

The adsorption of methanol on large water clusters

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Abstract

We have studied the adsorption of methanol monomers onto large water clusters by using the pick-up technique to deposit methanol onto water clusters formed in a supersonic expansion of pure water vapour. The clusters are ionised by electron impact and mass analysed. The major low-mass methanol-containing ion peaks (< 100 u) correspond to unclustered and unprotonated methanol and have similar cracking patterns to free methanol monomers, although there are some heterocluster ions observed containing no more than one water and two methanol molecules. The measured ion appearance potentials indicate that the methanol is directly ionised. In contrast to previous results for methanol adsorbed onto large argon clusters [F. Huisken and M. Stemmler, *J. Chem. Phys.* 98 (1993) 7680], we do not find any evidence for the formation of dimers or higher clusters of methanol on the water clusters.

1. Introduction

The study of mixed clusters, in which one species is in an excess of another, can provide a useful method of studying solute–solvent interactions. Using water as the solvent, it is possible to probe intermolecular hydrogen bonding in systems where the solute is an organic molecule (e.g. an alcohol) as prototypes for biologically important systems. There have been several previous studies involving mixed methanol–water clusters in which the stability of certain protonated methanol–water cluster ions has been noted [1–3] and related to particularly stable structures. Alcohols can act as both proton donors and proton acceptors and it has been shown [4] for methanol–water clusters that the methanol acts as a proton acceptor. Mass spectroscopy is commonly used to detect and identify neutral clusters and the observed low-mass fragment ions are often similar to those observed for the unclustered species. However, there are examples [5] of intracluster ion–molecule

reactions taking place that modify the relative intensities of the methanol ion fragments compared with those for an unclustered methanol molecule; for example, when methanol is incorporated in inert clusters, such as Ar or CO_2 .

Scoles and co-workers [6] have shown that it is possible for species to be incorporated into a host cluster in two ways. It can either occupy a site within the bulk of the cluster (matrix-like or solvated behaviour) or it can be located on the surface of the cluster. The former case generally results when a premixture is co-expanded with an inert gas through a supersonic molecular beam source. The second case can be achieved using the pick-up method [7] in which molecules are deposited onto the surface of a cluster after the supersonic expansion. Huisken and co-workers [8,9] have recently used the pick-up method to study methanol molecules adsorbed onto the surface of large argon clusters using a combination of mass spectroscopy and infrared molecular beam depletion spectroscopy. They find that, in addi-

tion to being able to place methanol monomers onto the surface of the argon cluster, it is possible, at high methanol concentrations, to create dimers, trimers and tetramers of methanol on the surface.

In this Letter, we report a mass spectrometric examination of methanol molecules deposited on large water clusters, $(\text{H}_2\text{O})_n$ ($50 < n < 700$), using the pick-up technique. In this case, we are able to compare the effect of methanol–water hydrogen bonding on the behaviour of the surface adsorbed methanol–water cluster compared with methanol adsorbed on inert argon clusters and to discuss the processes that occur upon electron impact ionisation of the cluster.

2. Experimental

Water clusters were produced by the supersonic expansion of pure water vapour from a temperature controlled reservoir (< 420 K) through a 0.3 mm conical nozzle giving stagnation pressures, P_0 , up to 2 bar. The temperature of the nozzle was maintained a few degrees hotter than the reservoir and lead tubes. The source chamber was pumped by an unbaffled oil diffusion pump ($2800 \text{ dm}^3 \text{ s}^{-1}$) and a high efficiency cryo-panel ($\approx 0.1 \text{ m}^2$) cooled by liquid nitrogen. The central part of the beam was sampled by a 1.0 mm diameter skimmer positioned 23 mm from the nozzle. After passing through two further stages of differential pumping, the beam entered a

detection chamber where it was monitored by a quadrupole mass spectrometer (VSW Mass Analyst, 0–300 u, 1 mA emission). The beam was modulated by a rotating chopper (8 ms period) before entering the quadrupole detection chamber and the signal from the mass spectrometer processed by a lock-in amplifier (Brookdeal 411/422/450) and then digitised for storage and processing on a PC. The electron energy of the ioniser could be varied to allow the appearance potential for particular ions to be measured. The electron energy scale was calibrated by measuring the appearance potentials for argon and water monomer ions.

