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Adsorption of Organic Molecules on Large Water Clusters

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The sticking efficiencies for a range of organic molecules (methanol, propan-2-ol, acetone, acetaldehyde, formic acid, benzene, trimethylamine, and ethene) onto large water clusters, containing several hundred water molecules, have been determined using a supersonic molecular beam expansion to generate the water clusters and the pickup technique to deposit the organic molecule onto the cluster. It is believed that the organic molecule remains adsorbed onto the surface of the cluster and is not incorporated into the bulk of the cluster. The relative sticking coefficients are found to correlate with the magnitudes of the interaction energy for the organic molecule and water. It is suggested that the higher sticking efficiencies (e.g., for formic acid and acetaldehyde) may result from the molecules forming more than one hydrogen bond to the water cluster.

Introduction

The takeup of gases into liquid and solid aerosols is of fundamental importance in a wide range of atmospheric processes including tropospheric ozone formation, the destruction of stratospheric ozone, and the formation of cloud condensation nuclei. In this paper, we report results for the accommodation of a range of organic molecules on large water clusters generated by a supersonic molecular beam expansion. The organic species is deposited on the cluster after the expansion is complete using the pickup technique. The study of mixed clusters, in which one species is in excess of the other, can provide a useful method for studying the processes by which solute and solvent species interact and for determining the criteria by which solvation takes place. In addition to the pickup technique, mixed clusters can also be prepared by coexpansion of a dilute mixture of the solute and solvent which generally gives incorporation of the solute into the bulk of the solvent cluster. However, in the pickup technique, the solute molecule is initially deposited onto the surface of the cluster, and a variety of conditions will determine whether it is then incorporated into the bulk of the cluster or remains on the surface. This paper expands on some results for the attachment of methanol onto large water clusters reported previously.[1] Ionized water clusters containing different organic species have been studied by several groups.[2−5] The uptake of a wide range of organic species by water droplets has been studied by Davidovits and co-workers[6,7] and may provide some insight into the present study.

Experimental Section

The experimental procedure employed in these experiments was identical with that used in the previous study of the sticking of methanol onto large water clusters.[1] A schematic view of the apparatus is given in Figure 1. Water clusters were produced by the supersonic expansion of pure water vapor 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 dm^3 s^{-1}) and a high-efficiency cryopanel (surface area ~ 0.1 m^2) cooled by liquid nitrogen. The central part of the beam was sampled by a 1.0 mm diameter skimmer positioned 23 mm downstream 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 with electron impact ionization (VSW Mass Analyst, 0−300u, 70 eV electron energy, 1 mA emission). The form of the mass spectrum was found to be invariant with variation of the electron energy down to <10 eV, although there was an overall lowering of the total intensity of the ion signal. To improve the overall signal-to-noise ratio, the beam was modulated either by a rotating chopper (8 ms period) in the final differential pumping chamber before entering the quadrupole detection chamber or by a tuning fork chopper (3.4 ms period) located in the buffer chamber immediately after the source chamber. In both cases, the signal from the mass spectrometer was processed by a lock-in amplifier (Brookdeal 411 / 422 / 450) and then digitized for storage and processing on a PC.

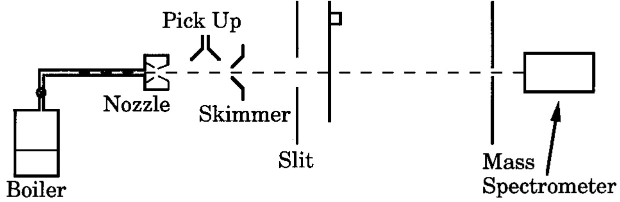

Figure 1. Schematic view of the apparatus employed in these experiments. Note that the rotating chopper was located as shown, but the tuning-fork chopper was placed between the skimmer and the slit.

In the source chamber, the water cluster beam was crossed by an effusive spray of the organic molecule issuing from a stainless steel tube (0.16 mm i.d.) located 15 mm downstream of the nozzle and 4 mm above the beam axis. This pickup source was operated with a backing pressure up to 8 mbar. Under these conditions, no dimers or higher clusters of the organic molecule are formed in the pickup source. In the absence of the water cluster beam, there was no detectable contribution from the organic molecule due to effusion from the pickup source alone, placing a limit on the ratio of any effusive to “picked up” signal of < 0.5%.

