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## Laboratory Studies on the Formation of Carbon-Bearing Molecules in Extraterrestrial Environments: From the Gas Phase to the Solid State

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### 1. Introduction

A detailed knowledge of the formation of carbon-bearing molecules in interstellar ices and in the gas phase of the interstellar medium is of paramount interest to understand the astrochemical evolution of extraterrestrial environments (1). This research also holds strong implications to comprehend the chemical processing of Solar System environments such as icy planets and their moons together with the atmospheres of planets and their satellites (2). Since the present composition of each interstellar and Solar System environment reflects the matter from which it was formed and the processes which have changed the chemical nature since the origin (solar wind, planetary magnetospheres, cosmic ray exposure, photolysis, chemical reactions), a detailed investigation of the physicochemical mechanisms altering the pristine environment is of paramount importance to grasp the contemporary composition. Once these underlying processes have been unraveled, we can identify those molecules, which belonged to the nascent setting, distinguish molecular species synthesized in a later stage, and predict the imminent chemical evolution of, for instance, molecular clouds.

Laboratory experiments under controlled physicochemical conditions (temperature, pressure, chemical composition, high energy components) present ideal tools for simulating the chemical evolution of interstellar and Solar System environments. Here, laboratory experiments can predict where and how (reaction mechanisms; chemicals necessary) in extraterrestrial environments and in the interstellar medium complex, carbon bearing molecules can be formed on interstellar grains and in the gas phase. This paper overviews the experimental setups utilized in our laboratory to mimic the chemical processing of gas phase and solid state (ices) environments. These are a crossed molecular beams machine (3) and a surface scattering setup (4). We also present typical results of each setup (formation of amino acids, aldehydes, epoxides; synthesis of hydrogen terminated carbon chains as precursors to complex PAHs and to carbonaceous dust grains in general; nitriles as precursor to amino acids).

## 2. Surface scattering machine

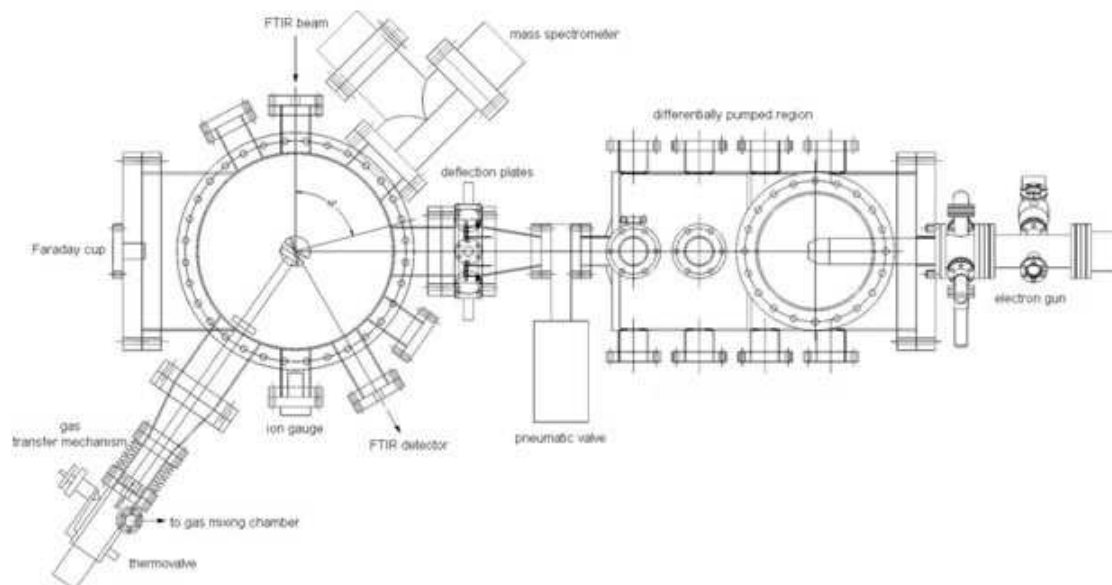


Fig. 1.— Schematic top view of the surface scattering machine.

