EUV Photolysis of Ice Analogs of Astronomical Interests

In the last decade, much progress has been made in laboratory simulation study of chemical processes that occur in astronomical environments and in planetary systems. These simulations include the study of photon irradiation and charged particle impact, implantation, and sputtering of ices and icy grains, processes which are fundamental to an understanding of the formation and evolution of the chemical composition of the material in our solar system, and throughout the universe generally. Figure 1 depicts the evolution of an interstellar grain in a dense molecular cloud including photon irradiation, which process the ice mantles forming complex organic molecules.

Since Greenberg pioneered the investigation of photon-induced chemical reactions in mixed ice systems there have been quite a few studies in recent years. However, all of these studies, with the exception of those of Wu *et al.*, utilized the microwave discharge hydrogen lamp which provides mainly the atomic hydrogen Lyman-α line at H I 121.6 nm and the molecular hydrogen band emissions in the spectral region between 140 nm and 200 nm. It is well known that the photons produced by the hydrogen lamp are not energetic enough to ionize most of the molecular ices. The extreme ultraviolet (EUV) light defines the spectral region from soft x-Rays to 106 nm. Therefore, absorption of EUV photons involves excitation of the inner valence shell electrons, the ionization continua, the multiple electron transition (MET) states, and the core electrons resulting in the production of single and multiple ionizations, neutral and ion fragments, which can be either in the ground electronic state or excited electronic states. It is thus expected that many chemical reactions will take place following EUV photon absorption. In other words, the quantum yields for photon-induced chemical reactions by the EUV photon irradiation should be much higher than for those irradiated by the VUV-visible irradiation. However, it is also known that the VUV solar flux of the atomic hydrogen Lyman-α line is 2 to 3 orders of magnitude larger than the solar emission features in the EUV region. It is therefore possible that the production rates of certain chemical species in the icy environment using the present day solar VUV and the EUV photon irradiation fluxes could be comparable. Furthermore, it is important to point out that because various singly, doubly, multiply charged and/or electronically excited photofragments are produced in the EUV irradiation, it is possible that new molecular species may be synthesized by the EUV irradiation, but not necessarily by the VUV counterpart.

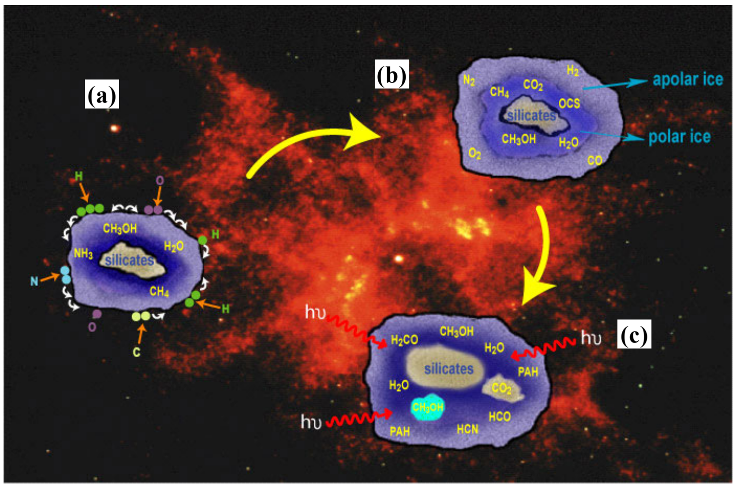

Fig. 1: *Evolution of a dust grain in a dense molecular cloud. (a) Gas-phase species condense on the surface of a cold grain and chemically react to form new molecules. (b) Depending on the gas-phase atomic H abundance, polar or apolar ice mantles are formed giving a layered onion effect. (c) UV photons from a protostar may process the ice mantles.*

We have carried out laboratory simulation experiments of pure ices of CO, N_2, NH_3, and CH_4, and mixed ices of N_2+CH_4, CO_2+H_2O, C_2H_2+H_2O, CO+NH_3+ H_2O, and CO+N_2+CH_4 at 10 K in search of the productions of radicals, such as the NH_2, N_3, CH_2, CH_3, saturated and unsaturated hydrocarbons, HCN, aldehydes, alcohols, etc. It is particularly interesting to look into the photon-induced reactions in mixed icy systems with N_2 and NH_3 as the host since life in the universe may have been synthesized from C, H, O, and N atoms. Our research goals include the identification of new photolyzed products, measurements of production yields for the new species and depletion yields for the parent icy molecules, the possible photon-induced chemical reaction mechanisms, and the applications of the laboratory data to the interpretations and modelings of astronomical observation. In this highlight report we wish to use the case of CO ice as an example to illustrate the exciting results obtained from works carried out at NSRRC.