In previous experiments,[8] we have characterized the properties of the water cluster beam. The velocity of the beam is ~1000 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 of

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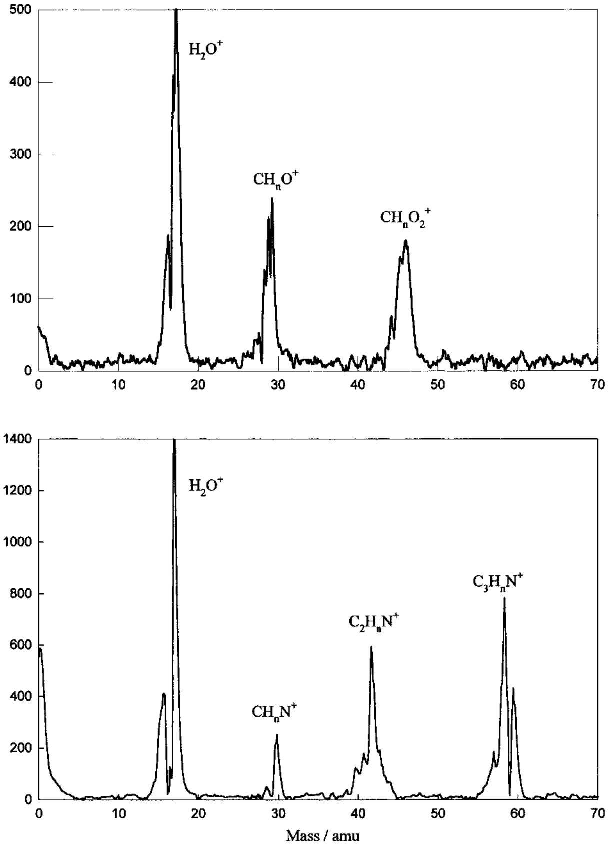

Figure 2. Mass spectra for the low mass peaks (0−70u) resulting from electron impact ionization of formic acid (upper panel) and trimethylamine (lower panel) adsorbed onto a water cluster containing approximately 200 water molecules ($P_0 \sim 1.2$ bar). The pickup source pressures were 7.8 and 2.7 mbar for formic acid and trimethylamine, respectively.

cluster size with water stagnation pressure has also been determined using a pulsed ionization time-of-flight technique.[8] For a stagnation pressure of 1.6 bar, the cluster beam has a bell-shaped size distribution with $\bar{m} \sim 625$ and a full width at half-maximum of ~600 monomer units typical of clusters formed by cluster−cluster coalescence and stabilized by evaporative cooling.[9] Electron diffraction studies[10] show that clusters of a few hundred water molecules have an amorphous structure, while clusters composed of several thousand water molecules exhibit a diamond cubic form. Clusters formed from pure water expansions are also found by the electron diffraction studies to reach a limiting internal temperature of 180 K.[10]

The sticking of the following organic molecules onto the water clusters was investigated: methanol, propan-2-ol, acetone, acetaldehyde, formic acid, benzene, trimethylamine, and ethene. With the exception of acetaldehyde which was purified by distillation, the liquid samples were used as obtained from the supplier (BDH), stored in glass ampules, and degassed by repeated freeze−pump−thaw cycles. Ethene (Argo International) was introduced into the gas line from a lecture bottle via a regulator and needle valve.

Results

The efficiency of the pickup process for the various gases was determined by monitoring, with the quadrupole mass spectrometer, a major ion peak corresponding to the organic molecule as a function of pickup source pressure for a given water stagnation pressure. Typical mass spectra for water clusters containing formic acid and trimethylamine are given in Figure 2, and the results of the pickup experiment are shown in Figure 3 for a water stagnation pressure of ~1.2 bar, corresponding to a cluster size of $\bar{n} \sim 200$ water molecules. The data have been corrected for any variation in the flux of the water cluster beam determined by monitoring the water cluster ion peaks and for the relative ionization efficiencies of the different organic molecules. It can be seen that the curves for methanol, propan-2-ol, formic acid, acetone and ethene are roughly similar, while the relative intensity for acetaldehyde is greater at a given pressure and those for benzene and trimethylamine are lower. It was shown previously[1] for methanol, that the form of the pickup intensity versus pressure curve was independent of water cluster size in the range $\bar{n} \sim 50-450$. This behavior was also confirmed for benzene and trimethylamine.