To investigate the formation of astrochemically and astrobiologically relevant molecules in low temperature, extraterrestrial ice analog samples, we carry out radiolysis experiments in a contamination free ultra high vacuum stainless steel chamber (Fig. 1) (5). The chamber can reach pressures down to  $5 \times 10^{-11}$  torr by use of a magnetically suspended turbo molecular pump that is backed by a scroll pump. All pumps used are oil-free to ensure no hydrocarbon contaminants enter the system. Temperatures of 10 K are reached using a two-stage closed-cycle helium refrigerator that is interfaced directly to a polished single crystal silver mirror onto which the gases are condensed. The silver substrate is suspended by a differentially pumped rotatable feedthrough, which aligns the wafer in the center of the main chamber. Gas condensation is carried out at 10 K and generally at a pressure of  $1.0 \times 10^{-7}$  torr to a total thickness of about 200 nm. The experiment proceeds by irradiating the ice samples isothermally with 5 keV electrons for one hour to simulate the radiation effects in the aforementioned environments. The progress of the reaction is monitored using a Fourier Transform Infrared Spectrometer (FTIR). The spectrometer has a wavenumber range of 10,000-500  $\text{cm}^{-1}$  and operates in absorption-reflection-absorption mode with a reflection angle of 75 deg from the normal relative to the mirror surface. The infrared spectra of the ice were recorded online and in situ at an integrated time of 2.5 minutes and at a resolution of 2  $\text{cm}^{-1}$ . After irradiation the sample is left at 10 K to check the stability of the resulting molecules. In the final phase of the experiment, the sample is warmed at a rate of 0.5 K  $\text{min}^{-1}$  in an attempt to observed reaction, dissociation, and/or sublimation of the molecular species. Molecules that have sublimed may then be observed with the mass spectrometer that is directly attached to the reaction chamber. This procedure allows us to get

information on i) newly formed molecules in the gas phase (QMS) and solid state (FTIR), ii) the production rates, iii) the kinetics and dynamics involved, and iv) the underlying reaction mechanisms.

### 3. Crossed beams machine

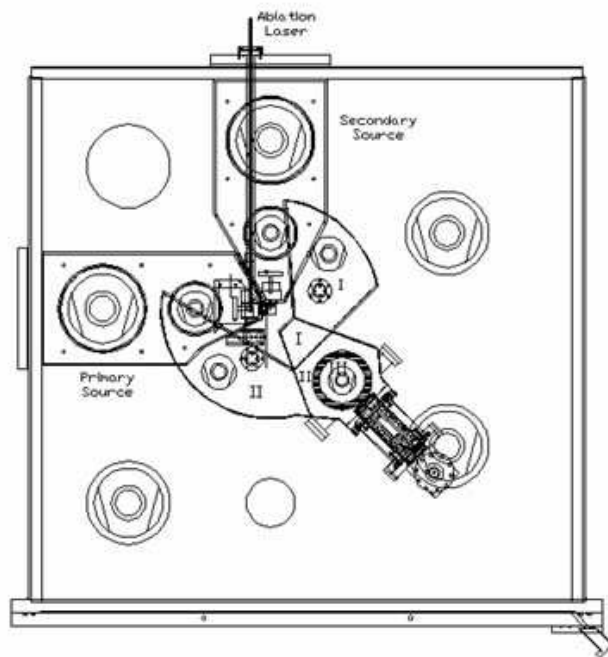


Fig. 2.— Schematic top view of the crossed beams machine.

