Cross-cutting analysis tools

Overview

The industrial revolution deserves credit for improving the lives of humans through the invention of many new and innovative technologies, from nylon to cell phones, but is also to blame for the climate change problem that is now ensuing. However, innovation can also rescue us by providing revolutionary solutions to the carbon capture problem through novel materials synthesis, characterization, theory and analysis. Such innovation will require efforts that exceed our current activities in scope and magnitude. In this section we discuss some of the key elements needed to strengthen materials characterization and analysis to meet the needs of the science and engineering goals for carbon capture 2020 and beyond.

Some key messages emerged from the workshop. First, while we need to develop new tools to understand and overcome new scientific challenges, there is also a lack of access to currently available tools and expertise that is inhibiting progress. In particular, it is becoming more important to apply integrated state-of-the-art characterization tools that complement each other, and assemble the information at the basic signal level so that the integrated data can guide interpretation and modeling. Second, new tools should be developed to address specific challenges. We have identified some of the cross-cutting analytical information needed for several promising carbon capture technologies below. Third, techniques must be developed to recognize unique events from the ensemble response that is most often measured. It is the properties of unique events that we want to optimize, especially in complex and disordered materials that are the hallmark of many desirable materials. And finally, it is imperative that advanced characterization, advanced synthesis and processing and advanced computation come together in a joint effort to produce the materials needed for efficient carbon capture.

In what follows, we outline some Priority Research Directions that must be pursued in order to obtain critical pieces of information for characterizing, understanding and ultimately improving upon some promising carbon capture technologies. The Priority Research Directions we outline are the following:

- Physical and chemical analysis techniques that can be applied *in situ* on relevant temporal and spatial scales
- Advances in interfacial and thin film characterization
- Characterization and understanding of near-surface fluid properties
- Methods for generating an atomic scale view of gas-host structures and kinetics

- Methods for the characterization and control of nanoscale synthesis in 1- and 2 dimensions

Priority Research Directions

Physical and chemical analysis techniques that can be applied *in situ* on relevant temporal and spatial scales

Processes for carbon capture typically operate under conditions of elevated temperature, pressure gradients, high volumetric flow rates of complex gas or liquid mixtures, and often occur in the presence of mechanical stress, impurities and debris. The thermodynamics and kinetics of the capture process under these conditions is very different from typical laboratory environments. To develop fundamentally new processes, or improve the efficiency and reliability of existing processes, necessitates characterizing materials behavior *in situ* under these extremely difficult conditions. While there are experiments today that characterize materials *in situ*, the capabilities and access are quite limited. It is not only critical for us to examine structure and properties *in situ*, but also to catalog the dynamics involved in the molecular capture and regeneration of the potential host for the molecular interactions including both physisorption and chemisorption.

Accurate information on structural and dynamic properties *in situ* is critical to enable materials by design for breakthrough improvements in key transport, reaction and thermodynamic properties under actual conditions of operation.
New analysis tools are critically required for studying structural and dynamic properties of materials under a wide a range of pressure (P), temperature (T) and other (x) conditions. Such studies may include, for example, varying P-T conditions with the material in contact with fluids, in the presence of reactive or corrosive gases, and over many cycles (ageing). This capability will also be critical as we explore the ability to effect separations with conditions other than P and T, as outlined earlier in this document. The ability to study materials under realistic P-T-x conditions will impact not only carbon capture but also in broad areas of energy research including catalysis, fuel cell energy conversion and energy-efficient materials synthesis. To achieve this aim, characterization techniques must be developed that can be applied *in situ* over the relevant span of time and spatial scales.

The structural and dynamics properties of gas capture materials (including sorbents, membranes and complex fluids) is what determines the key thermodynamic and kinetic properties necessary for proper performance. The gap between model systems and realistic conditions can be bridged by *in situ* experiments. Some advanced materials characterization methods are already

particularly suited to *in situ* experiments, for example hard x-rays and neutron beams that can penetrate bulk materials. But in many cases there is a lack of adequate capability to hold samples under the needed conditions. Thus, research is needed to develop appropriate sample chambers for use with a much broader variety of characterization tools. Another approach would be nanoscale probes (nano "Mars Rovers") that might be fully immersed in the environment, and hold self-contained measuring capabilities.

Even with optimal *in situ* sample environments and appropriately matched probes, there are limitations today in the temporal and spatial resolution of measurements that must be overcome. The time-scales of importance to carbon capture science and engineering span over 18-orders of magnitude. From femtoseconds (10^{-15} seconds) associated with an absorption event up to many seconds time required for diffusion of heat and mass through critical systems. Similarly, length scales of interest span many orders of magnitude--from below the atomic scale, needed to understand the binding of gas-host with sub-atomic positional precision and compare with theory, to the mm range of porosity in solid adsorbents. Thus, for complex materials, we will need a variety of different techniques to fully characterize *in situ* behavior, and it is particularly important to combine more than one technique at the same time, or at least under the same conditions on the same sample. Examples of analysis techniques that will play a role in the analysis of carbon capture materials are outlined below.

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Comment: While we discuss techniques that are available today, what advances are needed?

