Highly localized H$_2$O librational motion as a far-infrared spectroscopic probe for microsolvation of organic molecules

The most prominent spectroscopic observable for the hydrogen bonding between individual molecules in liquid water is the broad absorption band detected in the spectral region between 300 and 900 cm$^{-1}$. The present work demonstrates how the associated large-amplitude out-of-plane OH librational motion of H$_2$O molecules also directly reflects the microsolvation of organic compounds. This highly localized OH librational motion of the first solvating H$_2$O molecule causes a significant change of dipole moment and gives rise to a strong characteristic band in the far-infrared spectral region, which is correlated quantitatively with the complexation energy. The out-of-plane OH librational band origins ranging from 324.5 to 658.9 cm$^{-1}$ have been assigned experimentally for a series of four binary hydrogen-bonded H$_2$O complexes embedded in solid neon involving S-, O- and N-containing compounds with increasing hydrogen bond acceptor capability. The hydrogen bond energies for altogether eight binary H$_2$O complexes relative to the experimental value of 13.2 ± 0.12 kJ mol$^{-1}$ for the prototypical (H$_2$O)$_2$ system [Rocher-Casterline et al., J. Chem. Phys., 2011, 134, 211101] are revealed directly by these far-infrared spectroscopic observables. The far-infrared spectral signatures are able to capture even minor differences in the hydrogen bond acceptor capability of O atoms with slightly different alkyl substituents in the order H-O-C(CH$_3$)$_3$ > CH$_3$-O-CH$_3$ > H-O-CH(CH$_3$)$_2$ > H-O-CH$_2$CH$_3$. 

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Low Temperature DeNOx Technologies for Power and Waste Incineration Plants

Formation of NOx is inevitable during high temperature combustion processes in air. NOx is of increasing environmental concern due to its participation in detrimental photochemical reactions, which lead to ozone layer depletion. NOx emissions also cause acid rain, contributes to smog formation and induces respiratory diseases in humans. There is no doubt that anthropogenic effects are contributing to the global climate change. The largest contributor to anthropogenic greenhouse gas emissions is CO₂, been of great interest as a method to decrease global CO₂ emissions. Some of the fuels that have drawn particular interest over the past decade is biomass and municipal waste. While the CO₂ emissions are decreased by a transition to these fuels, other problems are caused by it. Potassium present in many of the alternative fuels lead to severe deactivation of the catalyst used for NOx abatement. Consequently, NOx abatement is currently not possible when these are used exclusively. Since NOx gasses are strong pollutants, the increased emission caused by using these alternative fuels is highly undesirable and hinders a more widespread use of alternative fuels. The work presented here has primarily been concerned with finding an alternative solution to NOx abatement for biomass and waste incineration. The optimal solution to this would be a tail-end deNOx unit, which operates at low temperatures (60-140°C). Previous work has shown that ionic liquids (ILs) are promising absorbers and can selectively absorb flue gas constituents such as CO₂, SO₂ and NO. Utilisation of ILs is severely limited by high viscosities, which hinders mass transfer across phase boundary layers. Dispersion of the IL onto a porous support has been suggested as a possible solution to this problem. In the present work, a vast variety of supported ionic liquid phase (SILP) materials have been tested in NO breakthrough experiments. Based on the obtained results, an attempt was made to understand the chemical and physical properties governing the SILP performance. Based on these investigations, characteristics of the optimal support were suggested. It was found that hollow-sphere silica (HS) had properties close to what was considered optimal, therefore it was decided to investigate this support material further. Synthesis of the support material and subsequently SILP formulations utilising the HS-support material were carried out in collaboration with Prof. Dai at Oak Ridge National Laboratory. The resulting HS-SILP performed significantly better than any other SILP formulation tested in NO breakthrough experiments. Based on this performance, it was suggested that the HS-support could be ideal for selective absorption of other gasses using SILP absorbers. Some SILP formulations were found to have significant oxidative capabilities, willingly oxidising NO to higher NOx species. It was found that the observed effect was due to alcohol residuals in the SILP material from the impregnation process, despite careful evaporation and drying. In order to investigate this effect further, the effect of several alcohols were screened and showed promising results. Therefore, an experimental setup was built to investigate if the oxidation would occur under continuous flow conditions, and to determine the steady state oxidation rates. Significant steady state conversions were found under continuous flow conditions, with a high turn over number for methanol. The reaction proceeded over all porous surfaces, but the use of a SILP material seemed to increase the rate of oxidation significantly.

Absorption and oxidation of nitrogen oxide in ionic liquids

A new strategy for capturing nitrogen oxide, NO, from the gas phase is presented. Dilute NO gas is removed from the gas phase by ionic liquids under ambient conditions. The nitrate anion of the ionic liquid catalyzes the oxidation of NO to nitric acid by atmospheric oxygen in the presence of water. The nitric acid is absorbed in the ionic liquid up to approximately one mole HNO₃ per mole of the ionic liquid due to the formation of hydrogen bonds. The nitric acid can be desorbed by heating, thereby regenerating the ionic liquid with excellent reproducibility. Here, time-resolved in-situ spectroscopic investigations of the reaction and products are presented. The procedure reveals a new vision for removing the pollutant NO by absorption into a non-volatile liquid and converting it into a useful bulk chemical, that is, HNO₃₋.
Alternative NOx abatement, finding a suitable method

This project explores the possibility of removing NOx through one of several strategies utilising the unique properties of ionic liquids (ILs), including absorption and oxidation of NOx to nitric acid.

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Combined oxidation and absorption of nox by an ionic liquid tandem process.
The present invention relates to a new strategy for capturing NOx using a two-step process.

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Absorption of Flue-Gas Components by Ionic Liquids

Gas separation by ionic liquids (ILs) is a promising new research field with several potential applications of industrial interest. Thus cleaning of industrial off gases seems to be attractive by use of ILs and Supported Ionic Liquid Phase (SILP) materials. The potential of selected ILs for absorption of NOX, CO2 and SO2 are demonstrated and the possible mechanism of absorption described on the molecular level. Special focus regards the interaction of the ILs with water vapor, which is an important feature in envisaged application of flue gas cleaning in power plants, waste incineration plants, cement and glass factories as well as on board ships.

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