

# Photo-stimulated desorption from water and methane clusters on the surface of solid neon

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Photo-stimulated desorption of ions from methane and water heterocluster on the surface of solid neon was studied. The desorption yields of the variety of photo-desorbed species showed strong dependence on the composition and the size of the mother cluster. It was found that the presence of a water molecule in the cluster significantly enhanced, or was almost essential for, the desorption of any species observed. Systematic investigation of the correlation between the cluster size and the desorption yield of each ion has revealed the mother cluster which yields the each desorbed ion.

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68.43.Tj Photon-stimulated desorption;  
82.33.Fg Reactions in clusters.

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## 1. Introduction

The role of the ice surface as a stage of chemical reaction has been studied in the wide variety of fields such as interstellar astrophysics [1], atmospheric science [2,3], and biological science. Specifically in the interstellar astrophysics [4], it is considered that the ice surface of the interstellar dust provides the stage where a complex organic molecule is synthesized from simple molecules. Dynamics induced by electronic transitions, such as desorption, dissociation, or chemical synthesis, at the water cluster which contains organic molecules have been studied in conjunction with the photochemistry at ice particles in cosmic space and in the atmosphere.

We have studied the photo-stimulated desorption (PSD) from the clusters prepared on the surface of a solid rare gas, which is condensed on a copper substrate cooled by liquid helium in an ultra-high vacuum chamber [7]. Our experimental method has the advantage in controlling the cluster size and of high density of specimens in comparison with a molecular beam experiment. The sample is excited by vacuum ultraviolet light with a photon energy between 12 and 310 eV and a pulse width of 10 ns, which is generated by a laser plasma light source [6]. The mass spectrum of photo-desorbed ions is measured by a time-of-flight (TOF) method. There are variety of species in the photo-desorbed ions from the coadsorbed system of water and methane; protonated water clusters,  $(\text{H}_2\text{O})_n\text{H}^+$ , me-

thane clusters,  $(\text{CH}_4)_n\text{CH}_k^+$ , heteroclusters of water and methane,  $(\text{H}_2\text{O})_n(\text{CH}_4)_m\text{CH}_k^+$ , and the ions of synthesized species, methanol, ethane, or ethylene.

In the present study, the relation between the desorbed species and the composition of the mother cluster has been systematically studied. The result shows that a water molecule plays an important role in the desorption process. The unique ability of our experimental method is also demonstrated.

## 2. Experimental method and apparatus

The experimental apparatus was composed of a vacuum ultraviolet (VUV) light source and a PSD chamber which contained a cryogenic sample holder and a detector for photo-desorbed ions.

The excitation source was a laser plasma vacuum ultraviolet light source (LPLS) [6]. A Q-switched Nd-YAG laser beam, 1024 nm of wavelength, was focused on a rotatable cylindrical tantalum target to produce metal plasma. The laser pulses were repeated at a frequency of 50 Hz with a pulse width of 10 ns, and a typical laser energy was 550 mJ/pulse. The light emitted from the plasma was monochromatized with a toroidal grating and an exit slit and was introduced into a PSD chamber. The beam line was differentially pumped to maintain ultra-high vacuum condition as low as  $10^{-8}$  Pa in the PSD chamber. Three toroidal gratings covered the wavelength range between 4 and

108 nm. Our LPLS apparatus provided a pulse photon beam with the photon number of  $10^6$ – $10^8$  photons/pulse, the pulse width less than 15 ns, and the wavelength resolution  $\lambda/\Delta\lambda$  of 50–100.

The copper substrate was mounted on the bottom of a liquid He reservoir. These were thermally connected and electrically insulated by a sapphire rod. The sample temperature was 5.9 K. The PSD chamber had three gas inlet ports for rare gases, water, and methane. Water and methane were deposited on a solid film of rare gas condensed on the copper substrate. The thickness of the rare-gas film and the amount of methane adsorbed were calculated from the exposure, namely, the product of a pressure in the chamber and an exposing time. Water, which was purified by multiple freeze-pump-thaw cycles, was effused from a small orifice directed toward the sample substrate. The coverage of water was estimated from the flow rate of water vapor with the cosine rule at the exit orifice. Here we assumed that the condensation coefficients of these gases were unity. The rare-gas film was deposited as thick as several hundreds molecular layers so that the effects of the copper substrate were negligible.