The crossed molecular beams technique represents the most versatile approach in the elucidation of the energetics and chemical dynamics of elementary reactions relevant to astrochemistry (1). In contrast to bulk experiments, where the reactants are mixed, the main advantage of a crossed beams approach is the capability to form the reactants in separate, supersonic beams. In principle, both reactant beams like carbon atoms (C), cyano radicals (CN), ethynyl radicals ( $C_2H$ ), carbon clusters ( $C_2$ ,  $C_3$ ) can be prepared in well-defined quantum states before they cross at a well-defined collision energy under single collision conditions. The species of each beam are made to collide only with the molecules of the other beam, and the products formed fly undisturbed toward the detector. These features provide an unprecedented approach to observe the consequences of a single collision event, preventing secondary collisions and wall effects. Crossed beams experiments can also help to infer those intermediates involved and provide reaction products together with their branching ratios critical input parameters in chemical reaction models of interstellar environments and of atmospheres of planets and their moons. Briefly, the main chamber of the crossed beams

machine consists of a stainless steel box and is evacuated to the low  $10^{-8}$  torr region (Fig. 2). The source regions, in which the supersonic reactant beams are generated, are located inside the main chamber. In the primary source, we generate the reactive, open shell species like carbon atoms (C), cyano radicals (CN), ethynyl radicals ( $C_2H$ ), or carbon clusters ( $C_2$ ,  $C_3$ ) via laser ablation techniques (1; 2). The ablated species are then seeded in a helium carrier gas released by a pulsed valve. A chopper wheel situated after the skimmer selects a part of the ablation beam of a well-defined peak velocity and velocity spread. Both beams pass through skimmers and cross perpendicularly in the interaction region. The reactively scattered products are monitored in the collision plane using a triply differentially pumped quadrupole mass spectrometer with an electron-impact ionizer in the time-of-flight (TOF) mode, i.e. recording the time-dependent intensity of ions at distinct  $m/z$ -ratios at different laboratory scattering angles. To extract information on the reaction dynamics, intermediates involved, energetics, and reaction products, we finally transform the laboratory data into the center-of-mass (CM) system.

#### 4. Results

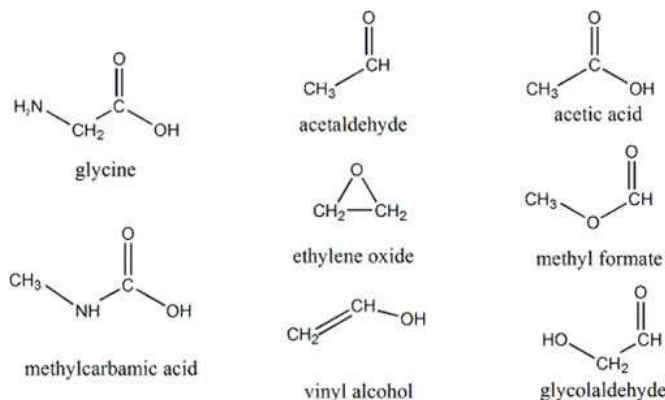


Fig. 3.— Structures of astrobiologically relevant species identified by our laboratory (7).

Our experimental setups are well suited for investigating chemistry that occurs in cold extraterrestrial ices (Figure 3), in cold molecular clouds, circumstellar envelopes, and in hydrocarbon-rich atmospheres of planets and their satellites (Figure 4). For example, in solid state experiments, identified species have obvious relevance in attempting to understand the abiotic synthesis of, for instance, amino acids and their isomers. Acetaldehyde and ethylene oxide have also been detected and have been suggested to play an important function in amino acid formation and in early metabolic pathways, respectively. The presence of ethylene oxide demonstrates the stability and the presence of formation routes to ring structures suggesting that sugars may also be easily formed. Currently work is being done to understand the synthesis of the  $C_2H_4O_2$  isomers, acetic acid ( $CH_3COOH$ ), methyl