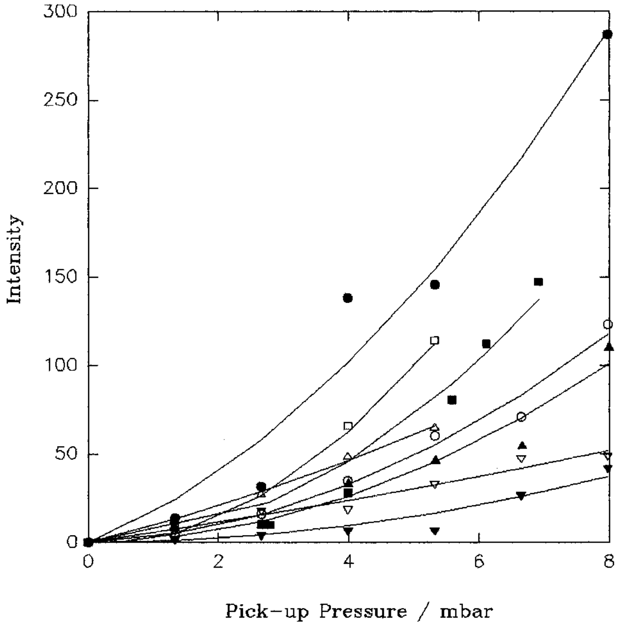

Figure 3. Variation of the relative intensity of the adsorbed molecules versus pickup source pressure for a water stagnation pressure of ~1.2 bar ($\bar{n} \sim 200$). (○) methanol; (■) propan-2-ol; (●) acetaldehyde; (□) formic acid; (▼) benzene; (▲) ethene; (▽) trimethylamine; (△) acetone.

The pressure dependence of the pickup intensity, *I*, can be fitted to a quadratic in the pickup pressure, *p*:

$$I = ap + bp^2 \quad (1)$$

As shown by Goyal et al.[11] in their study of SF_6 on helium clusters using the pickup method, the probability of a single molecule being picked up by the cluster will depend linearly on the pressure in the pickup region. To produce a cluster that has picked up two molecules requires a further collision of a cluster that already contains one molecule with the pickup gas; the probability of picking up further molecules is independent of how many molecules have been already picked up. The production of clusters containing two picked-up species will then depend quadratically upon the pickup source pressure. The ratio of the coefficients *a* and *b* in (1) will give the relative proportion of clusters having picked up one and two molecules, respectively. This defines the mean number of molecules attached to the water clusters, $\bar{n}$. A list of these numbers is given in Table 1. At any given pressure, the curves in Figure 3 give the relative sticking efficiencies for the various gases, using the coefficients, *a* and *b*, from eq 1. These are evaluated at 5 mbar and listed in Table 1, relative to methanol taken as unity.

In our previous study of the adsorption of methanol onto water clusters,[1] we noted that the dominant organic ions formed upon

TABLE 1: Sticking Efficiencies for the Various Species onto a Cluster of $\bar{n} \sim 200$ Water Molecules Expressed Relative to the Efficiency for Methanol, Evaluated for a Pickup Pressure of 5 mbar[a]

molecule	relative sticking efficiency	mean no. of molecules picked up, $\bar{m}$
acetaldehyde	2.8	1.5
formic acid	2.1	2.0
propan-2-ol	1.4	2.0
acetone	1.2	1.3
methanol	1.0	1.8
ethene	0.8	1.9
trimethylamine	0.6	1.1
benzene	0.3	2.0

[a] The mean number of molecules of each species, $\bar{m}$, attached to the water cluster is also listed.

ionization of the cluster corresponded to a single methanol without any associated water molecules. This is in contrast to the results obtained when methanol–water clusters are produced by coexpansion of a premixture of methanol, water, and an inert gas where the mass spectrum shows[2,5] intense sequences of protonated heterocluster ions of the type $(CH_3OH)_m(H_2O)_nH^+$. We found that the cracking pattern of the methanol ions from ionization of the cluster is almost identical with that resulting from the ionization of an isolated gas-phase methanol molecule. A similar behavior is observed for all of the other organic species studied here. In all cases, the ionization potential of the organic species is lower than that for water, and it would appear that the positive charge resides upon the organic molecule which is rapidly detached from the cluster upon ionization without undergoing any ion–molecule reactions with the cluster. This behavior is characteristic of surface adsorbed species produced by the pickup method and contrasts to the ionization of methanol–water clusters formed by coexpansion where the methanol is embedded in the bulk of the cluster.