Photo-desorbed cations were accelerated by the electric field between the positively biased substrate and the entrance of a drift tube at ground potential, and were detected by a channeltron electron multiplier placed at the other end of the drift tube. A TOF spectrum was recorded on a multi channel scaler and was converted to a mass spectrum, where the mass resolution  $m/\Delta m$  of about 100 was achieved. The signal intensity of each desorbed ion was normalized by the excitation light intensity which was continuously monitored by the photoemission current from a gold-plated mesh inserted in the beam line.

### 3. Experimental results and discussions

#### 3.1. Pure water clusters and desorption mechanism

A typical TOF mass spectrum of PSD ions from water physisorbed on solid Ne is shown in Fig. 1, where the fractional coverage of water was 0.05 monolayer (ML) and the excitation photon energy was 70 eV. In the spectrum are the series of protonated water clusters,  $(\text{H}_2\text{O})_n\text{H}^+$ , as the main species and the trace of  $\text{H}_2\text{O}^+$  and  $\text{Ne}^+$ . Coulomb repulsion between two adjacent ions is essential for the desorption of an ion from the surface of a molecular crystal [7]. The excitation of a doubly charged ion followed by the charge exchange, via either a simple charge transfer or an intermolecular Auger process, results in the formation of the adjacent ion pair. In the case of water physisorbed on Ne solid, the direct double photoionization of Ne, whose threshold energy is 62.5 eV [5], leads to the ionization of a water cluster on the surface. On the other hand, in regard to a pure water cluster, the ionized water cluster has an excess vibrational energy and ejects OH to become the protonated water cluster,  $(\text{H}_2\text{O})_n\text{H}^+$ , which desorbs from the surface [6].

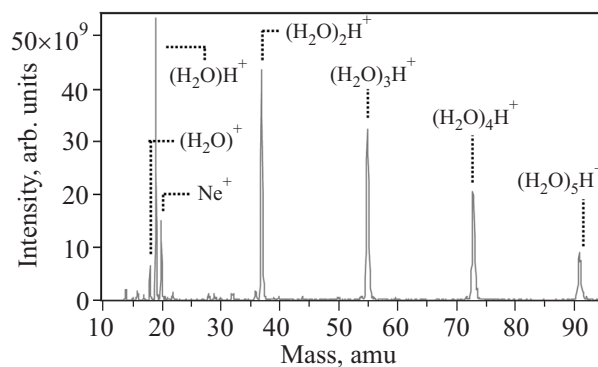


Fig. 1. A mass spectrum of photo-desorbed ions from water physisorbed on solid neon. The film thickness of solid neon was 250 monolayers (ML), the amount of adsorbed water 0.05 ML, the photon energy 70 eV.

The distribution of the size  $n$  of the protonated water clusters,  $(\text{H}_2\text{O})_n\text{H}^+$ , depended largely on the amount of water physisorbed as shown in Fig. 2. These protonated water clusters were prominently observed from a very thin water film as thin as 0.1 ML or less, but little from a monolayer film, and neither from thick ice films nor the surface of solid ice. This result shows that the ions observed here are originated from isolated water clusters on the surface of solid neon. The coverage dependence of the cluster size distribution obtained as Fig. 2 makes it possible to control the mean size of the clusters to be studied by choosing the amount of water deposited.

