respect to the 2.27 μm band, after increasing irradiation doses. We suggest that this effect may be observed on Centaur Pholus.

Key words. Solar System: Kuiper Belt - Comets: general – Methods: laboratory – Molecular processes

1. Introduction

Cosmic ion irradiation is believed to be one of the processes driving the evolution of surface materials on TNOs (Trans-Neptunian Objects) or Kuiper-Belt Objects (Strazzulla et al. 2003). A fast ion passing through a solid releases its energy in the target by elastic interactions with the target nuclei and by inelastic collisions causing ionisations and excitations. Many molecular bonds are broken along the ion-track and, in a very short time (one picosec or less), the radicals and molecular fragments recombine giving rise to a rearrangement in the chemical structure. As a consequence, in addition to the alteration of the chemical and lattice structure of the target material, new molecular species (not present before irradiation) are formed.

Thus, based on simulation experiments carried out in the laboratory, some prediction can be made on which molecules can be expected to be present in the surface layers of TNOs.

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"Laboratorio di Astrofisica Sperimentale" at the Catania Astrophysical Observatory, has been active starting from the eighties in the experimental study of the effects induced by fast ions in solids (frozen gases, carbonaceous and organic materials, silicates, etc.) of astrophysical interest and not. The results have been applied to various astrophysical scenarios. Some results relevant to the chemical evolution of surface materials of TNOs are summarized here.

2. Experimental facilities

Most of the available experiments are designed to be performed inside a scattering chamber in both vacuum (better than 10^{-7} mbar, or 7.5×10^{-8} torr) or controlled atmosphere, and at temperatures ranging from 10 K up to 300 K.

The experiments are temperature cycling of samples in the range 10-300 K, and ion irradiation of solids and frozen gases, using a Danfysik 200 kV implanter. Many different projectile ions can be used.

The analysis facilities can be operated "in situ" in most cases, enabling us to follow the evolution of the samples along the experiments. The "in situ" techniques used to analyze the effects of irradiation are Infrared, Raman and UV-Vis-NIR spectroscopy (Brunetto & Strazzulla 2005).

3. Synthesis of byproduct molecules on TNOs

Very few frozen molecular species have been detected on TNOs, among them water ice and recently methane ice (Licandro et al. 2006). Therefore ion irradiation experiments can be performed on those ice mixtures that are observed on "relatives" of TNOs such as short-period comets, Centaurs, Pluto and Triton.

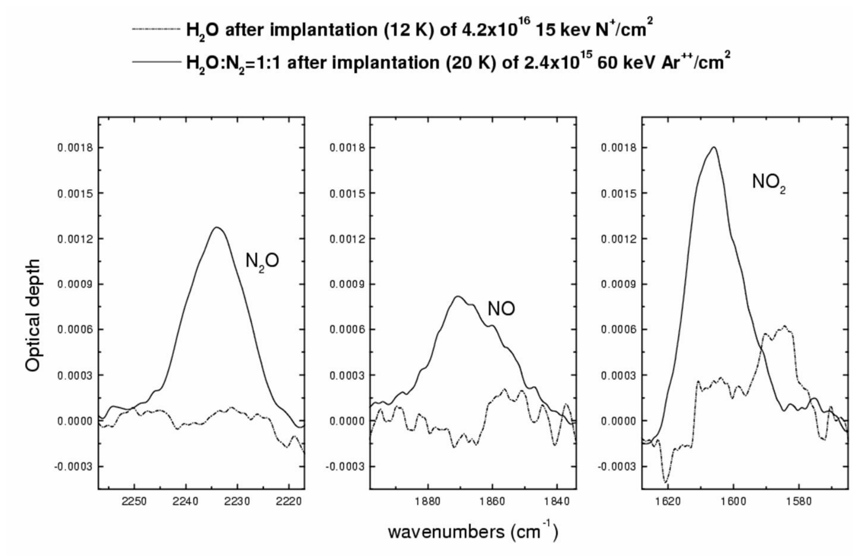
Comets have a composition, measured in the gas phase from sublimating molecules, similar to that observed on icy grains mantles in dense molecular clouds. They are water-rich with significant contribution of CO_2, CO, methanol and other hydrocarbons. Comets appear to be nitrogen poor.

