Vacuum Ultraviolet Photodissociation of Acetylene in Solid Ne

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Titan, the largest moon of Saturn, has a very dense atmosphere (1.6 atm) consisted of N_2 (~98.4 %), CH_4 (~1.6 %), and other trace gas. To date, except N_2 and CH_4, species have been identified in Titan including C_2H_2, C_2H_4, C_2H_6, C_4H_2, C_6H_6, C_6N_2, C_2N_2, HCN, and HC_3N. These species are likely synthesized by photo-induced chemical reaction of high abundance of N_2 and CH_4. When the amounts of these trace molecules is large enough, they begin to form aerosols. The photochemistry of C_2H_2 plays an important role in the Titan's atmosphere because it absorbs photons efficiently as wavelength shorter than 200 nm. Thus, the assistance for decomposition of CH_4 with C_2H_2 in Titan's atmosphere has been proposed. Our investigation of photodissociation of C_2H_2 with various photon energies and formation and identification of large carbon clusters and hydrides in the low temperature might be useful in the photochemical models for simulating the composition of atmosphere of Titan and the source of aerosols.

We irradiated samples of C_2H_2 in solid Ne at a ratio 1/1000 near 3 K with VUV light from the synchrotron and identified the photoproducts via IR absorption spectra. Photolysis of C_2H_2 in Ne matrix yielded photoproducts containing large carbon species up to C_8 upon irradiation with 171 nm and up to C_{12} upon irradiation with 130 and 114 nm. The formation of large carbon clusters was generated from combination of photofragments, but not from photolysis of clusters of C_2H_2 in the same cage. Our investigation of irradiation of acetylene dispersed in solid Ne with various photon energies might be valuable in modeling the photochemistry in the atmosphere in Titan.

Acetylene shows a vibronic structured absorption spectrum, in the wavelength region 155-190 nm and complex diffused bands mainly dominated by four Rydberg series below 155 nm to 108 nm, the first ionization potential. The photodissociation at 193 nm of acetylene involving the transition $A^1A_u \leftarrow X\ ^1\Sigma^+_g$ has been well investigated and suggested the involvement of the triplet manifold in the *A*-state predissociation. However, the investigation of the photolysis wavelength except 193 to 121 nm is very limited. The undulator beam from synchrotron radiation has advantages of more intense intensity and easily tuneable photon energy in the VUV region. Thus, we aim to study the photolysis effect of acetylene with higher photon energy. The selected photolysis wavelengths are 171, 130, and 114 nm corresponding to excitation of acetylene to $B\ ^1B_u$, (3R'+3R"), and (6R+6R"), respectively.

The photochemical behavior of species isolated in matrices might be distinct from that in the gaseous phase. In the gaseous phase at small pressure, fragments have little chance to collide with each other upon photodissociation, whereas photofragments produced in a matrix and without enough energy to escape are typically constrained within the matrix cage; this phenomenon is so-called cage effect. In this study, the photoproduct containing four or six carbon atoms observed in the experiment performed with irradiation of C_2H_2 in Ne matrix at 171 nm might be properly formed by photodissociation of dimer or trimer of acetylene in the same matrix cage, but the formation of C_8-species is not easily due to less probability of forming tetramer in the matrix sample of C_2H_2/Ne (1/1000).

The observation of large carbon clusters from irradiation of a matrix sample with VUV light for higher photon energy suggests that photofragments deposited excess energy after receiving VUV photons possess the high mobility inside the matrix and allow one to bring together atoms or molecules of rather different nature. The interactions between atoms and molecules are far stronger than those between molecules and rare gas matrix. Thus, molecules and atoms recombine efficiently to form clusters. In addition, formation of carbon clusters and hydrides with a linear structure indicates the addition for synthesizing a long carbon chain experienced with one or two carbon atoms step by step.

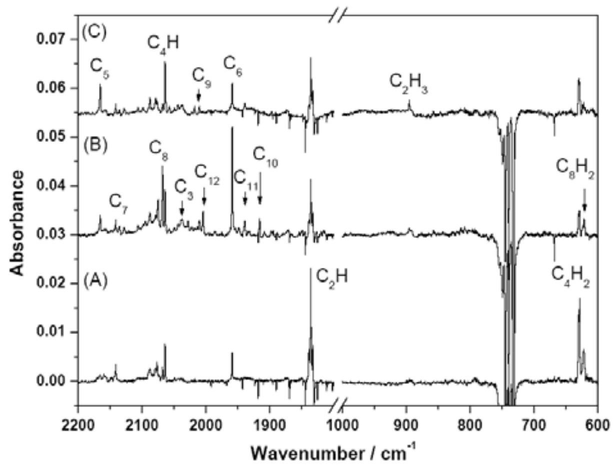

Fig. 1: Difference infrared spectrum of C_2H_2 in solid Ne upon irradiation at (A) 171 nm, (B) 130 nm, and (C) 114 nm for 50 min. Some assignments are noted.