#### 3.2. Water and methane coadsorbed on solid Ne

An example of TOF mass spectrum of PSD ions from water and methane coadsorbed on solid Ne is shown in Fig. 3, where the coverage of water and methane were 0.01 and 0.2 ML, respectively. Besides the species observed in the spectrum from the pure water system (Fig. 1), a variety of ionized species appeared in the spectrum; methane ions,

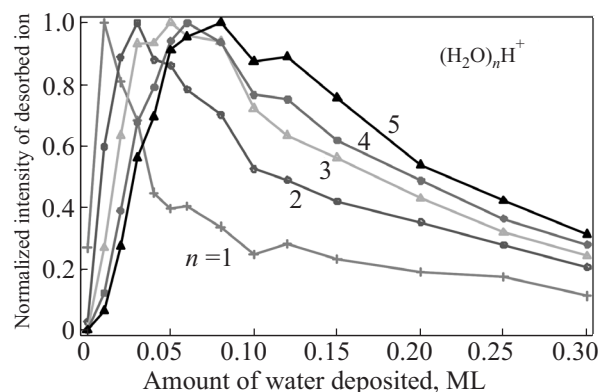


Fig. 2. The relative size distribution of the protonated water clusters,  $(\text{H}_2\text{O})_n\text{H}^+$ , of the size  $n$  between 1 and 5 as a function of the amount of water deposited. At each coverage, the peak heights appeared in the TOF mass spectrum were normalized by that of the largest intensity. The excitation photon energy was 70 eV.

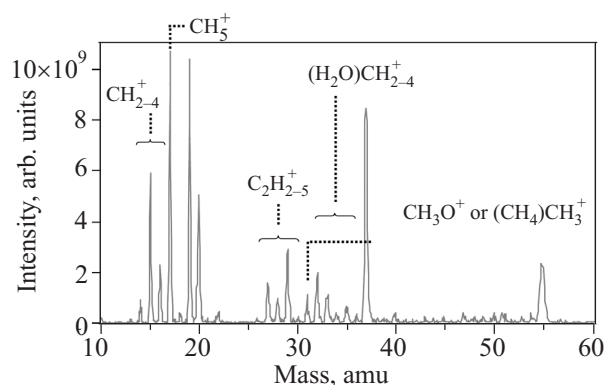


Fig. 3. A TOF mass spectrum of photo-desorbed ions from 0.01 ML of water and 0.2 ML of methane coadsorbed on solid Ne. The photon energy was 70 eV.

methane cluster ions, heterocluster ions of water and methane, and ions of ethane, ethylene, or methanol which is likely to be synthesized in the cluster. It was also found that the relative and the absolute yields of each ion depended greatly on the amount of both water and methane deposited. It suggests that there are some specific relations between each desorbed species and the size of its mother cluster  $(\text{CH}_4)_m(\text{H}_2\text{O})_n$ .

We have performed the systematic measurement of the yield of each ion by varying two parameters  $m$  and  $n$ , which were controlled by the amount of methane and water deposited, to reveal the mother cluster for each desorbed species. The contour map of Fig. 4 shows the desorption yields of the ion with the mass of 15 amu, namely  $\text{CH}_3^+$ , which were extracted from 90 TOF mass spectra which

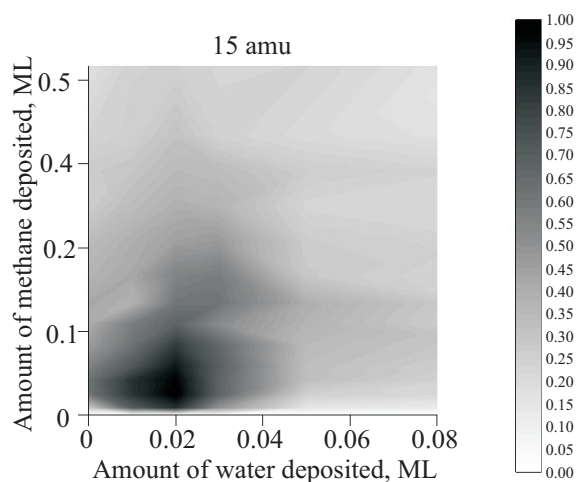


Fig. 4. A contour map of  $\text{CH}_3^+$  desorption intensities at various coverages of water and methane on the surface of solid neon. The excitation photon energy was 68 eV. Each signal intensity was normalized by the light intensity monitored during PSD experiment and the contour scale is normalized by the maximum intensity, that is, the signal intensity obtained with 0.02 ML water and 0.03 ML methane in this map.

