

Volatile organic compounds in gas phase as a probe of the chemistry occurring in solid phase

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Abstract

This contribution focuses on the monitoring of Volatile Organic Compounds (VOC) subliming after the warm-up of photo-processed ice analogs using the VAHIIA experimental set-up. This system uses a GC-MS that provides unprecedent data on the molecular diversity formed from ice processing. A quantification of VOC is also provided allowing the investigation of the impact of the solid phase chemistry on the VOC distribution in the gas phase. For the first time we can experimentally demonstrate that the gas composition is directly impacted by the ice composition and that the variation observed in the gas phase are directly explained by the reactivity occurring in the solid phase. These first results open new perspectives in using the gas phase as a direct probe of the solid phase reaction/composition.

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 using corresponding rotational spectra, 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 [1,2]. They consist in simulating the astrophysical environment where astrophysical ices are processed. The first step concerns the formation of an ice analog at low temperature (10-80 K) and pressure (10⁻⁸ mbar) with the most abundant molecules detected in

interstellar and cometary ices. The second step consists in submitting this ice to various energetic processes such as ultraviolet photons simulating the internal ultraviolet field inside cold molecular clouds. The processed ice is then warmed-up, which simulates the evolution of an astrophysical icy grain around a hot region (star, hot cores and corinos). All along this warming, volatile compounds desorb from the grain enriching the gas phase. During these experimental simulations, the characterization of compounds released in the gas phase can thus give important clues on molecules that can be formed in the considered environment and where they would be observed if their abundances are sufficient.

2. Molecular diversity released in the gas phase by methanol ice processing

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 as well as experiments using single photoionization reflectron time of flight mass spectrometry were used to identify 15 volatile organic compounds from methanol photo-processed ices while more molecules are expected [3]. To obtain more information on the VOC formed during astrophysical ice processing, an analytical approach (VAHIIA system) has been developed to increase the number of photoproduct identifications and to allow their direct quantification [4]. This approach consists in using a gas chromatograph coupled to an ion trap mass spectrometer (GC-MS) for the online analysis of these COV. This technique enables the separation of compounds from complex mixtures using the GC, and their identification using their mass spectrum. We will show how this system provides the identification and quantification of photoproducts

formed after the VUV irradiation and the subsequent warming of a pure CH₃OH ice [5].

3. Impact of ice composition on the VOC distribution of the gas phase

Next to methanol, various molecules form the icy mantle of dust grains. It is well known that the composition of the ice impacts the chemistry occurring in the solid phase and the different organic molecules that formed during the ice processing. We performed experiments by modifying the ice composition by adding to methanol, H₂O and/or NH₃. Using the VAHIIA set-up, we monitored the evolution of the distribution of VOC detected in the gas phase by quantifying their abundances. Using this protocol, we were able to observe the impact of the ice composition on the VOC distribution of the gas phase. The evolution observed is directly related to the chemistry occurring in the solid phase and is directly impacted by its composition. The monitoring of the gas phase could thus be used to indirectly probe the composition of the solid phase. We will present our first results focusing on VOC including CHO atoms and formed from ices including H₂O, CH₃OH and NH₃ [6].

4. VAHIIA 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. 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) [4].

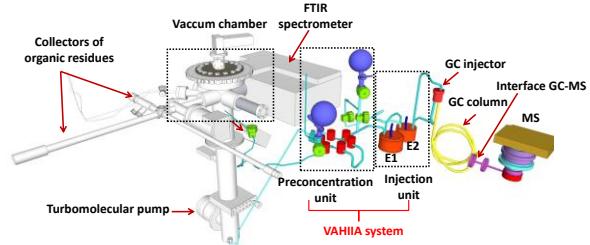


Figure 1: The VAHIIA system for VOC analysis.

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