We choose to present the spectra of the difference of absorbances, which were obtained by subtraction of the absorbance spectrum of the sample before irradiation from that of the irradiated sample. In Fig. 2 we show a plot of spectra of the difference of absorbances in the 2500-1900 cm^{-1} region after 30.4 nm photolysis of pure CO ices at 10 K under different photon irradiation times. The new peaks are obviously due to absorption of photon-induced chemical reaction products. The spectral positions of the new features at 2242 cm^{-1}, 1989 cm^{-1}, 2347 cm^{-1}, and 2062 cm^{-1} are attributed to the chemical species of C_3O_2, C_2O, CO_2, and CO_3, respectively. The identities of the features are also indicated in Fig. 2. The dips correlate with the absorption features of the parent ice molecules indicating their losses due to photon-induced chemical reactions. The main dip at 2139 cm^{-1} is due to the depletion of the parent CO icy molecules while the much smaller dip at 2092 cm^{-1} is due to the depletion of the isotopic ^{13}CO parent molecules. As one can see the magnitudes of the peaks and dips increase with increasing photon irradiation time, i.e., photon dosage. The absorbances of all above observed features become more prominent as the irradiation increases over the photon dosages investigated in the present work. The dip at 2139 cm^{-1} becomes less pronounced as photolysis time increases to 80 minutes. This can mainly be attributed to the change of surface conditions including re-deposition of CO molecules onto the ice surface.

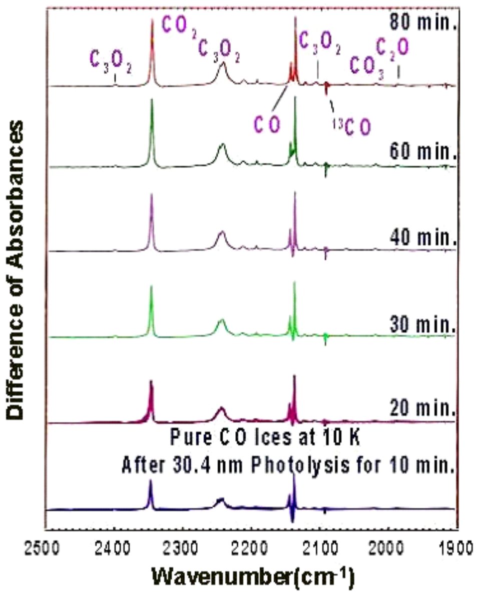

Fig. 2: The spectra of the difference of IR absorbances after the 30.4 nm photon irradiation of pure CO ices at 10 K for 10, 20, 30, 40, 60, and 80 minutes, respectively. The identified IR absorption features are marked in the top spectrum.

To determine the quantitative dependence of the production yield as a function of photon dose we first measure the product column density that is obtained by dividing the integrated peak of the change of absorbances with the absorption band strengths. The infrared band strengths used for the present analysis are taken from the literature. For example, the band strength of CO at 2139 cm^{-1} is A(CO, 2139 cm^{-1}) = 1.1 x 10^{-17} cm/molecule, CO_2 at 2344 cm^{-1} is A(CO_2, 2344 cm^{-1}) = 7.6 x 10^{-17} cm/molecule, and C_3O_2 at 821 cm^{-1} is A(C_3O_2, 821 cm^{-1}) = 1.3 x 10^{-16} cm/molecule. The photon dose in units of photons/cm^2 is obtained by dividing the integrated numbers of photons impinging on the ices by the photon beam size at the ice sample which is 0.16 cm^2. A typical plot of the product column density (cm^{-2}) as a function of photon dose

