Probing the Nature of Grain Surface- and Photo-Chemistry by Laboratory Simulation

W.A. Schutte

Raymond and Beverly Sackler Laboratory for Astrophysics, Leiden Observatory, P.O. Box 9513, 2300 RA Leiden, The Netherlands

Abstract. The experimental results that have been obtained in simulation experiments of grain surface- and photochemistry are reviewed, and ways to include these in models of dense cloud chemistry are indicated.

1. Introduction

Observations of the absorption features in the infrared spectra of obscured sources have yielded an inventory of interstellar ices (Gibb et al. 2000). The question of the origin of the frozen molecules is, however, still largely open. In this paper we review the current experimental knowledge on the nature of grain surface processes and UV processing, and indicate ways for using this into models of dense cloud chemistry.

2. Grain Surface Chemistry

For a typical grain dimension of 0.1 μm, and a typical density of 10^4 cm^{-3}, a few molecules or atoms will land on a grain each day. Except for He, these particles will stick at 10 K with an efficiency close to unity (Tielens & Allamandola 1987). H, C, N, O as well as H_2 are sufficiently light to overcome barriers, migrate over the surface (Tielens & Hagen 1982; Tielens & Allamandola 1987) and react with the ice species. Larger species are generally considered immobile. The main surface reactions for O- and C-bearing species are schematically summarized in Figure 1 (Tielens & Hagen 1982; Hasegawa et al. 1992).

Experimental simulation of grain surface reactions involves the bombardment of a cryogenic ice sample with a beam of cooled atoms. Atom beams are produced by dissociating molecules (H_2, O_2, N_2) by microwave discharge, radiofrequency discharge, DC discharge, or by heating (e.g., Hiraoka et al. 1994). The cooling of the beam can be achieved in the final part of the deposition tube. Analysis of the sample can be done in-situ by infrared spectroscopy, or by mass spectroscopy during warm-up and sublimation.

There are some aspects in which experiments cannot duplicate the interstellar conditions. In a dense cloud the atomic H flux is $\sim 10^5$ H atoms cm^{-2} s^{-1}, and no more than a single H atom will be present on a 0.1 μm grain at any given time. In this case, the H atom will react even if only a single reactive species is present. However, the beam intensity in the laboratory is so high ($\sim 10^{19}$ H atoms cm^{-2} s^{-1}; Mennella et al. 1999) that recombination of atomic H on the
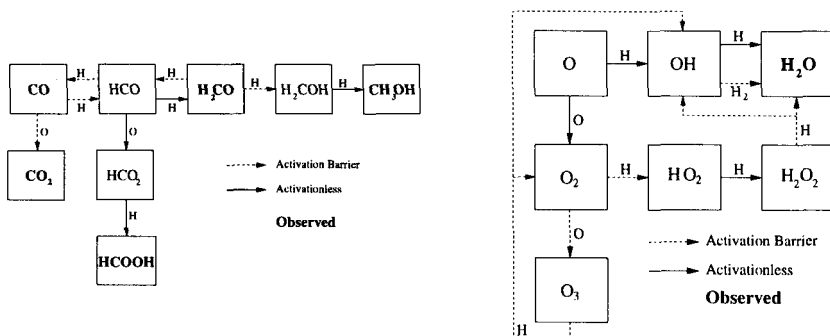
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Figure 1.   Schematic representation of grain surface chemistry starting with CO (left) and with O or O_2 (right).

surface of the sample will dominate the H loss. The efficiency of reactions with the sample material will therefore be much lower in the laboratory situation, preventing a direct quantitative application of the results. Only if a theoretical estimate is made of the survival time for H atoms on the sample surface, the experimental results could be calibrated. A second experimental limitation is production of atoms in an excited state, e.g., O ^{1}D.

Hiraoka et al. (1994; 1998) studied the bombardment by atomic H of plasma activated N_2, CO and N_2O. These samples contain a few percent of N, C, and O, respectively, and were 10 - 30 molecular layers thick. The experiment yielded NH_3, CH_4 and H_2O, respectively, with abundances of $\sim$1 %. This indicates a high conversion of the atoms to hydrated species, consistent with the absence of reaction barriers. An additional implication is that atomic H can penetrate the bulk and react *inside* the ice. A further study concerned the hydrogenation of CO (Hiraoka et al. 1995; 1998). The yields of H_2CO and CH_3OH were $\sim$ 0.01 % and 0.002 %, respectively. As discussed above, these low yields do not necessarily imply that this proces is also inefficient under interstellar conditions.

