

Untangling the Formation Mechanisms of Biorelevant Molecules in the ISM with Photoionization Reflectron Time-of-Flight Mass Spectrometry

Marko Förstel^{1,2} and Ralf I. Kaiser^{1,2}

¹W. M. Keck Research Laboratory in Astrochemistry, University of Hawaii at Manoa, Hawaii, HI, 96822, USA

²Department of Chemistry, University of Hawaii at Manoa, Honolulu, Hawaii, HI, 96822, USA
email: ralfk@hawaii.edu

Abstract. Exploiting reflectron time of flight mass spectrometry coupled with single photon ionization of the subliming molecules (PI-ReTOF-MS) during the temperature programmed desorption (TPD) and combining these data with on line and in situ infrared spectroscopy (FTIR), a versatile experimental approach has been established to elucidate the formation pathways of complex organic molecules in interstellar analog ices upon interaction with ionizing radiation at astrophysically relevant temperatures as low as 5 K.

Keywords. laboratory astrophysics, isomer specific detection, tunable photoionization

An understanding of the formation of complex organic molecules (COM) in the interstellar medium is of core value to the astronomy community upon multiple levels (Whittet *et al.* (2011), Walsh *et al.* (2014), Vasyunina *et al.* (2014), Bacmann *et al.* (2012)). Our experimental program advances the knowledge of the most fundamental processes leading to the synthesis of COMs, among them biorelevant molecules such as amino acids, dipeptides, sugars and vitamins, on ice-coated interstellar grains (ICIGs) in cold molecular clouds and in star forming regions (Charnley, Ehrenfreund & Kuan (2001), Aikawa *et al.* (2008)). Our experimental approach also allows us to differentiate between structural isomers of specific molecule and to measure their branching ratios and rate constants of formation. Together with this information, these isomers can serve as a molecular clock and tracers in defining the evolutionary stage of cold molecular clouds and star forming regions (Garrod, Weaver & Herbst (2008)). Finally, since COMs have also been identified in the Murchison meteorite (Botta, Bada & Ehrenfreund (2002)), our project might bring us closer to understanding the extent to which key classes of COMs might have been synthesized exogenously in the ISM, (partly) incorporated into parent bodies of, e.g., Murchison, and then delivered to early Earth.

The aforementioned goals are achieved by systematically replicating the conditions of ICIGs as present in cold molecular clouds and toward high- and low-mass star forming regions in a next-generation ultra-high vacuum surface scattering machine. Interstellar ice analog samples at astrophysically relevant temperatures as low as 5 K are exposed to ionizing radiation in the form of energetic electrons. We follow a radically different approach than traditional infrared spectroscopy (FTIR) and electron impact mass spectrometry by interfacing complementary detection schemes to a single machine. Individual COMs subliming into the gas phase upon warm-up of the samples are identified via a reflectron time-of-flight mass spectrometer (ReTOF-MS) coupled with soft photoionization by

simultaneously monitoring the decay signal of relevant functional groups in the condensed phase via FTIR (Maity, Kaiser & Jones (2015), Jones, Kaiser & Strazzulla (2014)). The energy of the ionizing photon can be controlled within a resolution of at least 0.01 eV allowing to photoionize subliming molecules according to their ionization energies. The ideally fragment-free isomer-specific detection of individual isomers represents the key advantage of soft single photon ionization compared to traditional mass spectrometry with electron impact ionization. Since the subliming molecules and structural isomers can also be separated via fractionated sublimation, the sublimation sequence along with the correlation of the ionization energy with the m/z ratio of the product represents a versatile and powerful approach to uniquely identify the complex organic molecules formed.

The exposure of simple astrophysical model ices containing carbon monoxide (CO), methanol (CH₃OH), methane (CH₄), and ammonia (NH₃) to energetic electrons leads to the formation of several key molecules as important representatives of biorelevant sugars (glycolaldehyde; HCOCH₂OH), polyalcohols [glycerol; HOCH₂CH(OH)CH₂OH], and amides (formamide; HCONH₂; urea; H₂NCONH₂) (Kaiser, Maity & Jones (2015), Abplanalp *et al.* (2015), Förstel *et al.* (2015)). Besides the generic identification of these structural isomers, we were also able to derive, in some instances, reaction mechanisms leading to COMs by fitting the system of coupled differential equations of the newly formed molecules. Most importantly, these COMs can be formed at 5 K within the ices via non-equilibrium processing involving, for instance, suprathermal hydrogen atoms and the excited triplet state of, for instance, carbon monoxide (CO) and/or acetylene (C₂H₂). To a certain degree, the low temperature matrix also stores reactive radicals such as formyl (HCO) and hydroxymethyl (CH₂OH). Upon annealing of the ices, these radicals can diffuse and might recombine. Based on our results, these thermal routes represent less prominent pathways leading to complex organic molecules within the processed ices.

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