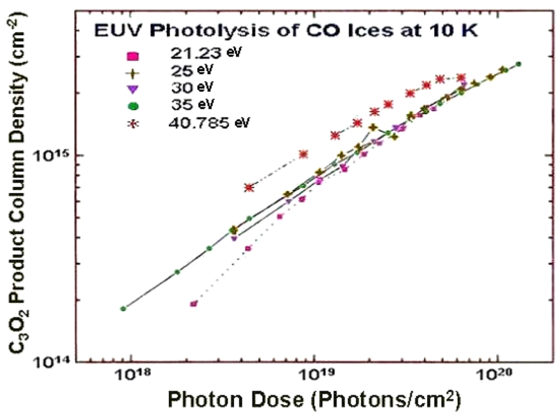

Fig. 3: The product column densities of C_3O_2 produced in the pure CO ices at 10 K by photolysis as a function of photon dose at several EUV photon energies.

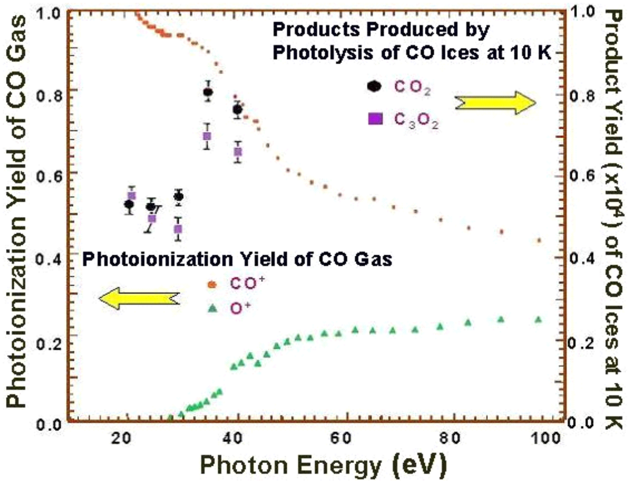

***Fig. 4:** The product yields of CO_2 and C_3O_2 produced through photolysis of CO pure ices at 10 K. The photoionization yields of CO^+ and O^+ produced through photoionization and photodissociative ionization of gaseous CO molecule are also plotted for comparison.*

(photons/cm^2) is shown in Fig. 3 for EUV photolysis of pure CO ices at several photon energies. The slope determined from such a plot gives the production yield per photon. Within the presently studied photon dose range the product column density of C_3O_2 appears to deviate from a linear increase at a photon dosage of about 4 x 10^{19} photons/cm^2 for photolysis at 30.4 nm (40.78 eV). The product column densities for CO_2 depend less linearly than that of C_3O_2 as a function of photon dose under the present experimental conditions. The determined product yields per photon for CO_2 and C_3O_2 are 7.5 (±0.4) x 10^{-5} and 6.5 (±0.4) x 10^{-5}, respectively, by photolysis at 30.4 nm and 5.2 (±0.4) x 10^{-5} and 5.4 (±0.4) x 10^{-5} by photon irradiation at 58.4 nm.

In order to understand the correlation between the production yields of a given new product and the electronic states of the CO molecule we have carried out the photolysis study at several EUV photon energies, namely, at 40.78, 35.0, 30.0, 25.0, 21.23, 11.27, and 10.196 eV. The product yields of CO_2 and C_3O_2 produced through photolysis of CO pure ices at 10 K are displayed in Fig. 4 along with plots of the photoionization yields of CO^+ and O^+ produced through photoionization and photodissociative ionization of gaseous CO molecule. A step-like increase in the production yields can clearly be observed in the photon energy between 30 eV and 35 eV which correlates with the excitation of the MET states of CO gas molecule. This increase has also been observed in the fluorescence excitation functions produced through photoexcitation of CO gas in the 28-45 eV regions. From Fig. 4 we find that the photon-induced chemical reactions in the CO ice systems involve the following production mechanisms: (1) excited neutral parent molecule, (2) excited neutral photofragments, (3) ion photofragments and/or parent ion molecule, (4) excited ion photofragments and/or excited parent ion molecule, (5) multiply charged ion photofragment and/or multiply charged parent ion, (6) photoelectrons produced through photolysis in the ice sample, and (7) neutral photofragment with non-thermal kinetic energy. In the presently studied photon energy range the most important mechanisms responsible for the observed prominent increase in the production yields are mechanisms (4) and (5).

BEAMLINE
03A High Flux VUV beamline

EXPERIMENTAL STATION
Matrix-Isolation/FTIR System end station

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