3.   UV Photochemistry

It is generally accepted that a weak cosmic ray induced UV field of $\sim 10^3$ photons cm^{-2} s^{-1} is present in dense clouds (Prasad & Tarafdar 1983). Furthermore, Galactic radiation may penetrate into the cloud (Whittet et al. 1998). To illustrate the potential effects, Figure 2 shows the infrared spectrum of an ice mixture $H_2O/CO/NH_3 = 100/24/20$, direct after deposition at 10 K, and after a
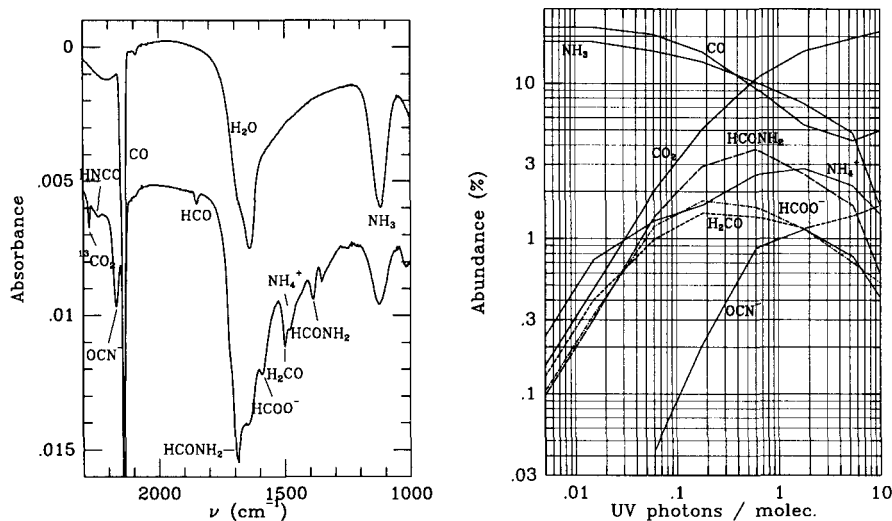
Figure 2.   Experimental results of the UV photolysis of $H_2O/CO/NH_3$ = 100/24/20 at 10K. Left: IR spectrum before irradiation (top) and after a dose of 3×10^{17} photons cm^{-2} ($\approx$ 0.6 photons/molec.). Right: Abundances vs. dose.

(low) dose of 3×10^{17} photons cm^{-2} (i.e., $\sim$ 0.6 photon/molec.). The irradiated sample shows strong features of photoproducts (see further below).

Infrared spectroscopy allows quantitative monitoring of the abundance of the various products. This can be achieved by integrating the spectral features, and converting to column densities using the intrinsic band strength (Schutte 1999, and references therein; Kerkhof et al. 1999). As an example, Figure 2 shows the abundances as a function of UV dose for $H_2O/CO/NH_3$ = 100/24/20. These data were obtained from the database of photolysed ices of the Sackler Laboratory for Astrophysics, available under:
http://www.strw.LeidenUniv.nl/~lab.

Figure 3 gives schematics of the photochemistry for two types of astrophysical ice analogs, $H_2O/CO/NH_3$ (Grim et al. 1989), and $H_2O/CH_3OH/NH_3$ (Bernstein et al. 1995). For details we refer to the original papers.

Future advances should include the analysis of the products which sublime during warm-up. Mass spectroscopy and/or gas chromatography has the potential to detect with high sensitivity the more complex and less abundant products for which infrared spectroscopy is not sensitive. Such studies could provide a database for comparison with hot cores in star-forming regions and with comets.

The data from infrared spectroscopy give detailed information of the abundances of the products as a function of dose. It should be possible from this to make a semi-empirical description of the photochemistry including parameters like the UV destruction and formation cross-section of species in various matrices (cf., Gerakines et al. 1996). In this way a quantitative prediction of the photochemistry for a wide range of ice mixtures may be achieved.
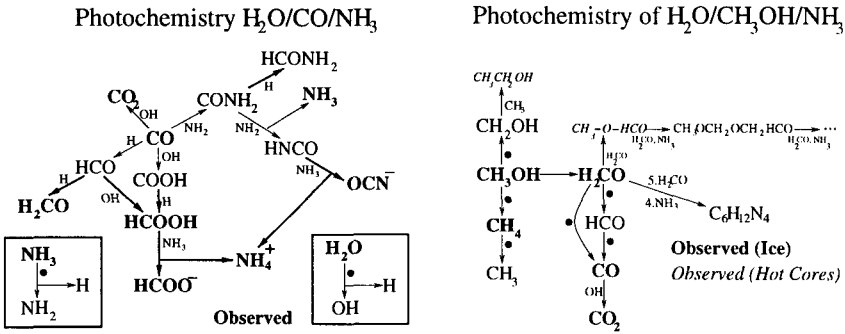
Photochemistry H$_2$O/CO/NH$_3$ Photochemistry of H$_2$O/CH$_3$OH/NH$_3$

Figure 3.   Schematic representation of the reaction channels during 10 K UV photolysis of the ice mixtures H$_2$O/CO/NH$_3$ and H$_2$O/CH$_3$OH/NH$_3$.

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