On the other hand the surface of Pluto and Triton are nitrogen rich although, locally, ice segregation could have formed surface spot rich in different molecules (Owen et al. 1993). In addition to the dominant solid nitrogen and solid methane, CO and CO_2 have been detected on Triton's surface. Pluto has some CO and no CO_2.

The spectrum of the Centaurus Pholus has been matched with five components among which are 15% of water ice and 15% of methanol ice. Thus in addition to silicates and carbon, the icy materials that are of particular interest for TNOs are mixtures dominated by water and/or hydrocarbons and/or nitrogen.

In the upper panels of Fig. 1 we show that irradiation of $H_2O:N_2$ mixtures leads to the formation of N_2O, NO and NO_2 (Ottaviano et al. 2000). Although nitrogen and water are likely to be rapidly spatially segregated, because of their very different thermodynamic properties, we believe that, due to seasonal sublimation and re-condensation observed for example on Pluto and Triton, the highly volatile nitrogen is deposited on the entire surface of the objects, i.e. including the water-rich spots. It has been shown that, when condensed on amorphous water ice, N_2 diffuses in at temperatures of about 30 K, thus realizing an $H_2O:N_2$ mixture. This is demonstrated by the appearance of a sharp water feature in the IR spectra at about 1.88 μm that is easily distinguishable from the broad one of polymeric water centered at about 2 μm. Irradiation of $H_2O:CH_4:N_2$ mixtures (see lower panel of Fig. 1) leads to the formation of several species among which CO, CO_2, HCN, HNCO, N_2O and CN bearing species (Palumbo et al. 2004).

The formation of several new species among which carbon dioxide and suboxides, nitrogen oxides, and a number of CN bearing species have been also observed in irradiated $CO:N_2$, $CH_4:N_2$, and $CO:CH_4:N_2$ mixtures (Moore & Hudson 2003; Palumbo et al. 2004). Laboratory experiments have also shown that carbonic acid (H_2CO_3) can be expected on objects with surface area rich in $H_2O:CO_2$ mixtures (Brucato et al. 1997).



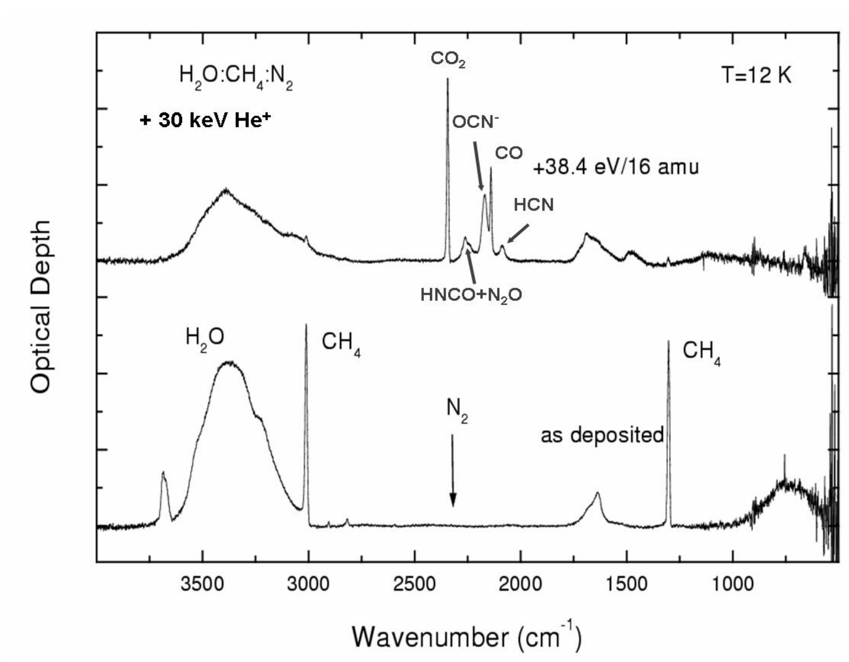


Fig. 1. Upper panels: formation of N_2O, NO and NO_2 after ion irradiation of H_2O:N_2 icy mixtures, compared to irradiation of water ice. Lower panel: ion irradiation of H_2O:CH_4:N_2 icy mixtures, with the production of CO, CO_2, HCN, HNCO, N_2O and CN bearing species.

