ESF – SimBioMa – Science Meeting – Final Report

Title: *Vibrational Spectroscopy of Complex Systems*

Organizers: Damien Laage & Ward Thompson

Summary

The workshop brought together theoretical and experimental chemists working on the applications of vibrational spectroscopy to a variety of condensed phase systems. Nonlinear vibrational spectroscopies were particularly highlighted. These techniques can provide a detailed picture of the dynamics in liquids, both of the liquid molecules in neat form or in a heterogeneous environment as well as of solute behavior. Systems discussed at the workshop included water, ice, organic liquids, salt solutions, water-vapor interfaces, reverse micelles, small peptides, proteins, and hydrated DNA. These represent problems that are of interest in theoretical/experimental method development, environmental chemistry, and biological function, as a few examples.

While the scope of the workshop was limited to vibrational spectroscopy, it is well-known that the insight that can be gained into a particular structural or dynamical feature depends on the technique used. Hence, the workshop brought together researchers working on multiple techniques to discuss the overlap and complementarity of the various approaches. These included linear infrared (IR) and Raman spectroscopy, pump-probe spectroscopy, 2- and 3-dimensional IR, and vibrational sum-frequency generation. A key challenge in the spectroscopy of complex systems in general, and nonlinear spectroscopy in particular, is the translation of the spectra into a molecular-level description of structure and dynamics. This issue was a key motivation of the workshop, which thus involved a mixture of experimentalists and theorists. This connection between modeling and measurement was a significant theme of the workshop, both in the talks and the discussions.

Description of the scientific content of and discussion at the event

Presentations

The presentations covered a range of the key issues in vibrational spectroscopy from both the experimental and theoretical points of view. Prof. Hynes (ENS, France and U. of Colorado, USA) described work on the reorientation of water around amphiphilic solutes. He and his collaborators have used molecular dynamics simulations to examine the origins of slower dynamics observed in experimental measurements by several groups. He described how, within their extended jump model, they can decompose the effects of the hydrophobic moieties on the solutes, which are primarily associated with excluded volume, and the hydrophilic groups, which can restrain or accelerate dynamics through differences in hydrogen bond strengths. These results provide a molecular-level description for vibrational pump-probe anisotropy measurements in these systems.

Another key topic discussed was the use of vibrational spectroscopy to probe protein structure. This is an area that is still emerging as numerous efforts are underway to develop approaches based on vibrational signatures that can complement NMR and X-ray structure determinations. Dr. Moran (U. of Wisconsin, USA) described experimental efforts in this direction based on isotopic labeling. By clever placement of, for example, ^{13}C isotopes in the protein backbone and probing the vibrational frequencies involving those atoms, they can gain access to structural information. A different approach was proposed by Prof. Corcelli (Notre Dame U., USA) based on simulations. He showed how deuteration of C-H bonds could provide information about structure, and dynamics, in proteins and other systems.

Prof. Elsaesser (Max Born Institut, Germany) described their recent experiments aimed at understanding the dynamics of DNA using nonlinear vibrational spectroscopy. Their approach is to examine how different vibrational modes within DNA are coupled to other modes, both within DNA and in surrounding waters. They examined both NH stretches in the base pairs as well as the phosphate groups. Their results show sometimes quite complex dynamics involving intramolecular vibrational redistribution, spectral diffusion, and vibrational energy transfer. These results point to both the information content contained in the spectroscopic signals and the need for theory-experiment collaboration to uncover the molecular-level details.

Prof. Morita (Tokohu U., Japan) presented his simulated sum-frequency generation (SFG) spectrum of the air-water interface that is in very good agreement with recent experiments which report the real and imaginary part of the susceptibility determining the SFG intensity. A key feature of these results is the presence of a positive value of the imaginary part at comparatively low frequencies for the OH stretching vibration. He not only presented simulations that reproduced this feature, but provided a clear physical picture of the molecular behavior accounting for it. Namely, he was able to show it was due to a cooperative effect between two hydrogen-bonded molecules. As the hydrogen-bond donating molecule undergoes an OH stretching vibration, it enhances the polarizability of the accepting molecule perpendicular to that OH stretch. This is a novel and convincing description. Profs. Geissler (U. of California-

Berkeley, USA) and Skinner (U. of Wisconsin, USA) also presented key approaches to simulating SFG spectra, while Prof. Bakker (AMOLF, Netherlands) presented exciting new results on 2D-SFG, a long-standing goal of interfacial spectroscopy.

