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WHAT CAN WE LEARN FROM RAMAN SPECTROSCOPY AND MODEL CALCULATIONS ON ROOM TEMPERATURE IONIC LIQUIDS?

Rolf W. Berg*[a]

[a]Department of Chemistry, Technical University of Denmark, Kemitorvet, B-207, DK-2800 Lyngby, Denmark

*rwb@kemi.dtu.dk

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Abstract

Traditionally room temperature ionic liquids (RTIL's) also involve inorganic hygroscopic substances that need to be contained under protective atmospheres, e.g. in sealed ampoules. Experimental methods to study the chemistry inside closed ampoules are limited, and one popular technique has been and still is Raman scattering because the laser light easily passes through the glassy ampoule wall. The method is of course equally valuable for non-hygroscopic substances and mixtures and "green liquids".

Raman spectra - though characteristic for most compounds - do not give direct chemical evidence (species formulae, quantities, structures, etc.). The resulting spectra must be interpreted to let chemical information be deduced - sometimes from subtle comparisons between different systems and experiments with carefully selected standard compounds.

A rather new requisite in the research landscape is now the quantum mechanical calculation software [1]. This software allows everyone - on an ordinary PC after some trial and error - to calculate the most stable equilibrium geometries of guessed chemical structures and to depict their normal vibrations and the fundamental Raman and IR spectra.

These new calculations form the basis for a better understanding of quite complicated chemical systems such as liquids. Many groups of researchers have recently started to use such a methodology: They compute structures and Raman spectra of various ions (the RTIL's themselves and eventual solutes) and compare with the experimental spectra, hoping that this will lead to a better understanding of the behaviour of the liquid.

The number of possible cation-anion combinations is very high. A review of the present status cannot be given within the limits of this presentation, but some examples that reflect the typical situation will be given. After an introduction to the calculation methods used [1], some examples will be shown — among others new own results on aluminum-oxy-chloride ions (see the Figure), as well as our already published results [3] on 1-alkyl-3-methylimidazolium cations with halogenide or complex inorganic anions. It will be mentioned that conformational isomerism and hydrogen bonding are important in these RTIL systems.
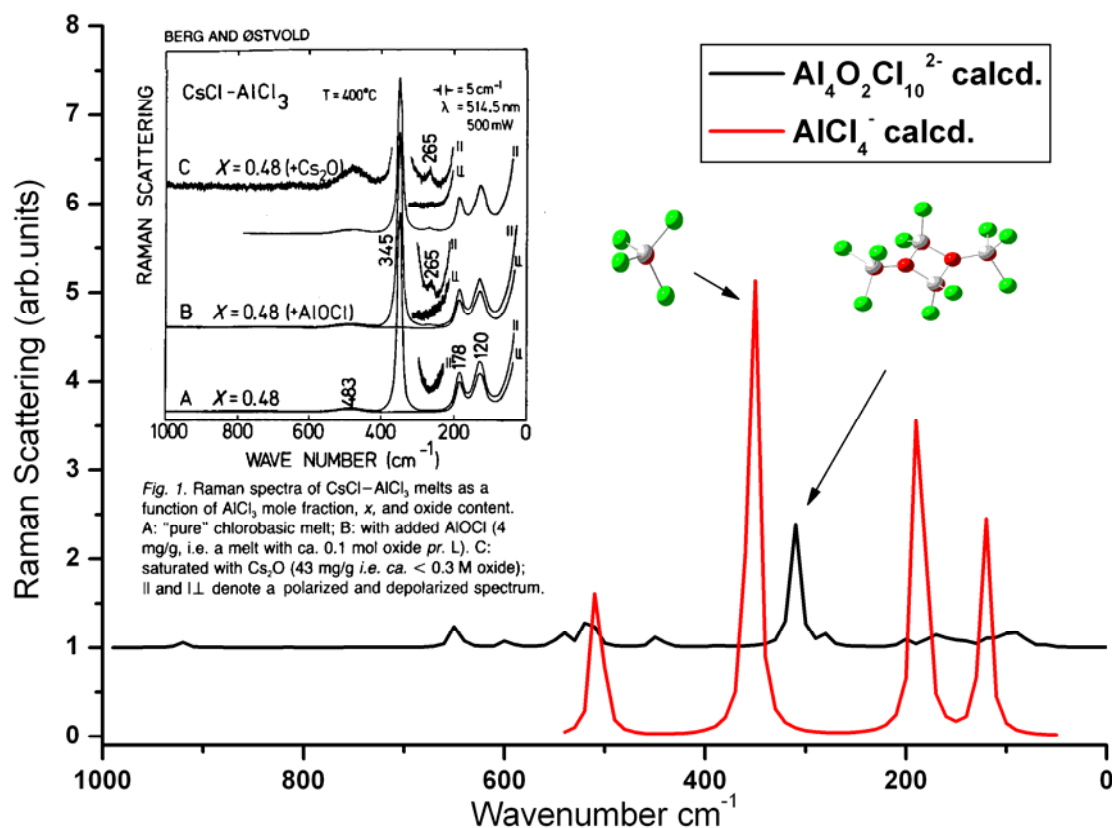
Figure. Example of experimental Raman spectra of CsCl-AlCl$_3$ melts with oxygen contaminations and new model calculated structures and spectra. The experimental data are from ref. [2].

Then some other interesting systems will be discussed: The spectra and *ab initio* calculation results on liquid methanesulfonic acid, CH$_3$SO$_2$OH, have shown [4] that the liquid must consist of dimer associated molecules. In an extension of the same kind of reasoning, finally we present preliminary results (spectra and calculations) aiming at an understanding of what goes on in a liquid methanol-sulfuric acid mixture. The results will be interpreted to show that a whole lot of associated molecules will exist in such a mixture.

Finally at the same time we hope to demonstrate the beauty and strength of present days animation of normal modes of vibrations in the molecules.

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