4. Band profile and relative intensity modification

In addition to formation of new molecular species, ion irradiation can modify the infrared signature (band profiles and relative intensity) of pre-existing molecular species. This is not surprising since the shape, peak position and the intensity of the IR bands depend on the chemical composition and the structure of the matrix.

As an example (see Fig. 2), ion irradiation of pure methanol ice and methanol mixed with water has shown that the methanol band at 2.34 μm strongly decreases with respect to the one at 2.27 μm (Brunetto et al. 2005). Methanol has been tentatively identified on the Centaur Pholus (Cruikshank et al. 1998): the methanol band around 2.27 μm was observed, while the band at 2.34 μm was not present. The fact that the 2.34 μm band has not been observed could be indicative of ion irradiation processes (Brunetto et al. 2005).

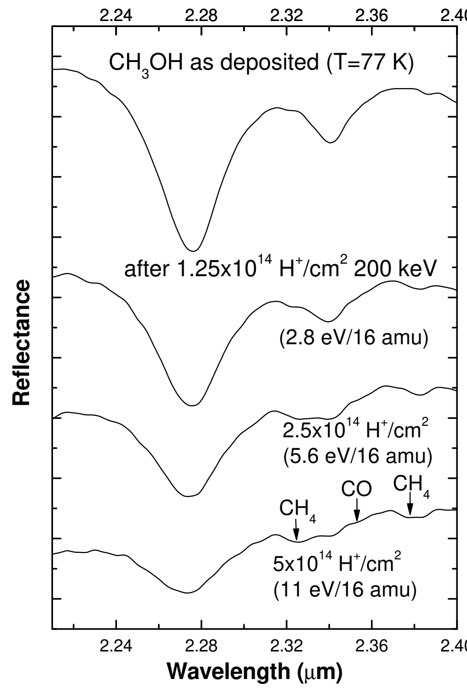


Fig. 2. NIR reflectance spectra (2.2-2.4 μm) of irradiated methanol at T = 77 K, offset for clarity. The methanol bands decrease, in particular the one at 2.34 μm; bands appear from newly formed CO and CH_4. The spectrum gets redder as the ion fluence increases.

5. The organic crust

When the carbon content is significant in the ice mixture, ion irradiation leads to the formation of an organic residue that is left over the substrate after warm up to room temperature. The results indicate that whatever the initial hydrocarbon is, it is converted into a refractory insoluble residue.

Based on these experimental results, it has been suggested that a comet exposed to background particle irradiation develops an outer web of non-volatile material which will lead to the formation of an organic crust. Recently it has been suggested that, due to irradiation processing, TNOs could have a crust even thicker and/or developed much rapidly than previously estimated for comets in the Oort cloud (Strazzulla et al. 2003). Comparing the observed spectral slopes of Centaurs and TNOs with laboratory data, it has been recently found that about 70% of the considered objects may have developed an irradiation mantle (Brunetto et al. 2006).

In situ Raman spectroscopy of carbon-containing ice mixtures reveals that the organic crust is already forming during irradiation at low temperature and its formation does not require the warming of the sample (Palumbo et al. 2004; Ferini et al. 2004). This supports the hypothesis that an organic crust could be already formed during the TNOs long residence far from the Sun.

6. Conclusions

Ground based observations already show the presence of ion irradiation effects on outer Solar System objects (e.g. modification of the NIR bands, formation of the organic crust, etc.).

Basing on laboratory simulations, a plethora of not yet identified species are likely to be present because of ion irradiation of TNOs, and these will be probably detected in the close future, also with the help of ongoing missions (e.g. NASA mission New Horizons).

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