Discussions

Exciting experimental data is emerging regarding hydration dynamics around DNA and proteins, some of which was discussed at the workshop. However, deriving molecular-level insight from these experiments will require theoretical efforts strongly coupled to the experiments. Among the features that need to be explored for DNA are the signatures of the hydration structure around the phosphates and base pairs as well as the roles of resonant vibrational energy transfer, heat transfer, and intramolecular vibrational redistribution (IVR). A nascent collaboration between Prof. Elsaesser and the organizers was furthered at the workshop.

The low frequency, intermolecular, vibrational modes in water was another topic that elicited considerable discussion. The spectroscopic features associated with these motions are broad and can thus be hard to interpret. While a clear picture is not forthcoming the discussion focused on some of the areas in which theory and experiment can combine to address the outstanding issues, particularly how the spectroscopic features can be used to obtain information about the water environment.

Significant discussion was devoted to the potential for obtaining protein structural information from vibrational spectroscopy, particularly nonlinear versions. As noted above, the talks presented some approaches based primarily on isotopic substitution. The discussions explored the ultimate potential/limitations on these methods for extracting structural information as well as the barriers to progress. Different viewpoints were expressed and the answers are as yet unclear. Agreement was found in the idea that solutions will come from a combination of experimental and theoretical approaches.

Presentations by Profs. Skinner, Torii, and Elsaesser sparked discussion about the spectral signatures of resonant vibration-vibration energy transfer. A number of issues were raised. These include how important are these effects; the answer appears to depend quite strongly on the spectroscopic observable. The description of these effects can be computationally expensive and new method developments, perhaps dependent on the spectroscopic measurement, are needed. The effects are also system-dependent (*e.g.*, they can be dramatic for ice but considerably less-so for liquid water) and understanding this will require further experimental and theoretical study.

A significant topic of discussion was the simulation of and molecular interpretation of measured sum-frequency generation (SFG) spectra. Profs. Skinner and Morita proposed two, somewhat different explanations for a low-frequency feature in the SFG spectrum of the water-air interface. The resolution of these different interpretations, one involving three-body effects and the other an anisotropic polarization, will require more theoretical study. Prof. Geissler presented a study indicating that simulations of SFG spectra, typically done using a slab of material, depend on how one chooses to define the top and bottom halves of the slab. This development has significant implications for such calculations. Finally, Prof. Bakker proposed a new interpretation for the double-peaked structure in the hydrogen-bonded

region of the water-air interface SFG spectrum. He attributed it to a Fermi resonance between the stretching mode and the water bend. Verification of this mechanism will require new theoretical modeling as current approaches neglect this effect.

Assessment of the results and impact of the event on the future direction of the field

The objectives of the workshop were: 1) to stimulate the development of advanced theoretical frameworks to analyze and interpret a new generation of experiments, 2) to encourage experimentalists to design new experiments to probe phenomena predicted by theory and simulations, and 3) to combine the views of theoreticians and experimentalists to discuss potential solutions to long-standing issues, including for example how to specifically probe solvent molecules at interfaces (*e.g.* biomolecule, nanoscale framework).

The strong point of the workshop was the informal discussions, both in the 15-minute periods designated for each talk and during the breaks and meals. A key feature of these discussions was the interaction between experimentalists and theorists. In this way, objectives 1 and 2 were met, for example through productive discussions on themes such as sum-frequency generation measurements of interfaces and determination of protein structure from vibrational spectroscopy.

In terms of weak points, the workshop could have benefited from a longer time-scale, e.g., an additional day, for the meeting with greater time for informal discussions. This might have permitted greater progress as ideas fermented and percolated through the group of participants.