Discussion

In their pickup experiments with SF_6 and large argon clusters, Scoles and co-workers[12] found that there were two ways in which SF_6 could be incorporated into the cluster; either the SF_6 molecule was incorporated into the bulk of the cluster i.e., solvated or matrix-isolated in argon, or it was adsorbed onto the surface of the cluster. These two states could be distinguished by the infrared spectrum of the SF_6 chromophore. If the SF_6 was picked up during the early stages of the argon cluster expansion, it became solvated. However, if the pickup took place late in the expansion process, the argon clusters had adopted a rigid structure and the SF_6 was adsorbed onto the surface. This was commonly the case for large argon clusters. Huisken and Stemmler[13] have studied the deposition of methanol onto large argon clusters by the pickup technique using infrared molecular beam depletion spectroscopy. They find that the methanol infrared absorption spectra are little shifted from the gas phase and conclude that the methanol occupies a surface-adsorbed state rather than a matrix or solvated state. However, corresponding studies[14] for water deposited onto large argon clusters find that the infrared absorption bands for water are close to those found for water in argon matrixes indicating that the water is solvated by the argon atoms.

Del Mistro and Stace[15] have performed a molecular dynamics study of the pickup process by simulating the interaction between an argon cluster with 20 atoms, Ar_{20}, and an acetonitrile molecule. Two limiting cases were examined; in the first, the acetonitrile molecule was placed almost at rest upon the surface of the cluster and in the second, the cluster experienced a head-on collision with the acetonitrile molecule. In the first case, the acetonitrile molecule stayed upon the surface of the argon cluster for about 0.3 ns, and then local melting occurred and the molecule was "solvated" at the surface of the cluster but was never fully encapsulated within the cluster. In the second encounter, the acetonitrile molecule penetrated the cluster and was solvated in the bulk of the cluster within 40 ps of the collision; the cluster was stabilized by evaporative cooling involving the elimination of a single argon atom. They considered the extrapolation of their results to the behavior of larger clusters in a pickup experiment. For the head-on collision, the relative kinetic energy of the encounter does not increase significantly with the increasing mass of the cluster but quickly reaches a limiting value for clusters with more than a hundred monomers. This is a consequence of the fact that the cluster beam reaches a terminal velocity with increasing size as we noted for our water cluster beam.[8] In this case, the behavior will be determined by the increased ability of the large cluster to act as a heat sink accommodating the collisional energy without melting. In our case, for the organic molecules interacting with the large water cluster, the momentum might be insufficient to drive the molecule into the water cluster and local heating coupled with any hydrophobic interactions may result in the organic molecule floating to the surface.

Le Roy and co-workers have shown[16] that a critical consideration as to whether a molecule will be solvated or remain on the surface of a cluster is the relative strength of the solute–solvent interaction compared with the solvent–solvent interaction. If the solvent–solvent interaction is greater than that between the solvent and solute, solvation will not be energetically favorable. Even when solvation is energetically favorable, this has to balanced with a potential loss in entropy when the molecule leaves the surface and enters the bulk of the cluster and also the possibility that the energy gain may not be sufficient to cause the cluster to melt and accommodate the molecule by solvation. This latter behavior is seen in the ab initio calculations[17] on $Cl^-(H_2O)_{14}$ clusters where even though the $Cl^-\cdot H_2O$ interaction energy is greater than the H_2O-H_2O interaction energy by ~ 12 kJ mol^{-1}, there is no overall gain by disrupting the H_2O hydrogen-bonded network in order to solvate the Cl^- ion which instead adopts a position on the surface of the cluster. Such behavior is also observed in molecular dynamics simulations of $Cl^-(H_2O)_{14}$ clusters[18] and has been recently confirmed by infrared spectroscopy of small $Cl^-(H_2O)_n$ clusters.[19] Considerations about having sufficient energy to melt the cluster before solvation can take place while important in a pickup experiment are unimportant in experiments where mixed clusters are formed by coexpanding the solute and solvent species.

