

Multiphoton Ionization of Mixed Benzene-Water-Methanol Clusters. Competitive Microscopic Solvation

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Clusters of benzene with polar molecules are observed from a supersonic jet expansion of a ternary mixture of benzene, water and methanol seeded in Helium. It is found that complex formation with methanol is strongly enhanced when a single water molecule is preadsorbed.

I. Introduction

The benzene molecule is a prototype system to study van der Waals interaction in weakly bound molecular complexes. Benzene seeded in a supersonic jet expansion readily forms complexes with noble gases [1], with smaller molecules [2] and clusters with itself [3]. As is known from clusters like anthracene, the organic molecule can act as a solute in a solvent of noble gases, showing distinct structure and solvation shells [4]. For the interaction with molecules which have a strong dipole moment or which are forming hydrogen bonds the clusters are of additional interest as these systems can be used to study hydrophobic bond formation by the stabilization of organic molecules in a polar solvent, and complexes of benzene with water or alcohols were already studied on the basis of ab-initio calculations [5].

In all the previous studies the complexation was performed between benzene and a single species of solvent. We now present the results of mixed clusters of benzene with water and methanol which show that the complex formation of benzene with methanol is strongly enhanced by the presence of water, i.e. the adsorption of methanol is assisted when one water molecule is preadsorbed. Here the study of a ternary mixture provides unique answers not provided by binary mixtures.

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II. Experimental

The experimental setup is described in [3]. A mixture of 60% benzene, 20% water and 20% methanol was seeded in Helium at 2 atmospheres as a carrier gas and expanded through a pulsed nozzle into the vacuum. The supersonic jet was skimmed and then entered a second chamber, where the clusters are ionized with a single dye laser which was frequency doubled to 259.3 nm. The ions are detected in a time-of-flight (TOF) mass spectrometer and the mass spectrum is recorded.

III. Results

The ionization of the clusters was observed when the laser frequency was adjusted 53 cm^{-1} to the red of the bare benzene molecule 6_0^1 near the 6_0^1 transition of the benzene-water-complex [2]. Figure 1 shows the mass spectrum, which is dominated by the benzene-dimer signal. In addition, one observes three sequences which arise from clusters of benzene-water-(methanol)_n with *n* from 0 to 8, (benzene)₂-water-(methanol)₂ with *n* from 0 to 5 and a weak sequence of benzene-(methanol)_n with *n*=1 to 2.

The striking result from this spectrum is that the clustering with methanol is strongly enhanced when one water molecule is adsorbed. The adsorption of methanol itself can also be observed but is very much weaker. Furthermore, the adsorption of more than one water molecule is not observed.

IV. Discussion

The observed spectrum arises from the seeded beam expansion of a ternary homogeneous mixture with only a small concentration of water and methanol. At high concentrations, water and methanol, which are not ionized at this laser frequency, are more likely to form clusters with themselves; and, in the mass spectrum only the features of benzene clusters themselves remain at a much lower intensity. The seed ratio chosen here permits one to detect the mixed clusters. The primary addition of water can be explained as a strong interaction of the benzene quadrupole with a negative partial charge on the carbon atoms and the

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Mixed Benzene-Water-Methanol Clusters

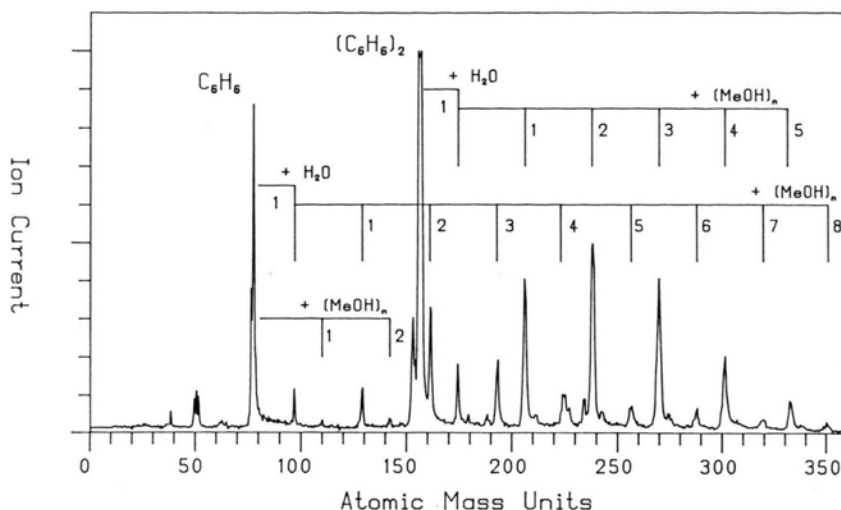


Fig. 1. Time-of-flight mass spectrum of benzene-water-methanol cluster: Excitation was performed at 259.3 nm and a TOF mass spectrum was recorded. Two sequences of clusters of methanol with the bare benzene molecule and the benzene dimer are observed after pre-adsorption of one water molecule. Adsorption of pure methanol was also observed but is found to be much weaker.

water dipole with a partial positive charge on the hydrogen atoms. The formation of hydrogen bonds in such a cluster is not the dominant part, as no higher clusters with more than one water molecule and benzene are observed.

The observation that the formation of clusters with methanol is enhanced by a single molecule of water is a new finding and is perhaps due to a strong polarization of the benzene by one water molecule, which in

addition to the larger van der Waals interaction of methanol helps to form these interesting mixed clusters. This is suggested to be an interesting method for the understanding of mixed solvents.

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Erratum

John C. Fetzer and Maximilian Zander, On the Use of Perhydrocoronene as a Matrix in the Luminescence Spectroscopy of Polycyclic Aromatic Hydrocarbons, *Z. Naturforsch.* **45a**, 814–816 (1990).

Recent experiments have shown that the observed sensitized coronene phosphorescence (reported in section 1.2 of the paper) is predominantly not due to intermolecular triplet-triplet but to singlet-singlet energy transfer between polycyclic aromatic hydrocarbon (PAH) guest molecules and coronene molecules following intersystem crossing from the first excited singlet state of coronene to its first excited triplet state. Energy transfer occurs probably by both dipole-dipole interaction between spatially separated PAH guest and coronene molecules and singlet exciton migration in PAH guest molecule microcrystals (aggregates) containing small amounts of coronene.