

Methanol photochemistry as a source of complex organic molecules in cometary environments

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Abstract

This contribution focuses on the identification and quantification of Volatile Organic Compounds (VOC) subliming after the warm-up of photo-processed methanol ice analogs using the VAHIA experimental set-up. Data obtained will help elucidating the presence of molecules in astrophysical environments such as comets, as well as estimating the detectability of methanol photoproducts in these environments based on a quantitative approach.

1. Introduction

Comets are of prime interest in the study of the origin of the planetary organic matter since they have preserved for a part the original material of the solar nebula which subsequently led to our solar system. The determination of organics in comets is an important objective for understanding the chemical evolution occurring during the solar system formation. However, probing such objects is a difficult task and data interpretation is quite complex. The chemical evolution of organic matter occurs also mostly in low- and high-mass protostellar envelopes known as hot cores and hot corinos. These regions are extensively observed using radio astronomy to identify their content in complex organic molecules, but here also data interpretation is often ambiguous. For enhancing data interpretations obtained from cometary missions and understanding the chemical reactivity that occurs in cometary environments and in hot cores, laboratory experiments have been developed. They consist in recreating the astrophysical environment where astrophysical ices are processed. Briefly, ice analogs are formed at low temperature (10-80 K) and pressure (10^{-8} mbar) with the most abundant molecules detected in interstellar and cometary ices. They are then submitted to energetic processes such as ultraviolet photons

simulating the internal ultraviolet field inside cold molecular clouds. Afterwards the ice analog is warmed-up leading to the desorption of volatile compounds enriching the gas phase of the vacuum chamber. The analysis of compounds released in the gas phase can help explaining the presence and formation of such molecules in astrophysical environments, and orient the search for these compounds by the scientific community.

Among the most abundant molecules detected in astrophysical ices, MeOH is important, since it is the most abundant source of reduced carbon available within these icy grains. Therefore, understanding the chemistry related to this molecule is an important challenge that would give essential clues on the cometary chemistry and on molecules that could be detected in this environment. Infrared spectroscopy coupled to Temperature Program Desorption [1] as well as experiments using single photoionization reflectron time of flight mass spectrometry [2] were used to identify 15 volatile organic compounds from methanol photo-processed ices while more molecules are expected. In this contribution, we have used the VAHIA system based on a gas chromatography coupled to mass spectrometry approach to screen and quantify photoproducts formed after the VUV irradiation and the subsequent warming of a pure CH_3OH ice.

2. VAHIA experimental set-up

When the ice analog formed in the high vacuum chamber is warmed-up, sublimating species are pumped to a **preconcentration unit** directly connected to the chamber [3]. This developed unit has two main objectives: firstly, preconcentrating analytes prior to the GC analysis; secondly, reaching a pressure sufficient to provide a GC analysis. Concretely, species are pumped out of the chamber using pneumatic valves and are then stacked in a

preconcentration loop submerged in liquid nitrogen. After preconcentration, the loop is then rapidly warmed-up to 70°C. Helium is then introduced in the loop to increase sample pressure and facilitate analyte transfer to the **injection unit**. This latter was developed in collaboration with Interscience Belgium and allows the introduction of the gaseous sample coming from the preconcentration unit into the GC injector classically conceived for liquid sample injections (Figure 1).

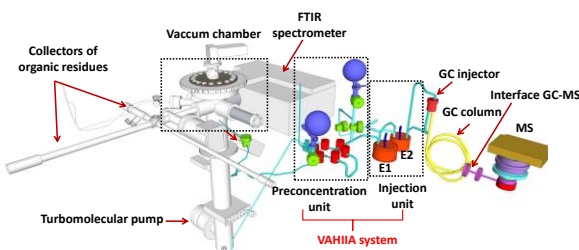


Figure 1: The VAHIIA system for VOC analysis.

3. Results

The GC-MS chromatogram of the photo-processed CH_3OH ice shows plethoras of peaks, which we identified based on their retention time and mass spectrum fragmentation pattern [4]. Identified photoproducts are constituted of 2 to 6 carbon atoms with various chemical functions, such as aldehydes (C2-C6), alcohols (C2-C5), ketones (C3-C6), esters (C2-C6), ethers (C3-C5) or carboxylic acids (C2). Almost all C3 to C6 compounds were not identified previously, highlighting the power of the VAHIIA experimental set-up to translate the complexity of photoprocessed ices. In addition to the identification process, we have focused on the quantification of all C1, C2 and C3 compounds that have been assigned since they are the most abundant, along with few C4 photoproducts. Our objective is to provide data on CH_3OH photo-dissociation, mainly the abundance of photoproducts with respect to the irradiated fraction of CH_3OH (branching ratios) and to the remaining CH_3OH fraction after irradiation (observational ratio). These results give essential information for helping data interpretation of the current Rosetta mission, as well as for assessing the different photo-dissociation pathways and diagnosing the conditions of molecule formation.

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