RUHR-UNIVERSITÄT BOCHUM

Aggregation and Dissociation of HCl in Methanol at sub-Kelvin temperatures in Superfluid Helium Clusters

Philipp Meyer
Microsolvatation & Microaggregation
Physical Chemistry 2 – Prof. Dr. Martina Havenith-Newen

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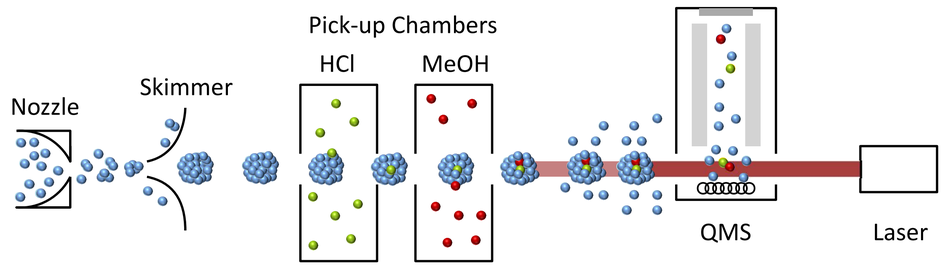
Introduction

The dissociation of acids in water is the foundation of many chemical and biological processes occurring in nature. One very common acid is hydrochloric acid, a solvated form of hydrogen chloride. Here, the proton and the chloride ion are separated by a solvent, most commonly water. This dissociation does not only occur in the laboratory or industrial reactors but also in living organisms, stratospheric clouds and interstellar space. The dissociation of hydrogen chloride in a non-bulk solvent environment has been an area of great interest over the past couple of years and has been studied using various methods and experimental setups. [1–4] Aim of this work was to lay the foundation in understanding the solvation process of HCl in methanol, the smallest alcohol and a common organic solvent. Like water, methanol possesses a strongly polarized OH bond which can form hydrogen bonds and exhibits similar physical properties. Because of the non-polar moiety which are only slightly polarized, dispersive interactions such as van der Waal's forces may also contribute to the packing arrangements of methanol clusters and could play a role in the dissociation process.

He-Cluster Setup

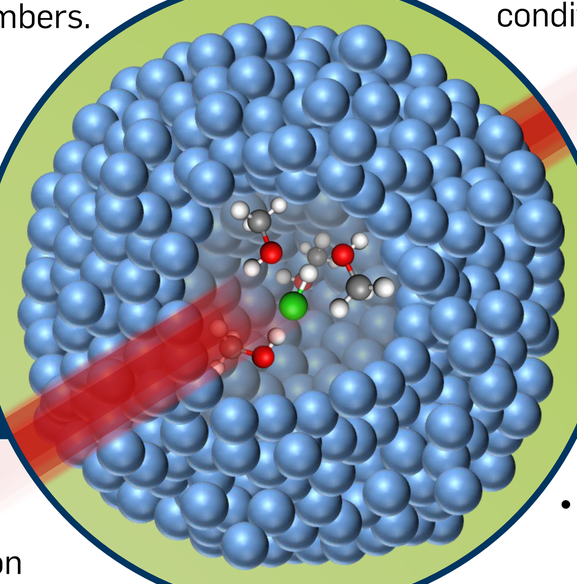


- Expansion of gaseous Helium through a precooled nozzle.
- Liquefication by evaporation to 0.37 K and formation of droplets.
- Selective pick up of HCl and Methanol in pick-up chambers.
- Interaction of guest molecule with Laser beam.
- Resonance leads to evaporation of Helium atoms.
- Smaller droplets are less likely to be ionized in QMS.
- Depletion therefore directly linked to frequency.

Motivation

- Dissociation as a fundamental chemical concept known for hundreds of years, yet not fully understood.
- "Smallest drop of Acid" with 4 molecules of water, major contributions by the groups of Prof. Havenith and Prof. Marx. [3]
- Remarkable discovery: Sequence of pick up has a huge impact. [4]
- Similar investigations possible for other solvents such as methanol?