In the source chamber, the water cluster beam was crossed by an effusive spray of methanol issuing from a stainless steel tube (0.16 mm inner diameter) located 15 mm downstream of the nozzle and 4 mm above the beam axis. This pick-up source was operated with a methanol pressure up to 7 mbar. Under these conditions, no dimers or higher clusters of methanol are formed in the pick-up source. In the absence of the water cluster beam, there was no detectable contribution from methanol due to effusion from the pick-up source alone, placing a limit on the ratio of effusive to ‘picked-up’ methanol of $< 0.5\%$.

In previous experiments [10], we have characterised the properties of the water cluster beam. The velocity of the beam is $\approx 1000 \text{ m s}^{-1}$. For this velocity, the transit time of a cluster molecule from the nozzle to the detector is ≈ 0.5 ms. The variation

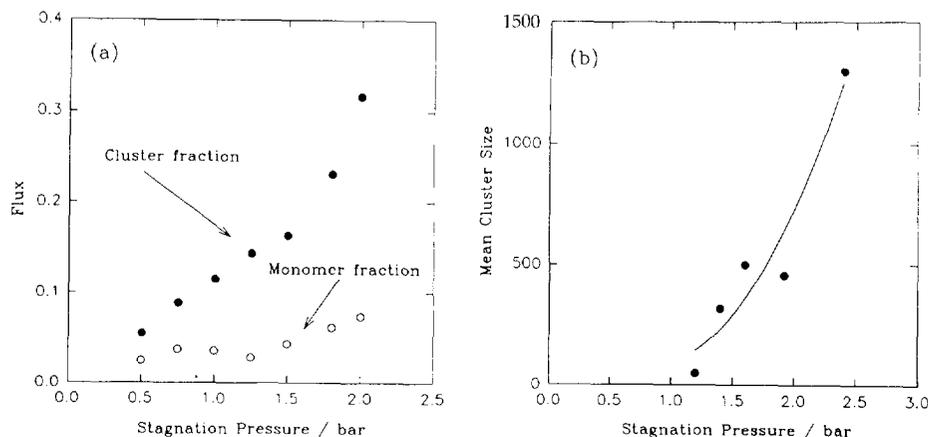


Fig. 1. The variation of the flux of water monomers and clusters (a) and the mean cluster size (b) with source stagnation pressure.

of the beam flux with stagnation pressure is shown in Fig. 1a and shows how the cluster fraction of the beam rises rapidly with stagnation pressure whilst the monomer fraction remains roughly constant. We have determined the variation of the mean cluster size, \bar{n} , with the source stagnation pressure using a pulsed electron beam time of flight method. Fig. 1b shows how the mean cluster size varies with stagnation pressure. For a stagnation pressure of 2.4 bar, the beam has a cluster size distribution with $\bar{n} \approx 1300$ and a full width at half maximum of ≈ 1000 monomer units. Electron diffraction studies [11] show that clusters of a few hundred water molecules have an amorphous crystalline structure whilst clusters composed of several thousand water molecules exhibit a diamond cubic form. Clusters formed from pure water expansions are also found to reach a limiting internal temperature of 180 K [11].

We have studied the fragmentation pattern of the mass spectrum produced by electron impact ionisation of the mixed methanol–water cluster beam and have investigated the intensity dependence of the various mass peaks as a function of both the water stagnation pressure and the methanol pick-up source

pressure. In addition, we have also measured the appearance potentials for some of the methanol-containing ions.

3. Results

A typical mass spectrum in the mass range $m < 100$ u for the methanol ‘picked-up’ by the water cluster beam is shown in Fig. 2. The major methanol-containing mass peaks that were observed in the mass spectrum are detailed in Table 1. These are in addition to the peaks corresponding to bare water cluster ions. The peaks with $m \leq 32$ u correspond to ionised methanol molecules. The peaks around $m = 50$ u can be associated with binary clusters ions containing one water and one methanol molecule and at $m = 83$ u, we find evidence for a cluster ion containing two methanol and one water molecule. Within the limits of our detection sensitivity, we do not find any other mixed cluster ions with different combinations of water and methanol molecules in the mass range 0–300 u; the maximum number of methanol monomers than we see in an ion

