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## **EUV-VUV Photolysis of Molecular Ice Systems of Astronomical Interest**

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### **ABSTRACT**

We wish to report laboratory simulation results obtained from extreme ultraviolet (EUV) and vacuum ultraviolet (VUV) photolysis of molecular ices relevant to the cometary-type ices and icy satellites of planetary systems. Specifically, we identify the type of molecules that form in the ices and/or those that come off the ice surfaces, quantify their production yields and destruction yields, understand their production mechanisms, and ascertain their significance in astronomical environments.

### **1. Introduction**

Recently, much progress has been made in the area of laboratory simulations of chemical processes present in astronomical environments and in planetary systems. The body of this work includes the study of photon irradiation and charged particle impact of ice grains and ices. Such studies are fundamental to the understanding of the evolution of the interstellar medium, and the chemical composition of primitive material in our solar system. Laboratory simulation has now become a major tool in deciphering these complex phenomena which could have many other important implications in astrophysics and astrobiology. We have

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carried out laboratory simulation studies of several ice systems. A brief summary of this research work is presented here. The experimental set up and experimental procedures have been previously described (Wu et al. 2002).

## 2. Results and Discussion

Using the FTIR spectrometry we have studied (a) pure ices such as pure  $CH_4$ ,  $CO$ ,  $N_2$ , and  $NH_3$  ices, (b) mixtures of two molecules such as  $H_2O + CH_4$ ,  $H_2O + C_2H_2$ ,  $H_2O + CO$ ,  $H_2O + CO_2$ ,  $CH_4 + NH_3$ ,  $CO + NH_3$ , and  $N_2 + CH_4$ , and (c) mixtures of three or more molecules such as  $H_2O + CH_4 + NH_3$ ,  $CO + CH_4 + NH_3$ ,  $H_2O + NH_3 + CH_4$ , and  $H_2O + CO + CH_4 + NH_3$ . Examples of the data obtained are shown in the following. The difference of absorbances of the  $CH_4 + H_2O$  (100:1) ice mixtures at 10 K produced by photolysis at the 58.4 nm (upper panel) and 30.4 nm (bottom panel) are shown in Fig. 1. The IR absorption features due to reaction products of  $CH_2$ ,  $CH_3$ ,  $C_2H_6$ ,  $C_3H_8$ ,  $CO$

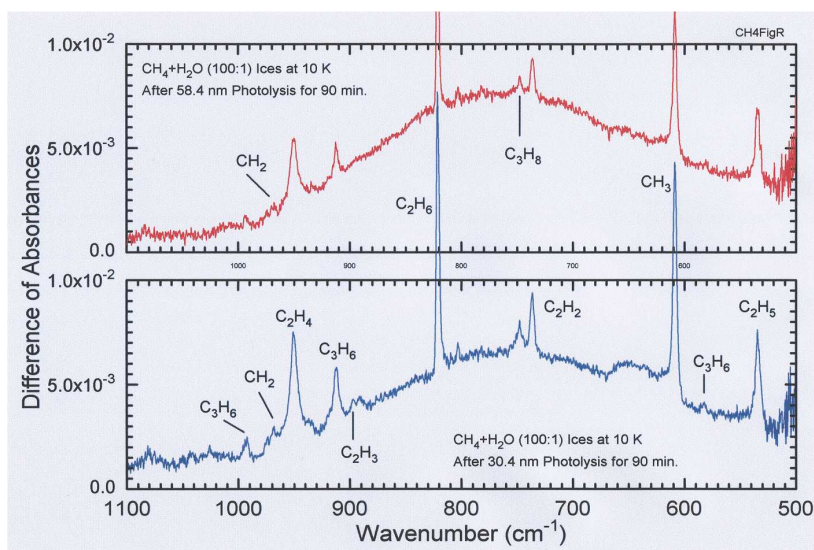


Fig. 1.— It displays the difference of absorbances of the  $CH_4 + H_2O$  (100:1) ice mixture at 10 K taken after irradiation by the 58.4 nm (upper panel) and 30.4 nm (bottom panel) photolysis

and  $CO_2$  are identified and indicated in the figure. We have also investigated  $CH_4 + H_2O$  (1:7) and  $CH_4 + H_2O$  (3:7) mixed ices. However, the products observed are mainly the  $CO$ ,  $CO_2$ , and  $H_2CO$ . Evidently the radicals such as  $CH_2$ ,  $CH_3$ , and  $C_2H_5$  are converted into  $CO$ ,  $CO_2$ , and  $H_2CO$  for the low  $CH_4$  to  $H_2O$  ratios. In photolysis of pure  $CO$  ices at

