Electron Spin Resonance (ESR) Studies of Atmospheric and Astrophysical Radicals

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Specific Aims

1. Study the reactions occurring on interstellar grains *via* ESR spectroscopy of astrophysically relevant species trapped in rare gas, water-ice, or carbon matrices.

2. Characterize the electronic structure and study the reactions of atmospheric species trapped in rare gas or water-ice matrices *via* ESR spectroscopy.

Interstellar Reactions

The interstellar medium contains a mixture of dust grains and gas-phase molecules. The dust grains consist of a carbon or silicate core surrounded by a carbonaceous mantle containing a variety of small molecules, such as H_2O, CH_4, and NH_3. These grains are believed to be sources of gas-phase molecules in the interstellar medium (Figure 1). Radical reactions on the grain surface require energy input from ultraviolet (UV) photons or cosmic ray particles. Product molecules are sublimed from the grain surface by additional incident radiation.

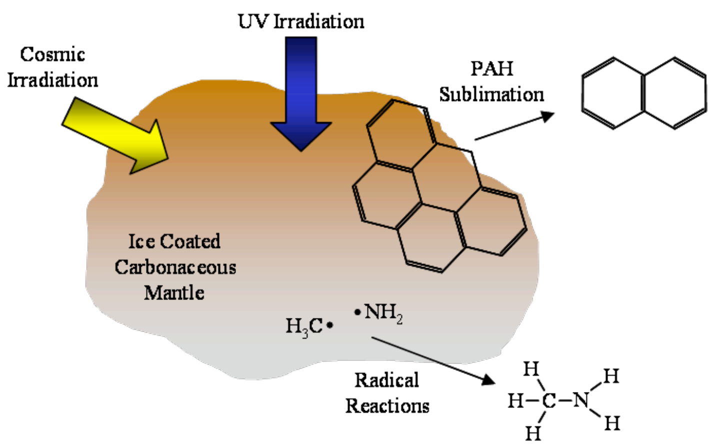

Figure 1. Examples of reactions occurring on the surface of interstellar grains.

In the gas phase, astrophysical molecules are proposed to form by the condensation of material in stellar winds. Condensation processes involving radical or ion-neutral reactions are the most likely due to the inherent low energy barriers. Ultraviolet photons, x-rays, and cosmic rays from stellar sources can fragment or ionize material in regions of high photon flux. The resulting radicals participate in a variety of reactions in the interstellar medium and planetary ionospheres. Thus, the study of these radical intermediates is crucial to understanding astrophysical processes.

Atmospheric Reactions

Atmospheric reactions involving small radicals occur both in the gas and condensed phases. Gas-phase radical reactions are initiated by the photodissociation of molecules by UV or cosmic radiation. This radiation can also ionize fragmented molecules in the upper atmosphere. The investigation of these ion-molecule and photodissociation reactions is necessary to understand various atmospheric processes, such as ozone destruction in the stratosphere. A great deal of atmospheric chemistry occurs on particle surfaces. Polar stratospheric clouds contain small, super-cooled particles consisting of H_2O, HNO_3, and H_2SO_4. The surfaces of these ice particles catalyze reactions of molecules and ions in the upper stratosphere. In the troposphere, dust, soot, and salt particles provide additional surfaces for atmospheric reactions. Consequently, the photochemical processes occurring on these surfaces are of considerable interest.

Matrix Isolation ESR Experiments

Because it approximates the collision-free astrophysical environment, matrix isolation spectroscopy has been widely applied to the study of interstellar species. The inert environment created in the matrix is also ideal for the study of reactive molecules and radicals present in the atmosphere. In our studies, neutral or ionic radical species will be generated by various techniques, such as laser vaporization, plasma ionization, or X-ray photolysis (Figure 2). These radicals will then be trapped in a low temperature (4 K), solid rare-gas matrix. Interstellar grain mantles will be simulated in the laboratory by depositing carbon with analyte molecules on a cold surface. Atmospheric ice particles will be reproduced by depositing analytes in water-ice matrices. In all cases, further reactions can be initiated by electron bombardment, UV photolysis, or matrix annealing. Electron spin resonance spectra will then be recorded for the matrix-isolated species.

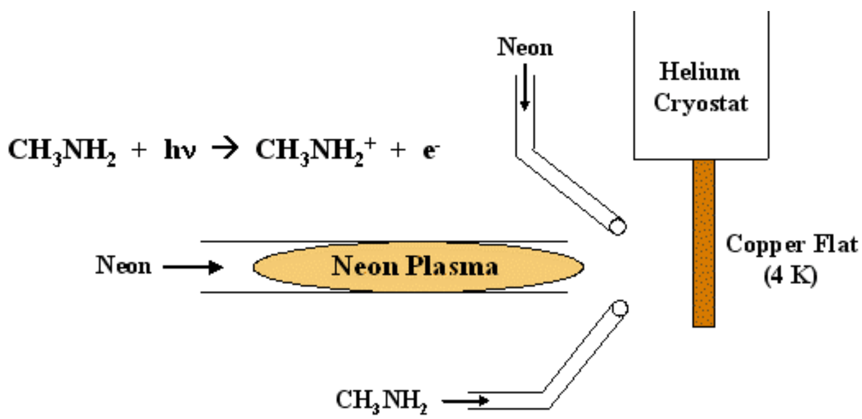

Figure 2. Apparatus used for the generation and study of methylamine cation ($CH_3NH_2^+$), a radical proposed as a precursor for amino acids in space.