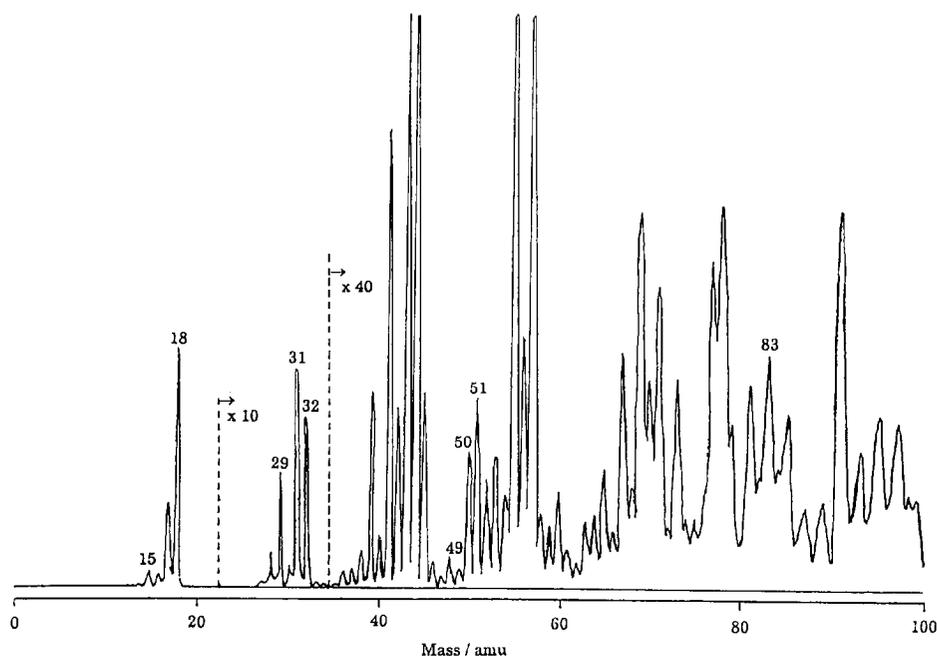


Fig. 2. A typical mass spectrum for the low mass peaks (0–100 u) resulting from electron impact ionisation of methanol adsorbed onto large water clusters recorded using an unmodulated system.

Table 1

Major methanol-containing ions detected from 70 eV electron impact ionisation of a methanol–water cluster beam. Typical conditions: water stagnation pressure = 2 bar, methanol pick-up source pressure = 5 Torr

Mass (u)	Ion
15	CH_3^+
29	CHO^+
30	CH_2O^+
31	CH_2OH^+
32	CH_3OH^+
49	$(\text{CH}_3)(\text{H}_2\text{O})\text{H}^+$
50	$(\text{CH}_2\text{OH})(\text{H}_2\text{O})\text{H}^+$
51	$(\text{CH}_3\text{OH})(\text{H}_2\text{O})\text{H}^+$
83	$(\text{CH}_3\text{OH})_2(\text{H}_2\text{O})^+$

is two. The peaks at $m = 50$ and 83 u are of comparable intensity and are about 2%–3% of the intensity of the peaks at $m = 31$ u. In their study of methanol adsorbed on argon clusters, Huisken and Stemmler [9] found evidence for a very intense peak at $m = 33$ u ($(\text{CH}_3\text{OH})\text{H}^+$), together with associated but less intense peaks at $m = 63$ and 64 u, which were attributed to the ionisation of methanol dimers adsorbed on the surface of the cluster. This assignment was confirmed by infrared molecular beam depletion spectroscopy based on studies [12] of pure methanol clusters. We do not find any evidence for significant concentrations of methanol dimers as the peak at $m = 33$ u is less than 2% of the intensity of the $m = 31$ peak and we do not detect any peaks at $m = 63$ and 64 u.

The variation of the intensity of various mass peaks with the water source stagnation pressure, P_0 , whilst the methanol pick-up source pressure was kept constant at 5 mbar is shown in Fig. 3. The peaks all rise with increasing stagnation pressure up to ≈ 2 bar from a threshold at 0.8–1.0 bar. Below this pressure, the clusters are too small to accept a methanol molecule without being deflected off the beam axis either by collision with the methanol or by evaporation of water molecules following the adsorption of a methanol molecule. Fig. 4 shows the variation in the intensity of the CH_3O^+ ion peak with the methanol pick-up source pressure for three different water stagnation pressures (corresponding to water clusters of different sizes). The data have been corrected for variations in the water cluster beam flux.