10 K, the chemical species produced were found to be primarily  $C_3O_2$ ,  $C_2O$ ,  $CO_3$ , and  $CO_2$  (Gerakines & Moore 2001). We have also studied the  $H_2O + CO$  mixed ice systems with two different compositions, i.e., 1:1 and 4:1, at 10 K in the photolysis at 40.78, 21.23, and 10.196 eV. The major products are  $HCO$ ,  $H_2CO$ ,  $HCOOH$ , and  $CH_3OH$ . That is to say, in the presence of  $H_2O$ , the suboxides are converted to aldehydes, acids, and alcohols. In the EUV photolysis studies of  $H_2O + C_2H_2$  (4:1) ices new molecules identified were mainly  $C_2H_6$ ,  $CO_2$ ,  $CO$ ,  $CH_3OH$ , and  $H_2CO$ . In addition, we have tentatively assigned several unidentified absorption features to  $HCO$ ,  $C_3H_8$  and  $C_2H_5OH$  (Wu et al. 2002). Several production yields produced through VUV and EUV photolysis of the above molecular ice systems are summarized in Table 1.

Table 1: Summary of the production yields produced through EUV photolysis of ice systems at 10 K

ICY SYSTEMS AT 10K	PRODUCT	$Y(PHOTON^{-1})$		
		30.4 nm	58.4 nm	121.6 nm <sup>a</sup>
$C_2H_2 + H_2O(1 : 4)$	$CO$	$2.8(\pm 0.2) \times 10^{-2}$	$4.6(\pm 0.2) \times 10^{-2}$	
	$CO_2$	$9.1(\pm 0.4) \times 10^{-3}$	$3.3(\pm 0.4) \times 10^{-3}$	
$CO_2 + H_2O(1 : 4)$	$CO$	$9.4(\pm 0.4) \times 10^{-3}$	$4.0(\pm 0.4) \times 10^{-3}$	$3.3(\pm 1.5) \times 10^{-2}$
	$H_2CO_3$	$5.7(\pm 0.4) \times 10^{-3}$	$2.3(\pm 0.2) \times 10^{-3}$	$3.1(\pm 1.6) \times 10^{-3}$
$PureCO$	$CO_2$	$6.1(\pm 0.3) \times 10^{-3}$	$5.8(\pm 0.4) \times 10^{-3}$	
	$C_3O_2$	$5.1(\pm 0.4) \times 10^{-3}$	$4.4(\pm 0.4) \times 10^{-3}$	
	$CO_3$	$2.3(\pm 0.3) \times 10^{-3}$	$2.8(\pm 0.4) \times 10^{-3}$	
$PureCH_4$	$CH_3$	$1.2(\pm 0.2) \times 10^{-3}$	$9.0(\pm 0.2) \times 10^{-4}$	
	$C_2H_2$	$6.4(\pm 0.5) \times 10^{-4}$	$4.6(\pm 0.5) \times 10^{-4}$	
	$C_2H_4$	$1.9(\pm 0.5) \times 10^{-3}$	$1.8(\pm 0.5) \times 10^{-3}$	
	$C_2H_6$	$2.9(\pm 0.2) \times 10^{-2}$	$2.2(\pm 0.2) \times 10^{-3}$	

<sup>a</sup>The mixed icy system has a composition of  $CO_2 + H_2O(1 : 1)$  at 18 K (Gerakines et al. 2000)

The EUV photolysis of the  $N_2 + CH_4$  (1:1) and the  $N_2 + CH_4$  (1:4) ice mixtures show IR absorption features belong to  $CH_3$ ,  $C_2H_4$ ,  $C_2H_6$ , and  $C_3H_8$ . The sharp  $HCN$  feature at  $2096 \text{ cm}^{-1}$  (Hudson & Moore 2000; Gerakines & Moore 2001) is clearly identified in the photolyzed  $N_2 + CH_4$  (1:1) ice sample although the peak size is relatively weak. A peak at  $2524 \text{ cm}^{-1}$  appears to be an unknown feature. Its identity is unknown at the present time.

One of the clear differences between the two different compositions is that the  $HCN$  peak at  $2096\text{ cm}^{-1}$  becomes too weak to be positively identifiable in the  $N_2 + CH_4$  (1:4) ice sample.

A comparison of the FTIR spectra of the differences of absorbances in the spectral region between  $1800$  and  $2200\text{ cm}^{-1}$  of the  $N_2 + CH_4$  (1:1),  $H_2O + CH_4 + NH_3$  (1:1:1), and  $CO + CH_4 + NH_3$  (1:1:1) ices at  $10\text{ K}$  produced through photolysis at  $30.4\text{ nm}$  is displayed in Fig. 2. The salient features are briefly mentioned here. First,  $HCN$  has been clearly