Final program

Monday, May 23

Morning Session

8:55 *Opening Remarks – Chair:* **Branka Ladanyi**

9:00 **Dominik Marx**, *Ruhr-Universität Bochum, Germany*
"Understanding THz Spectroscopy of Aqueous Solutions"

9:45 **Steve Meech**, *University of East Anglia, UK*
"Hydrogen Bond Structure in Aqueous Ionic Solutions"

10:30 Coffee Break

11:00 **Kelly Gaffney**, *SLAC National Accelerator Lab., USA*
"H-bond Switching and Ligand Exchange Dynamics in Aqueous Ionic Solution"

11:45 **Rossend Rey**, *University Politecnica Catalunya, Spain*
"Energy Relaxation Pathways in Liquid Water"

12:30 pm Lunch

Afternoon Session – Chair: **Erik Nibbering**

2:00 **Hajime Torii**, *Shizuoka University, Japan*
"Spectroscopic Phenomena Arising from Resonant Intermolecular Vibrational Coupling and the Related Electronic Motions"

2:45 **Sean Garrett-Roe**, *University of Zürich, Switzerland*
"Heterogeneous Dynamics of Liquid Water by Ultrafast Vibrational Spectroscopy (3D-IR) and Complex Network Analysis"

3:30 Coffee Break

4:00 **James Skinner**, *University of Wisconsin, USA*
"New three-body simulation model for water and its vibrational spectroscopy: clusters, liquid/vapor interface, and ice"

Tuesday, May 24

Morning Session – Chair: **Steve Meech**

9:00 **Thomas la Cour Jansen**, *University Groningen, Netherlands*
"Simulation of Nonlinear Vibrational Spectra in Condensed Phase Multi-chromophore Systems"

9:45 **Roger Loring**, *Cornell University, USA*
"Computing Nonlinear Vibrational Response Functions with Semiclassical Dynamics"

10:30 Coffee Break

11:00 **James Hynes**, *Univ. of Colorado, USA and ENS, France*
"Water Reorientation around Amphiphiles and 2D Infrared Spectroscopy"

11:45 **Erik Nibbering**, *Max Born Institut, Berlin, Germany*
"Exploiting and Exploring Photoacids: from Ultrafast Generation of Nature's Most Abundant Acid to Monitoring the Hydrogen Bond Structure in Solution"

12:30 pm Lunch

Afternoon Session – Chair: **Kelly Gaffney**

2:00 **Steve Corcelli**, *Notre Dame University, USA*
"Computational Studies of Infrared Probes of Amino Acid Protonation States"

2:45 **Sean Moran**, *University of Wisconsin, USA*
"Studying Complex Proteins with Novel Labeling Methods and 2D IR Spectroscopy"

3:30 Coffee Break (*Reimbursements for invited speakers)*

4:00 **Thomas Elsaesser**, *Max Born Institut, Berlin, Germany*
"Ultrafast two-dimensional infrared spectroscopy of hydrated DNA oligomers"

4:45 **Marie-Pierre Gaigeot**, *Univ. Evry, France*
"DFT-based molecular dynamics (DFT-MD) simulations applied to vibrational spectroscopy of floppy polypeptides in the gas phase and immersed in the liquid phase"

5:00 **Francesca Ingrosso**, *Univ. Nancy, France*
"Modelling the Infrared Spectra of Peptides in Solution: Semi-Empirical Born-Oppenheimer simulations"

8:00 Conference Dinner

Wednesday, May 25

Morning Session – Chair: **Steve Corcelli**

9:00 **Akihiro Morita**, *Tokohu University, Japan*
"Theory of Sum Frequency Generation Spectroscopy and Application to Liquid Surfaces"

9:45 **Huib Bakker**, *AMOLF, Amsterdam, Netherlands*
"Ultrafast Energy Transfer at Water Interfaces Studied with 2-Dimensional Surface Vibrational Spectroscopy"

10:30 Coffee Break

11:00 **Phillip Geissler**, *University of California-Berkeley, USA*
"Approximate views of hydroxyl stretching lineshapes: Insights they reveal and problems they expose"

11:45 **Rodolphe Vuilleumier**, *Ecole Normale Supérieure, Paris, France*
"Effective normal modes from finite temperature molecular dynamics simulations"

12:00 pm Lunch

Afternoon Session – Chair: **Huib Bakker**

1:30 **Michael Odelius**, *University of Stockholm, Sweden*
"Theoretical Simulations of X-ray Spectroscopy as a Local Vibrational Probe"

2:15 **Branka Ladanyi**, *Colorado State University, USA*
"Computer simulation of water dynamics in reverse micelles - connections to time-resolved IR spectroscopy"

3:00 *Concluding Remarks*