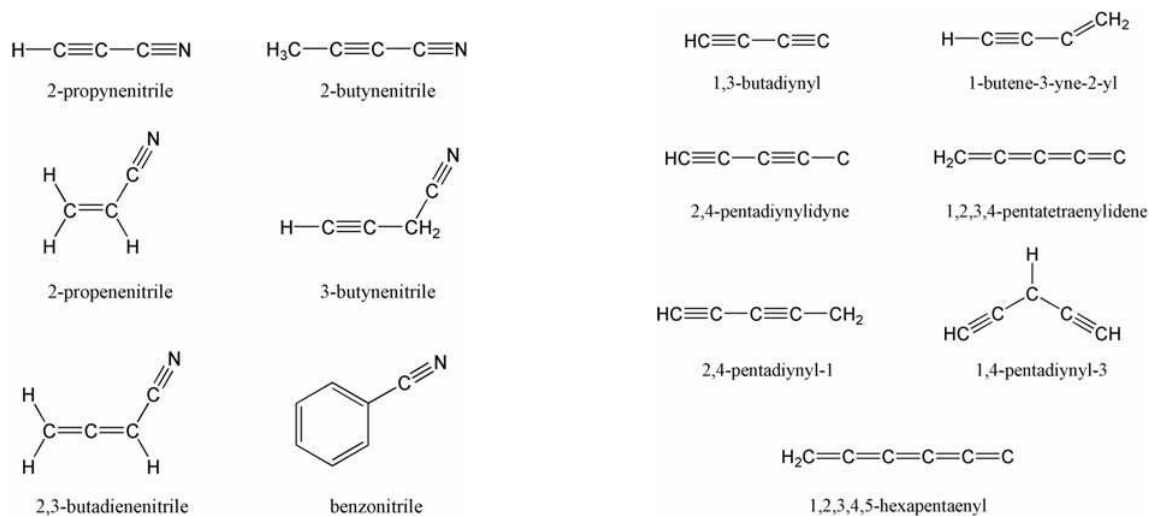


Fig. 4.— Left: Structures of nitriles relevant to the organic chemistry in Titan’s atmosphere and of cold clouds. Right: Structures of carbon-bearing molecules identified by our laboratory.

formate ( $\text{HCOOCH}_3$ ), and the simplest carbohydrate glycolaldehyde ( $\text{HCOCH}_2\text{OH}$ ) in interstellar and solar system ices. Through these and future experiments we can elucidate the reaction pathways relevant to a variety of environments and applications, including astrobiology. The gas phase experiments proposed various formation routes to nitriles in the interstellar medium and in Titan’s atmosphere (Figure 4, left panel) (2). The carbon bearing species synthesized via reactions of dicarbon and tricarbon molecules with unsaturated hydrocarbons provide vital building blocks to form polycyclic aromatic hydrocarbons (PAHs) and also precursors to more complex, carbon-based nanoparticles (interstellar grains) in the outflow of carbon rich stars as in IRC+10216 (6).

## REFERENCES

- R.I. Kaiser, *Chem. Rev.*, 102, 1309 (2002)  
 R.I. Kaiser, 34, 699 (2001)  
 X. Gu, Y. Guo, R.I. Kaiser, *Int. J. Mass Spectr. Ion. Processes* 246, 29 (2005)  
 C.J. Bennett, C. Jamieson, A.M. Mebel, R.I. Kaiser, *Phys. Chem. Chem. Phys.* 6, 735 (2004)  
 C.J. Bennett, Y. Osamura, R.I. Kaiser, *ApJ* 624, 1097 (2005)  
 X. Gu, Y. Guo, F. Zhang, A.M. Mebel, R.I. Kaiser, *Reaction Dynamics of Carbon-Bearing Radicals in Circumstellar Envelopes of Carbon Stars. Faraday Discussion 133: Chemical Evolution of the Universe* (in press 2006)  
 P. D. Holtom, C. J. Bennett, Y. Osamura, N. J. Mason, R. I. Kaiser, *ApJ* 626, 940 (2005). J. Bennett, Y. Osamura, M. D. Lebar, R. I. Kaiser, *ApJ* 634, 698 (2005). C.J. Bennett, R.I. Kaiser, *ApJ* 635, 1362 (2005)