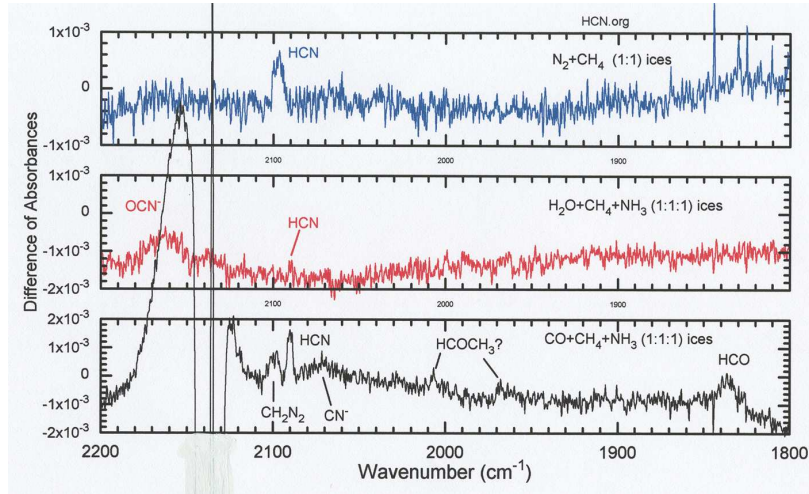


Fig. 2.— It displays a comparison of the FTIR spectra of the differences of absorbances in the  $1800 - 2200\text{ cm}^{-1}$  region of the  $N_2 + CH_4$  (1:1),  $H_2O + CH_4 + NH_3$  (1:1:1), and  $CO + CH_4 + NH_3$  (1:1:1) ices at  $10\text{ K}$  produced through photolysis at  $30.4\text{ nm}$

produced in the  $N_2 + CH_4$  (1:1) and the  $CO + CH_4 + NH_3$  (1:1:1) mixed ice systems at  $10\text{ K}$ , but it appears to be barely discernible in the  $H_2O + CH_4 + NH_3$  (1:1:1) solid ice sample under the present experimental conditions. The  $HCN$  spectral position in the  $N_2 + CH_4$  ice is about  $10\text{ cm}^{-1}$  higher than those of the other two ice samples because of different host-site conditions. Secondly, the feature of  $OCN^-$  is clearly observed from EUV photolysis of the  $H_2O + CH_4 + NH_3$  (1:1:1) mixed ice systems, see the middle panel. However, it is not clear whether the  $OCN^-$  is produced or not in the photolysis of  $CO + CH_4 + NH_3$  (1:1:1) ices. This is because its absorbance can possibly be buried by the strong peak of the parent  $CO$  molecules at  $2140\text{ cm}^{-1}$  (see the bottom panel). Thirdly, the  $CH_2N_2$  and the  $CN^-$  anions are uniquely observed in the photolysis of the  $CO + CH_4 + NH_3$  (1:1:1) mixed ice systems, the bottom panel. Further, we have tentatively identified the  $HCOCH_3$  from photolysis of the  $CO + CH_4 + NH_3$  (1:1:1) mixed ice systems. Therefore, by comparing the EUV photolyzed results of the ice samples of  $CO + CH_4 + NH_3$  (1:1:1) and  $H_2O + CH_4 + NH_3$  (1:1:1), we can conclude that the oxidizing power of  $H_2O$  in the icy environments is stronger than that

of  $CO$ . This is supported by the absence of  $CH_2N_2$ ,  $HCOCH_3$ , and  $HCO$  products in the spectra of the photolyzed  $CO + CH_4 + NH_3$  (1:1:1) ice samples at 10 K.

To determine the quantitative dependence of the production yield as a function of photon dose we first measure the product column density which is obtained by dividing the integrated peak of the change of absorbances with the band strengths. The photon dose in units of photons/cm<sup>2</sup> is obtained by dividing the integrated numbers of photons impinging on the ices by the photon beam size at the ice sample. The product yield per photon is determined from a plot of the product column density (cm<sup>-2</sup>) as a function of photon dose. In Table 1 we summarize the product yields of several ice systems that we have recently studied (Wu et al. 2003, 2002) and that of (Gerakines et al. 2000).

### 3. Conclusion

By comparing the EUV photolyzed results of the EUV photolysis of (a)  $CH_4 + H_2O$  (100:1),  $CH_4 + H_2O$  (1:7) and  $CH_4 + H_2O$  (3:7) ice systems; (b)  $CO$ ,  $H_2O + CO$  (1:1) and  $H_2O + CO$  (4:1) ices and (c)  $CO + CH_4 + NH_3$  (1:1:1) and  $H_2O + CH_4 + NH_3$  (1:1:1) ices, we conclude that the oxidizing power of  $H_2O$  in the icy environments is stronger than that of  $CO$ . Similar results are observed from photolysis at other EUV photon energies but with different production yields. The present results suggest that  $XCN$  can be readily produced in mixed ices containing  $H$ ,  $C$ , and  $N$  atoms. The intriguing photochemistry of ices deserves further investigations in order to improve our understanding of chemical evolution in cosmic environments.

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