Spectroscopy of solute-solvent complexes in helium nanodroplets

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Synopsis Infrared spectra of pure solvent clusters and solute-solvent complexes in helium nanodroplets are reported. Examples included pure methanol, mixed/methanol water clusters, and complexes formed between salts and solvents such as water. The latter pose considerable challenges in assigning the spectra, even for small complexes, but broadly fit with the idea that solvent molecules, such as H_2O and CH_3OH, form hydrogen bonds with the halide ion in alkali halide salts.

Alkali halides are archetypal salts. They readily dissolve in water to form fully ionic solutions when dilute. They also dissolve in other polar solvents, such as alcohols, but their solubility here is much less than in water.

We have used helium nanodroplets to explore the interactions between alkali halides and common solvents and how they develop as the number of solvent molecules is changed. Helium nanodroplets are suited to such microsolvation studies since they provide a convenient way to bring together the salt and the solvent in a controlled manner. Helium droplets also provide a means of recording spectra, through depletion spectroscopy, and in our case we have used infrared depletion spectroscopy.

Although relatively large $MX(S)_n$ complexes can be studied in this way, and might therefore be used to address the issue of solvent-separated ion-pair formation, our focus here is on small complexes and trying to understand the binding mechanism that exists between the solvent and the non-dissociated salt molecule. Several salts have been investigated and findings from a few specific cases, including NaCl [1,2] and CsI, will be presented.

For illustration Figure 1 shows an IR spectrum derived from a combination of CsI with methanol (MeOH) molecules. This spectrum spans both the CH (<3000 cm^{-1}) and OH (>3000 cm^{-1}) stretching regions and shows absorption features in both. Each spectrum was recorded in a specific mass channel (shown on the right above each spectrum) to provide a degree of discrimination between different sized complexes and therefore to help with the assignment of bands to specific complexes. The experimental work has been supported by a series of quantum chemical calculations which have sought to carefully identify all possible isomers of the complexes and then to predict their IR spectra.

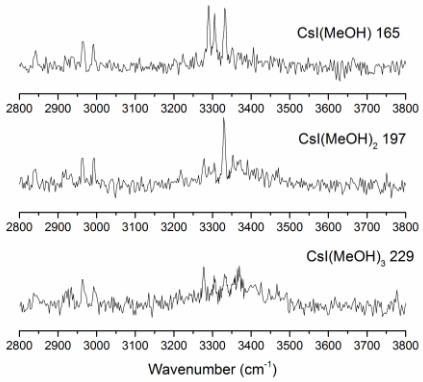

Figure 1. IR spectra of small $CsI(MeOH)_n$ complexes in helium nanodroplets.

The strong red shifts of the OH stretching bands relative to the free solvent molecules are indicative of the formation of ionic hydrogen bonds between the solvents and the salts, for both water and methanol. This has so far been found for all of the salts investigated. Specifically, hydrogen bonds form between OH groups in each solvent molecule and the anion in the salt molecule. However, even for some of the smallest complexes there are challenges in assigning the IR spectra and these will be discussed. These will be compared with IR data for pure and mixed solvent clusters, which have also been recorded in our laboratory [3].

References

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