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Raman Analysis of ice-gas co-deposits generated from mass spectrometry calibrated vapor mixtures

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INTRODUCTION

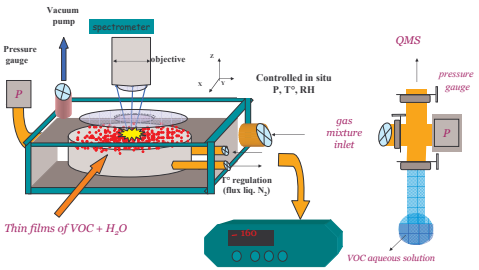
- Light volatile organic compounds (methanol, ethanol, formaldehyde) are intermediate products in the oxidation of atmospheric hydrocarbons. They are closely linked to the production of HOx, the main atmospheric oxidant. These trace gases interact with water and may affect the chemistry of the troposphere. Recent studies in polar regions showed that the concentration of several VOCs (HCHO, C_2H_4O etc) in the lower troposphere is higher than expected from model calculations. It is suggested that the source of these species is related to snowpack chemistry Hutterli et al., GRL, 1999, Dominé & Shepson, Science, 2002. Further, large missing source of formaldehyde have been reported in the upper troposphere. This has been tentatively explained by the heterogeneous oxidation of methanol on the ice surfaces Jaeglé et al.,JGR 2002.
- A characterization of the condensed phase of the ice-gas system is therefore necessary, more particularly of the equilibrium solubilities of gaseous species in ice. Indeed, the incorporation of dopants may induce changes in the ice structure that can lead to the ice amorphization, or to the formation of a hydrate crystal or a solid solution.

Previous work:

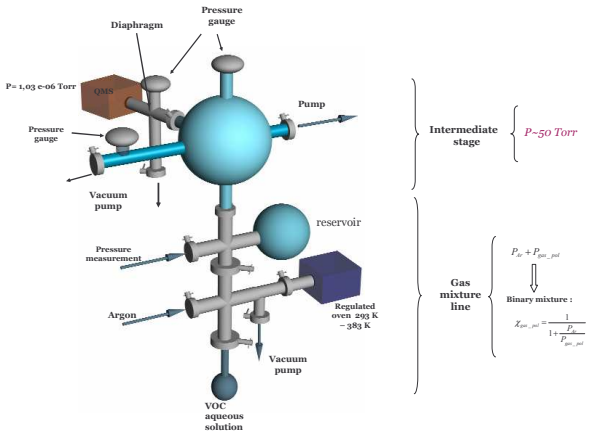
- Vapor deposited formaldehyde-ice mixtures investigated *in-situ* by micro-Raman spectroscopy *Chazallon et al., PCCP, 2007 (submitted)*
- Vapor deposited ethanol-H_2O ice mixtures investigated by micro-Raman scattering *Chazallon et al., VibSpec. 42, 206, 2006*
- Micro-Raman investigation of the formaldehyde-ice system, *Chazallon et al., J. Phys. Chem. B, **109**, 432, 2005*
- Raman characterization of the relative abundance of oligomers in the aqueous solutions, *Lebrun et al., J. Raman Spectrosc., **34**, 459, 2003*
- IR laser resonant desorption of formaldehyde-H_2O ices: hydrated cluster formation and velocity distribution *Mihesan et al. Surf. Sci., 566-568, 650, 2004, Ziskind et al. Appl. Phys. A, 79, 991, 2004*

RESULTS

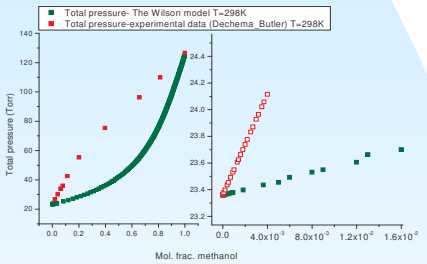
Raman experimental set-up



Mass spectrometry experimental set-up



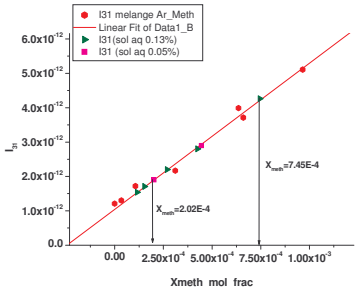
VLE equilibrium data of VOC aqueous solutions (H_2CO ,CH_4O)



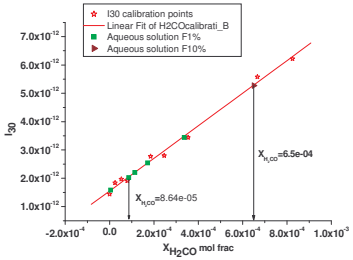
- Isothermal vapor-liquid equilibrium total pressure as a function of methanol water concentration.
- Aqueous solution of methanol are prepared and the gas phase collected above the solution at equilibrium is analyzed by mass spectrometry.