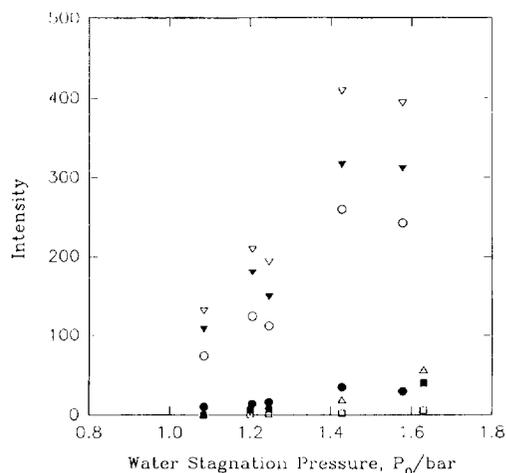


Fig. 3. The variation of the intensity of various mass peaks with the water stagnation pressure, P_0 , for a methanol pick-up source pressure of 5 mbar. (○) CHO^+ ; (●) CH_2O^+ ; (▽) CH_3O^+ ; (▼) CH_3OH^+ ; (□) $(\text{CH}_3\text{OH})(\text{OH})^+$; (■) $(\text{CH}_3\text{OH})(\text{H}_2\text{O})^+$; (△) $(\text{CH}_3\text{OH})_2(\text{H}_2\text{O})\text{H}^+$.

The signal is seen to increase with pick-up pressure up to ≈ 7 mbar and shows no dependence on cluster size. There is essentially no change in the intensity

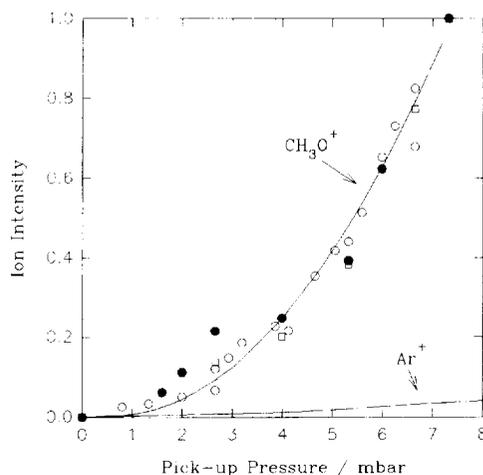


Fig. 4. The variation of the intensity of the CH_3O^+ ion peak with methanol pick-up source pressure for three water stagnation pressures, corresponding to different mean cluster sizes: (□) 50 water monomers; (○) 300 water monomers; (●) 450 water monomers. The three curves have been normalised to one another. This is compared with the Ar^+ signal resulting from the variation of argon pick-up source pressure. The signals have been corrected for the relative ionisation efficiencies of argon and methanol.

of the mass peaks corresponding to water cluster ions with methanol pick-up pressure.

An additional experiment was performed to attach argon atoms to water clusters in order to verify that the observed methanol signals result from methanol molecules that are attached to the water clusters rather than from methanol molecules that are entrained in a stream of water clusters. In this latter case, the signals from both systems (methanol or argon) would be expected to have a similar dependence on pick-up source pressure when appropriate corrections for the relative ionisation efficiencies are applied. As can be seen from Fig. 4, this is not the case and we conclude that our ion signals result from the attachment of the methanol or argon to the water clusters and that the difference in intensities reflects the different binding energies of methanol and argon to water (23 versus 2 kJ mol⁻¹) and the consequent effect that this has upon the adsorption efficiency.

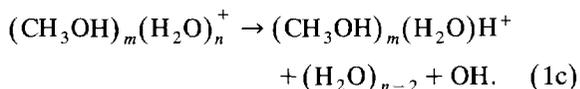
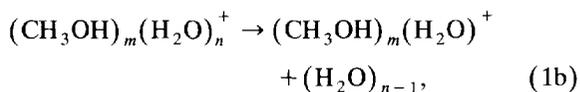
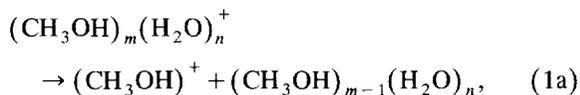
The measured appearance potentials for the CH₃O⁺ and CH₃OH⁺ peaks were found to be 11.0 and 11.5 eV, respectively, compared with the corresponding values [13] for unclustered methanol of 10.8 and 11.7 eV.