➢ Helium clusters provide excellent control of the reaction conditions and allow for high resolution IR spectroscopy.
➢ Useful for stratospheric studies, as droplets provide comparable conditions.
➢ Further our understanding in solvation mechanisms.

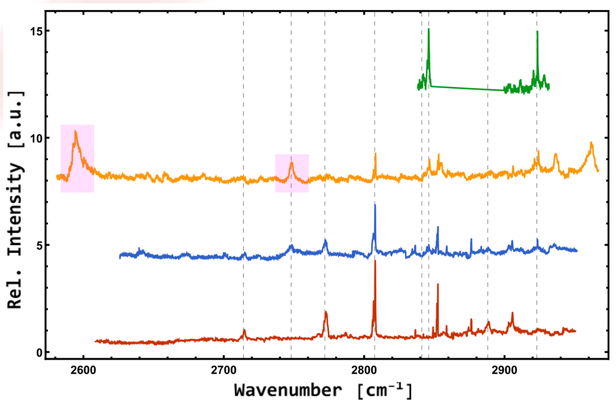


IR Spectroscopy

- Finely tunable lasers allow for a very high resolution.
- Mass spectrometer can be set to detect ion current on different mass channels resulting in varying signal intensities.

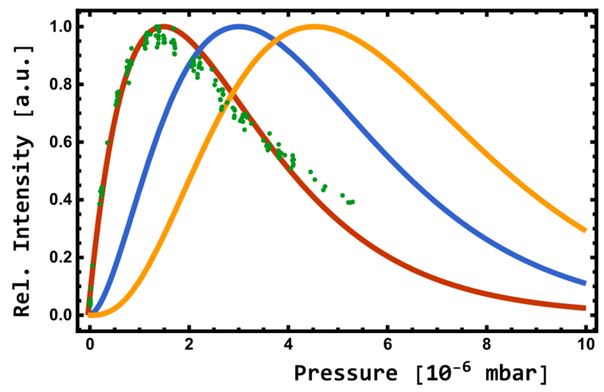
➢ Key Focus:
- Optimization of conditions.
- Confirmation of Setup.

➢ Measurements done for:
- MeOH at m/z =31
- HCl and MeOH at m/z = 31
- HCl and MeOH at m/z ≥ 10
- HCl at m/z ≥ 10



Pick Up Curves

- The amount of molecules in the droplet can be adjusted by varying the partial pressure in the pick-up chamber.
- Poisson distribution gives a good approximation for the pick-up.



➢ Signals can be assigned to number of molecules.

➢ Confirm repeatability of the setup.

➢ Example: 2905 cm^{-1}
- Monomer signal.
- Poisson fit for k= 1, 2, 3

Conclusion

Although no dissociation of hydrogen chloride in methanol could be observed, this work lays the foundation for further investigations into the dissociation behavior by confirming the methodology and experimental setup as in addition to the observation of new signals for an aggregated HCl-MeOH species. Possible follow-up experiments include the recording of pick up curves for the new signals as well as carrying out measurements with increased amounts of methanol to steer the system towards dissociation of HCl. It is also possible to use the gained understanding of the dissociation of HCl in water to try and observe solvation of other common acids such as sulfuric or nitric acid in future experiments. The unique environment of the superfluid helium droplets is a powerful tool to further our understanding of the reactivity of inorganic acids in water, alcohols and other polar organic solvents and provides extraordinary control over the experimental conditions.

References: [1] Vladimir E Bondybey and Martin K Beyer. "How many molecules make a solution?" In: International Reviews in Physical Chemistry 21.2 (2002), pp. 277–306. I [2] Melanie Letzner et al. "High resolution spectroscopy of HCl–water clusters: IR bands of undissociated and dissociated clusters revisited". In: The Journal of chemical physics 139.15 (2013), p. 154304. I [3] Anna Gutberlet et al. "Aggregation-induced dissociation of $HCl(H2O)_4$ below 1 K: The smallest droplet of acid". In: Science 324.5934 (2009), pp. 1545–1548. I [4] Devendra Mani et al. "Acid solvation versus dissociation at "stardust conditions": Reaction sequence matters". In: Science advances 5.6 (2019), eeav8179