For the majority of the organic species studied in this work, the solute–solvent interaction energy is smaller than the solvent–solvent (H_2O-H_2O) interaction, and it is thus unlikely that the organic molecules will enter the bulk of the water cluster and become solvated for the reasons discussed above. Thus, we believe that the organic species are deposited onto the surface of the cluster by the pickup process and remain there. The molecule will be adsorbed to the surface of the water cluster primarily by relatively weak interactions resulting from hydrogen bonding. This will be facilitated by the nature of the surface for water clusters of this size and temperature which is shown by molecular dynamics simulations[20] to have considerable surface irregularities with an abundance of nonbonding or "dangling" OH groups. Recent work[21] for crystalline ice has shown that similar irregularity extends to several subsurface layers and that certain adsorbates (C_2H_2 and H_2S) which can act as both proton donors and acceptors, induce ordering of the

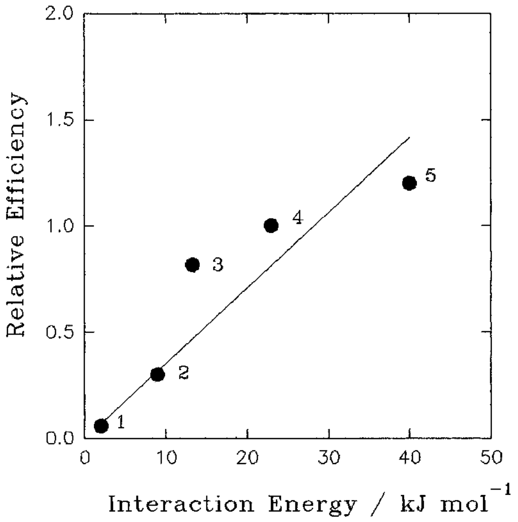

Figure 4. Correlation between the relative sticking coefficient for various molecules with large water clusters and the appropriate molecule−water interaction energies. 1, X ≡ Ar; 2, X ≡ benzene; 3, X ≡ ethene; 4, X ≡ methanol; 5, X ≡ acetone. The experimental data for Ar−H_2O comes from ref 1.

surface while weaker adsorbates (H_2, N_2, CO) do not. Studies of the adsorption of acetone onto ice films shows[22] that adsorption via hydrogen bonding is possible only on films with an amorphous surface structure having a high density of free surface OH groups. On a crystalline ice surface, there is only a physisorbed state of acetone. For relatively weakly bound species, it is common to assume that the surface is inert and that the important interaction is between the adsorbed molecule and the surface to a first approximation. Thus we might expect that there will be a direct correlation between the efficiency of adsorption and the interaction energy of the adsorbed molecule and a water molecule. Such a correlation is shown in Figure 4 between the measured relative sticking efficiency (from Table 1) and the interaction energy for the cases of argon, benzene, ethene, methanol, and acetone. The interaction energies are obtained from theoretical calculations of the appropriate pairs,[23−25] except for the case of benzene−water where a recent experimental determination[26] is used and for acetone−water where the value used is the desorption energy for acetone on an ice film.[22] It can be seen that there is a good correlation ranging from the very weak van der Waals interaction between Ar and H_2O, through the weak hydrogen bond between the OH group in water and the π electrons in benzene to the stronger hydrogen bonds between methanol and acetone and water. It is quite likely that the species with very large sticking coefficients relative to methanol (e.g., formic acid and acetaldehyde) are adsorbed to the water cluster via more than one hydrogen bond. Such behavior has been predicted[27] theoretically for formaldehyde with small water clusters, and it would be interesting to see if such structures persist for large clusters and are also observed in molecular dynamics simulations of such systems.

A final comment concerns the relationship between this present study and the takeup of organic molecules by water droplets studied by Davidovits and co-workers.[6,7] In the experiment, the uptake of a range of organic species in aqueous droplets is studied as a function of droplet temperature to obtain values for the enthalpies and entropies for the process. The uptake is determined by a combination of gas-phase diffusion, Henry's law saturation, and the mass accommodation coefficient, α, which is the probability that a molecule that strikes the surface will enter the bulk of the droplet. Poor agreement is obtained between the measured thermodynamic values and the corresponding quantities for solvation and the observed results are interpreted in terms of a model that invokes the formation of a critically sized cluster in the surface layer as a transition state before passing into the bulk. The critical size of this cluster with organic species depends not on the number of molecules in the cluster but on the number of potential hydrogen-bonding components. An obvious difference comes from the liquid nature of the droplet and the amorphous solid nature of the cluster which is closer to ice. However, there may be some similarities between the two processes due to localized melting in the cluster, the fluid nature of clusters of this type[28] and the possible coexistence between liquid and solid phases in a single cluster.[29]

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