4. Discussion

Our results indicate that it is relatively easy for a few methanol molecules to be adsorbed onto the surface of a large water cluster. The pick-up method generally deposits only a small number of species onto the surface of the cluster. Huisken and Stemmler [9] found evidence for up to four methanol molecules upon the surface of their argon clusters. The energy released in the adsorption process is accommodated by the evaporation of a few water molecules and we are sensitive only to those clusters which remain on the beam axis and are sufficiently long-lived to reach the detector ($\approx 500 \mu\text{s}$). We only detect the low-mass fragment ions ($m < 300$ u) resulting from the ionisation of the methanol–water clusters and have no information about any cluster ions of large mass that are formed. In this range, we find ions corresponding to unclustered and unprotonated methanol and a limited number of heterocluster ions containing no more than one water and two methanol molecules, indicating that our clusters have

adsorbed only a few methanol molecules. Following ionisation by electron impact, fragmentation, ion–molecule reactions and molecular rearrangement can take place within the ionised cluster leading to a product ion distribution that reflects the stability of the ions as much as it does the composition of the neutral cluster. Fragmentation will favour the channels leading to stable ions which are preferentially formed by the decomposition of the larger ions and which are then resistant to further decay.

The major processes producing low-mass ions following ionisation of our methanol–water clusters would appear to involve the evaporation of water molecules from the initially formed cluster ion to form ions containing at least one methanol molecule (m is a small number)



It is not possible to say whether the neutral products in (1) remain as large clusters or fragment further and we have no information about the production of any large cluster ions. We do not see any enhancement of the low-mass water cluster ions when methanol is attached to the cluster indicating that, in this mass range, the charge prefers to remain on the methanol. This is in agreement with the results of Meot-Ner [14] for mixed water–methanol cluster ions which show that neat methanol cluster ions are more stable than pure water cluster ions and that the replacement of a water molecule by a methanol is always exoergic. Because of the higher proton affinity of methanol, the proton prefers to be solvated by methanol rather than by water. Shi et al. [15] have shown that, for large water–methanol clusters, the dominant fragmentation pathway upon ionisation involves loss of water molecules rather than methanol, in accord with our finding that the dominant heterocluster ions only contain one water molecule. Ehbrecht et al. [8] also find evidence for ionic complexes containing one solvent Ar atom (e.g. Ar ·

Table 2

Relative product ion intensities from methanol ions from the ionisation of water /methanol clusters compared with the electron impact ionisation of pure methanol vapour

Ion	This work ^a	EI ^b
CH ₃ OH ⁺	80	75
CH ₂ OH ⁺	100	100
CH ₂ O ⁺	8	11
CHO ⁺	59	67

^a Methanol 'pick-up' on a large water cluster ($N > 100$)

^b Electron impact ionisation of monomer at 70 eV using the VSW quadrupole mass spectrometer and a methanol pressure of 1.0×10^{-5} mbar.

CH₃⁺, Ar · CH₂OH⁺) from the ionisation of methanol–argon clusters formed by the pick-up method. These would correspond to our peaks at $m = 49, 50, 51$ and 83 which contain a single water molecule.

Stace [5] has noted that the fragment ion cracking pattern observed upon the ionisation of a binary cluster is often very similar to that observed for a free molecule. That is certainly the case for the mass peaks at $m = 29–31$ u resulting from ionisation of our methanol–water cluster compared with the relative intensity pattern for pure methanol vapour ionised by the same quadrupole mass spectrometer, as listed in Table 2. This comparison would indicate that a single methanol adsorbed on a large water cluster behaves very much as a free methanol molecule, in contrast to the results for expansions of premixtures of methanol in Ar and CO₂, where the methanol fragmentation pattern is considerably modified. It would appear that the positive charge resides on the methanol molecule which is detached from the rest of the cluster upon ionisation. This might also present an explanation for the absence of protonated methanol ions, CH₃OH · H⁺, in our spectra. These are commonly observed in ionised water–methanol systems formed by the exothermic reaction

$$\text{CH}_3\text{OH}^+ + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{OH} \cdot \text{H}^+ + \text{OH}. \quad (2)$$

We can only speculate that there is essentially no interaction between the adsorbed methanol molecule and the water cluster and that, upon ionisation, the methanol is rapidly evaporated as an isolated ion or as a molecule which is then subject to secondary ionisation.