were obtained at the various combination of the amount of water deposited (0, 0.01, 0.02, 0.03, 0.05, and 0.1 ML) and that of methane (0, 0.01, 0.03, 0.05, 0.07, 0.1, 0.13, 0.16, 0.2, 0.25, 0.3, 0.35, 0.4, 0.5, and 0.6 ML). This result describes notable characteristics in the  $\text{CH}_3^+$  formation process clearly: (1) little  $\text{CH}_3^+$  comes from isolated  $\text{CH}_4$ , (2) coadsorption of small amount of water as low as 0.02 ML strongly enhances  $\text{CH}_3^+$  desorption, (3) however, a larger amount of water drastically reduces  $\text{CH}_3^+$  yield, and (4) these coverage dependencies are also the case for the amount of methane. It can be concluded that  $\text{CH}_3^+$  is efficiently yielded by a heterocluster  $(\text{CH}_4)_{1-2}(\text{H}_2\text{O})_{1-2}$ , which is the mother cluster of  $\text{CH}_3^+$  in other word, though it is difficult to determine its exact size.

The contour maps for the desorbed ions of the mass of 16, 17, and 31 amu are shown in Fig. 5 in the same scales of the coordinates and the contour of Fig. 4. The mother cluster for each ion can be deduced from the contour pattern which differs from ion to ion. The ion of 16 amu is not  $\text{O}^+$  but  $\text{CH}_4^+$  because it is observed without water, at the left end of Fig. 5, *a*, and not observed from pure water (Fig. 1). In contrast to  $\text{CH}_3^+$  desorption,  $\text{CH}_4^+$  comes from an isolated  $\text{CH}_4$  molecule. In other word, ionization of  $\text{CH}_4$  molecule does not yield  $\text{CH}_3^+$  but  $\text{CH}_4^+$ . The relatively small water-methane heterocluster,  $(\text{CH}_4)_{1-2}(\text{H}_2\text{O})_{1-2}$ , can also eject  $\text{CH}_4^+$  as is the case with  $\text{CH}_3^+$  desorption.

The ion of 17 amu is  $\text{CH}_5^+$ . The possibility of  $\text{OH}^+$  can be excluded because of no signal at low coverage of methane, namely at the bottom of Fig. 5, *b*. The contour pattern of  $\text{CH}_5^+$  is obviously different from both patterns of  $\text{CH}_3^+$  and  $\text{CH}_4^+$ . There is almost no signal from the clusters with one molecule of methane. Water molecule(s) in the cluster is also essential for the desorption of  $\text{CH}_5^+$ . In contrast to  $\text{CH}_3^+$  and  $\text{CH}_4^+$ , larger number of methane molecules in the cluster does not suppress the desorption yield. The mother cluster of  $\text{CH}_5^+$  can be deduced to be  $(\text{CH}_4)_{2-5}(\text{H}_2\text{O})_{1-2}$  from the above observation.

The species of 27 amu in Fig. 3 is  $\text{C}_2\text{H}_3^+$ ; any other combination of C, H, and O would be unacceptable. Its contour pattern, which is not shown here, is almost identical with that of  $\text{CH}_5^+$ . This means that the synthesis of ethane or ethylene occurs in the heterocluster composed of two or more methane and, at least, one water molecule.

The ion of 31 amu may be  $\text{CH}_3\text{O}^+$  or  $(\text{CH}_4)\text{CH}_3^+$  or both. The fact that the yield decreases as increasing methane concentration may exclude the possibility of a methane cluster ion. In addition, the close resemblance between the contour pattern of 31 amu species and that of  $\text{CH}_3^+$  suggests the same mother cluster for both species, namely  $(\text{CH}_4)_{1-2}(\text{H}_2\text{O})_{1-2}$ . From these observation, this species likely to be  $\text{CH}_3\text{O}^+$ , which is synthesized in the water-methane heterocluster.