Using a calibration curve made with binary mixture of pure methanol and argon whit a calculated molar fraction we want to verify the concentration of methanol in the gas phase predicted by Wilson model

Methanol calibration curve



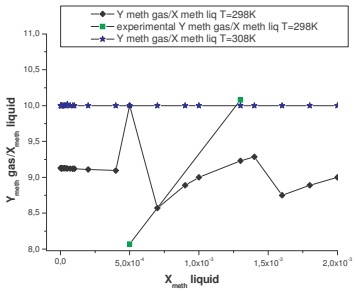
Formaldehyde calibration curve

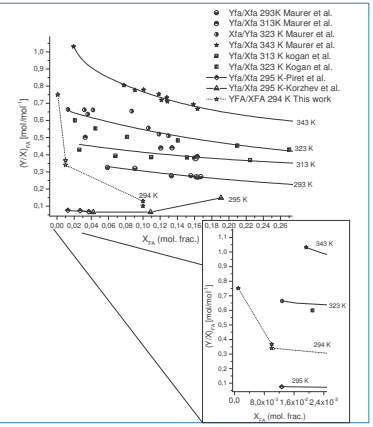


- With the partial pressure ratio, we can deduce the molar fraction Y_{VOC} gas in the binary gas mixture as analyzed by the mass spectrometer.
- The vapors collected above the solution are diluted until we are in the wanted molar concentration region. Using the calibration curve we find an experimental value for the molar fraction introduced in the mass spectrometer.
- By doing the backward mathematical calculation we find an experimental value for the methanol (formaldehyde) molar fraction in the gas phase above the aqueous solution.

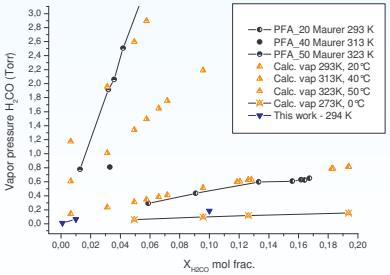
Partition coefficients

• Partition coefficients of Methanol/formaldehyde in the Methanol/formaldehyde-water system at different temperatures





Vapor liquid equilibrium data of H_2O-H_2CO aqueous solutions



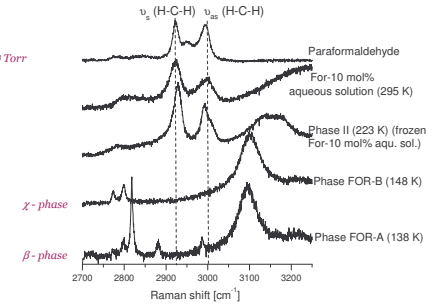
- Equilibrium vapor pressure of formaldehyde over formaldehyde aqueous solutions as a function of dissolved H_2CO concentration.
- A comparison with predicted values is shown, using

$$\log P_{H_2CO} = 9.942 - 0.953 (0.488)^{W/10} - 2905 / T$$

- Our data were determined by mass spectrometry / IR absorption

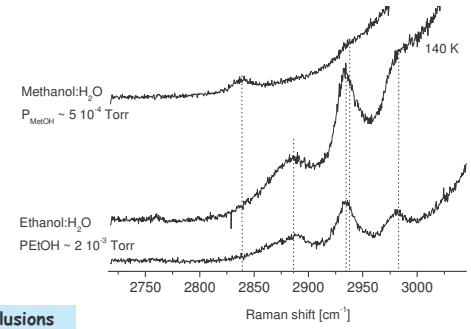
W = wt% of dissolved H_2CO, P in mm, T in K, Lacy, Electrochemicals Dept. E.I.Inc., unpublished results

Raman spectra of different formaldehyde-based compounds



• Comparison between Raman spectra of different formaldehyde-based compounds (see legend). The position (and attribution) of the vertical dotted lines indicate the symmetric νS and anti-symmetric νAS modes of C-H stretching observed in the liquid aqueous solution. Note the stricking spectral differences of hydrates crystallized in frozen solution (composed of hydrated oligomers) and hydrates formed by deposition of vapor collected above the solution (, and subsequent annealing (composed of molecular H2CO).

Raman spectra of co-deposited Methanol:H_2O mixture and ethanol:H_2O mixture



Conclusions

- Strong partitioning between liquid and gas phase at low concentration → need more experimental data to confirm
- Characterization of co-deposited hydrates of formaldehyde/methanol/ethanol phases underway