

## On the Formation of Clusters in Secondary Ion Mass Spectrometry of Molecular Solids

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Water strongly promotes the formation of ion clusters containing several undamaged methanol molecules during the sputtering of water-methanol layers condensed on titania at 120 °K.

Very large ion clusters have been observed in secondary ion mass spectrometry (SIMS) not only for elementary solids (metals<sup>1</sup> and rare gases<sup>2</sup>) but also for ionic (halides<sup>3</sup>) and molecular compounds (H<sub>2</sub>O,<sup>4</sup> NO,<sup>5</sup> CO<sup>5</sup>). We report here the observation by SIMS of new positive and negative ion clusters during Ar<sup>+</sup> bombardment of H<sub>2</sub>O, MeOH, and H<sub>2</sub>O-MeOH condensed from the gas phase onto TiO<sub>2</sub> kept at 120 K.

Up to now, only positive ion clusters of H<sub>2</sub>O have been observed.<sup>4</sup> We have now detected negative ion clusters such as OH<sup>-</sup>(H<sub>2</sub>O)<sub>n</sub>, n = 0–5, by SIMS. However they can only be

detected when the physisorbed water film is still conducting and thus only a few layers thick. They are not observed for an ice insulating film.<sup>6</sup>

For neat methanol, ion clusters have previously been observed by field desorption mass spectrometry (FDMS).<sup>7</sup> We have now observed an intense series of methanol ion clusters H<sup>+</sup>(MeOH)<sub>m</sub>, m = 1–17 (Figure 1). Additional series of less intense peaks are also present in the spectra. They are representative of the ions H<sup>+</sup>(H<sub>2</sub>O)(MeOH)<sub>m</sub>, HCO<sup>+</sup>(MeOH)<sub>m</sub>, CH<sub>3</sub>O<sup>+</sup>(MeOH)<sub>m</sub>, CH<sub>3</sub><sup>+</sup>(MeOH)<sub>m</sub>, and CH<sup>+</sup>(MeOH)<sub>m</sub>. The