The mother cluster for each PSD ion are summarized in Table 1. The symbol “+” denotes that the ion in the left column is efficiently yielded by the mother cluster above.

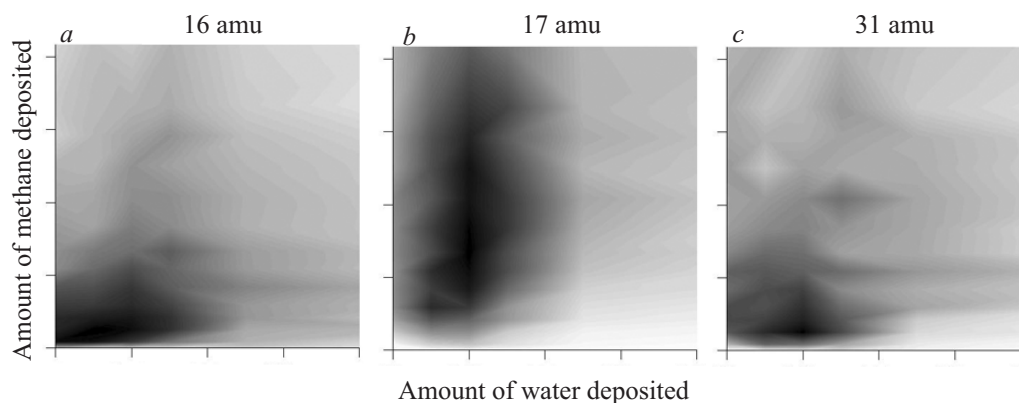


Fig. 5. Contour maps of the desorbed ions of the mass 16 (a), 17 (b), and 31 (c) amu. The scales of the coordinates and the contour are the same as Fig. 4.

Though these assignments are bold enough, and in addition, the cluster sizes were not exactly determined at this time, it was revealed that a water molecule plays crucial roles in the process. Firstly, one water molecule is essential for the desorption of the ions investigated here except the case of  $\text{CH}_4^+$  from the isolated  $\text{CH}_4$  molecule. Even for the case of  $\text{CH}_5^+$  and  $\text{C}_2\text{H}_3^+$ , those are likely produced from two adjacent methane molecules, the addition of one water molecule to the cluster is absolutely essential for the desorption of these species. It suggests that the ionized water molecule plays a key role in the chemical reaction in the clusters. From the contour pattern, however, it is also obvious that too many water molecules, which may be three or more, drastically reduces the desorption efficiency for every ion investigated in this study. Further investigation is necessary to reveal the detailed mechanism of the excitation and the relaxation in the heteroclusters.

Table 1. The mother clusters for each PSD ion. The most likely origin of each desorbed ion is denoted by "+".

PSD ions	Mother clusters		
	$\text{CH}_4$	$(\text{CH}_4)_{1-2}(\text{H}_2\text{O})_{1-2}$	$(\text{CH}_4)_{>2}(\text{H}_2\text{O})_{1-2}$
$\text{CH}_3^+$		+	
$\text{CH}_4^+$	+	+	
$\text{CH}_5^+$			+
$\text{C}_2\text{H}_3^+$			+
$\text{CH}_3\text{O}^+$		+	

#### 4. Summary

The photo-desorbed ions from the heteroclusters of water and methane on the surface of solid neon were analyzed by TOF mass spectrometry. In the mass spectrum were the ions originated from the photo-synthesized species, methanol, ethane, or ethylene. The mass spectrum of the desorption species depended greatly on the composition and the size of the cluster and each species had the specific mother cluster. It was found that the presence of a water molecule in the cluster strongly enhanced, or was almost essential for, the desorption of any species observed in the present study.

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