Our observation that the mixed methanol–water ions contain at most two methanol molecules is in contrast to the results for methanol–water clusters that are produced by co-expanding a mixture of methanol, water and an inert gas. The mass spectra of such clusters show [1,16] intense sequences of protonated methanol and heterocluster ions ((CH₃OH)_{*m*}H⁺ and (CH₃OH)_{*m*}(H₂O)_{*n*}H⁺) with large values of n and m unless the co-mixture is very dilute in methanol [4]. However, Ehbrecht et al. [8] have shown that there is enhanced production of unprotonated methanol ions upon ionisation of methanol–argon clusters formed by the 'pick-up' method. Because the ionisation potential of water is greater than that for methanol (12.6 versus 10.8 eV), it is likely that the positive charge will ultimately reside on the methanol. However, the mechanism of the methanol–water cluster ionisation is not clear. Three basic possibilities have been recognised: (a) direct ionisation of the methanol by the electron impact; (b) ionisation of the water cluster and transfer of the charge to the methanol; (c) intracuster Penning ionisation in which an excited state of water is created and the energy is transferred to the methanol causing ionisation. Ionisation of the host followed by migration of the positive hole to the solute has been postulated [17] for the ionisation of SF₆ in large helium clusters. Intracuster Penning ionisation is found to be responsible for the ionisation of methanol embedded in argon clusters [18]. Our measurement of the appearance potential for the ion peaks from our methanol–water cluster beam would seem to indicate that the methanol part of the cluster is directly ionised by the electron impact, in accord with our earlier observation that the surface adsorbed methanol behaves much like a free molecule little perturbed by its association with the water cluster.

However, comparison of measured appearance potentials for cluster ions with the gas-phase ionisation potentials may lead to misleading conclusions. For example, the ionisation potential of water clusters decreases from 12.6 eV for an isolated molecule to ≈ 11 eV for a cluster of four water molecules [19] and may have a very different value for a cluster of several hundred water molecules. If the methanol molecule is solvated rather than being adsorbed onto the surface, we might expect a modification of its

ionisation potential upon solvation. It is possible that direct ionisation of water as well as methanol can take place upon electron impact. The excess energy in these two ionisation events may be very different giving rise to different fragmentation pathways. In our experiment, we may only be sensitive to one such process and it would be interesting to investigate the formation of large cluster ions.

A significant difference between our results for the adsorption of methanol on water clusters and those of Huisken and Stemmler [9] for the adsorption of methanol on argon clusters is that we find no evidence in our mass spectrum for the presence of methanol dimers (or higher clusters of methanol) formed when two or more methanol molecules are separately adsorbed onto the cluster. Huisken and Stemmler suggest that, on the argon cluster, the two methanol molecules interact through their large dipole moments to form a dimer adsorbed on the cluster surface. Molecular dynamics calculations [20] for two methanol molecules on a water cluster of 63 molecules at 180 K show that whilst the molecules are fairly mobile and migrate on the surface, their motions are never correlated i.e. no dimer is formed. Physically, we can rationalise this observation by noting that the water–water hydrogen bond is stronger than the methanol–methanol hydrogen bond. The methanol–water hydrogen bonding will be intermediate in strength, implying that the methanol would prefer to bond to the surface water molecules rather than to another methanol. For methanol molecules on argon clusters, the situation will be reversed as methanol–methanol bonding will be stronger than methanol–argon.

Finally, the relatively free motion of methanol on the water surface observed in the molecular dynamics calculations may explain our observation that the mass spectrum shows peaks with relative intensities similar to those measured for free methanol molecules. The calculations show that the methanol molecules can at times be located at quite large distances (4–8 Å) from the surface water molecules. Knochenmuss et al. [21] in their study of 1-naphthol–water clusters have commented upon the fact that water clusters, $(\text{H}_2\text{O})_n$, with $n < 800$ are highly fluxional in their behaviour despite their low internal temperatures. It is possible for both solid and liquid phases to co-exist in a cluster and Berry [22] has

recently discussed clusters having a liquid-like surface layer and a solid-like core. Such behaviour would provide a possible description for our methanol–water system and would distinguish between the behaviour of methanol–water clusters formed by co-expansion of methanol and water where a relatively large number of methanol molecules are distributed in the bulk of the cluster which is often significantly cooled and those formed by the pick-up technique where only a few methanol molecules are deposited on the surface of a large water cluster. We are presently extending our study to include the adsorption of other organic molecules and molecules of atmospheric importance onto water clusters.

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