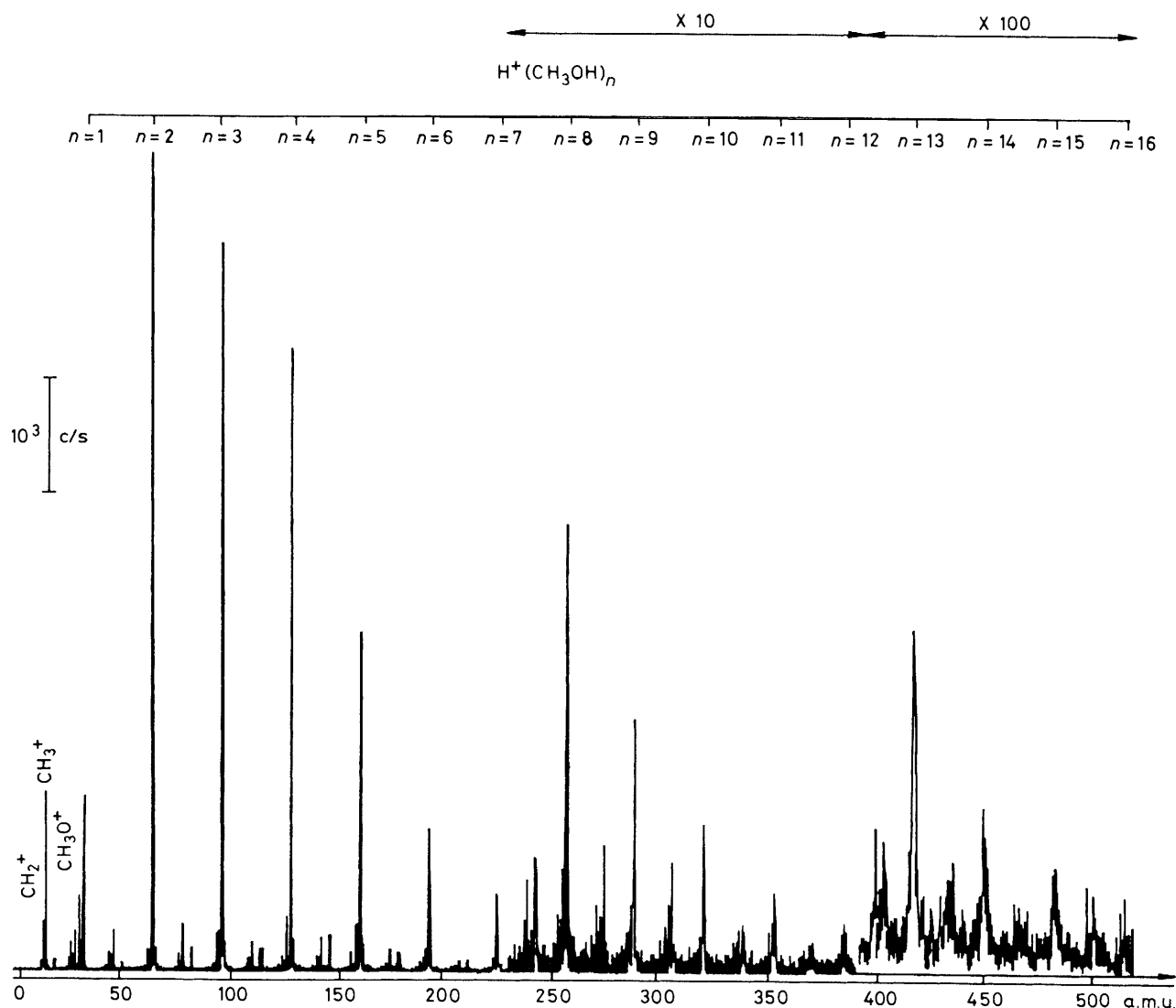


Figure 1. Positive SIMS spectrum of MeOH on TiO<sub>2</sub> at 120 K, Ar<sup>+</sup> 0.8 keV.

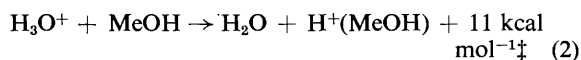
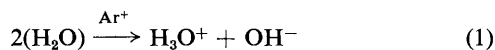
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two latter series could also be produced by ethanol impurities. The  $\text{CH}_3^+(\text{MeOH})$  peak has also been observed by Röllgen.<sup>7</sup>

Minute amounts of methanol in water (1:2000) produce intense signals for mixed clusters besides the  $\text{H}_2\text{O}$  and  $\text{MeOH}$  clusters with the following decreasing intensities  $\text{H}^+(\text{H}_2\text{O})_n > \text{H}^+(\text{H}_2\text{O})_n(\text{MeOH})_m > \text{H}^+(\text{MeOH})_m$ .

Increasing the amount of methanol (1:200) gives an intensity sequence  $\text{H}^+(\text{H}_2\text{O})_n(\text{MeOH})_m > \text{H}^+(\text{MeOH})_m > \text{H}^+(\text{H}_2\text{O})_n$ . At a water:MeOH ratio of 1:1, the sequence becomes  $\text{H}^+(\text{MeOH})_m \geq \text{H}^+(\text{H}_2\text{O})_n(\text{MeOH})_m > \text{H}^+(\text{H}_2\text{O})_n$ .

The high intensity of methanol-containing clusters may be tentatively explained by equations (1) and (2)<sup>8</sup>.



The protonated methanol is then solvated before ejection out of the condensed phase. The ion intensities observed here differ from those characteristic of ion-molecule reactions in the gas phase.<sup>8</sup> In addition, they are insensitive to pressure variations above the cold sample throughout the range  $10^{-8}$  to  $5 \times 10^{-6}$  Torr. These results lend much support to an interpretation of the spectra in terms of ion-molecule reactions in the condensed phase.

A mixture of  $\text{Me}^{16}\text{OH}-\text{H}_2^{18}\text{O}$  (1:200) shows no incorpora-

tion of  $^{18}\text{O}$  in methanol clusters which provides strong support for a direct ejection mechanism.

Thus we can conclude that (i) not only protons but also ionic fragments ( $\text{MeO}^+$ ,  $\text{HCO}^+$ ,  $\text{OH}^-$ ,  $\text{CH}_3^+$ ) can form stable ion clusters, as has been seen previously for inorganic salts<sup>9</sup> and (ii) water is a proton donor and therefore promotes the ion yield of the intact ejected molecular species.

In summary, water is a convenient promoting agent for SIMS molecular analysis of H-bond-forming molecules.

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† 1 kcal = 4.18 kJ.