Synchrotron X-ray: In situ high intensity light source methods are required to understand atomic arrangements and oxidation states of materials at pressure and temperature inside reaction or synthesis chambers, including capabilities for examining complex and amorphous materials (including XRD, PDF, XAFS, and others). The source brightness sets the lower limit for spatial and temporal resolution, because it determines the maximum number of particles per unit time that can be focused in a beam. Hard x-rays penetrate materials in a non-destructive manner. Less penetrating radiation like soft x-rays radiation could include introduction of large pressure gradients in short distances with skimmers to minimize the distance. Current synchrotron x-ray diffraction measurements can be collected on millisecond timescales with fast detectors and in nanoseconds with streak cameras. Major improvements in x-ray and neutron beamline brightness and instrumental sensitivity can be expected in the next two decades that will advance carbon capture science, including beamlines that will contribute in the ultrafast regime with free-electron lasers that will allow single events on the femtosecond scale with atomic level structural and chemical information. Conventional x-ray storage rings can be improved to produce high average brightness for time scales of 1 picosecond and above. Resolution at the nm range from x-ray sources is on the near horizon. Neutrons have a unique role because of their sensitivity to molecular gases, and increased flux at the new and future pulsed neutron sources, offers new opportunities.

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Environmental Electron Microscopy: Transmission or scanning electron microscopy can elucidate nanoscale morphology under conditions of gas binding or fluid contact. Transmission electron microscopy is capable of near-atomic resolution in gases, provided instruments and experiments are designed with a very short path length in the gas or in a thin film of liquid. Transmission electron microscopy has resolution below 0.1nm today, however the low penetrating power of this technique typically requires thin film samples. As such, it is well-suited for the examination of thin gas separation membranes. Special stages and optics utilizing recent improvements in aberration correction will likely be important in pushing the state-of-the-art *in situ* experiments.

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In situ solid state NMR: Solid-state nuclear magnetic resonance (NMR) can provide a wealth of structural details from atomic-level to macroscopic length scales, and dynamical details from picoseconds to kilosecond time scale[1,2]. The solid-state NMR methodologies most relevant to the characterization needs of CO_2 capture materials, such as metal organic frameworks (MOFs) or zeolite inorganic frameworks (ZIFs), can be found in a large literature of successful studies on heterogeneous catalysis[3]. NMR can provide numerous structural details such as the structure, organization, and dynamics of CO_2 and CO_2 binding sites, in addition to providing insights into kinetics, transport, and thermodynamic properties. Although NMR, in general, has relatively low sensitivity compared to other spectroscopic methods, it is particularly well-suited for the study of adsorbents with the type of high surface area materials that will be used for CO_2 capture. Additionally, solid-state NMR is particularly powerful in obtaining structural and dynamical details in disordered materials where conventional scattering approaches are ineffective. Magic-Angle Spinning (MAS) studies have even been successfully performed *in situ* at the kind of conditions [3] typical for power plant post-combustion flue gas and pre-combusion water-gas shift reactors.

[1] M. J. Duer, Introduction to Solid-State NMR Spectroscopy, Blackwell, Oxford, 2004.

[2] K.J.D. Mackenzie and M.E. Smith, Multinuclear Solid-State NMR of Inorganic Materials, Pergamon, 2002.

[3] M.Hunger, In situ flow MAS NMR spectroscopy: State of the art and applications in heterogeneous catalysis. Prog. NMR Spectros., 52:105-127, 2008.

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Neutron methods: Neutron diffraction is a powerful technique for determining the crystallographic locations of absorbed gases in materials. The Fourier-difference map method can be used to probe the time-averaged CO_2 locations in solid absorbers such as MOFs and ZIFs (Figure **).

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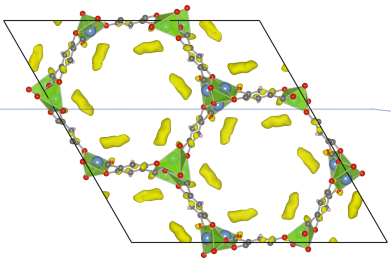
Neutron Fourier difference plot, clearly showing CO_2 molecules absorbed on the open-metal site of Mg-MOF74.



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Optical and infrared spectroscopies: A number of methods are already available to characterize vibrational or electronic molecular structure in reaction environments. However further improvements are needed to aid in the study and improvement of carbon capture processes. Optical and infrared spectroscopies have the advantages that they can be applied *in situ*, are highly sensitive, and can probe molecular and electronic structures to elucidate electrostatic forces involved in carbon capture, for instance. Nonlinear optical methods are especially needed with bond-specific structural resolution and quantitative conformational information. Multidimensional infrared and visible spectroscopies or surface sensitive sum-frequency spectroscopies, that span timescales from the ultrafast to the ultraslow will be important tolls for studying carbon capture. Developing spatially resolved non-linear optical spectroscopies would also aid in the characterization of carbon capture materials.

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Comment: Be a good place to expand state-of-the-art IR and optical methods.

(Sidebar) Viewing the nanoscale with synchrotron x-rays

Development of x-ray nanoprobes at synchrotron sources has potential for shedding considerable light on interactions between CO_2 and potential hosts. For example transmission x-ray microscopy (TXM) is a powerful tool for nondestructive *in situ* imaging with unprecedented spatial resolution and temporal resolution. This is the same idea as medical x-rays and CT scans which provide doctors with critical real-time *in situ* information on the internal structure of their patients. Using high resolution zone plates, state-of-the-art instruments can currently provide spatial resolution in the 30-60 nm range. A single two dimensional radiograph based on x-ray absorption contrast can be collected in a few micro-seconds at bright synchrotron x-ray sources. When collected over many angles, these two dimensional images can be reconstructed into three dimensional x-ray tomographic representations. As high energy x-rays are highly penetrating, TXM could be adapted for *in situ* monitoring within complex, changing physical and chemical environments.

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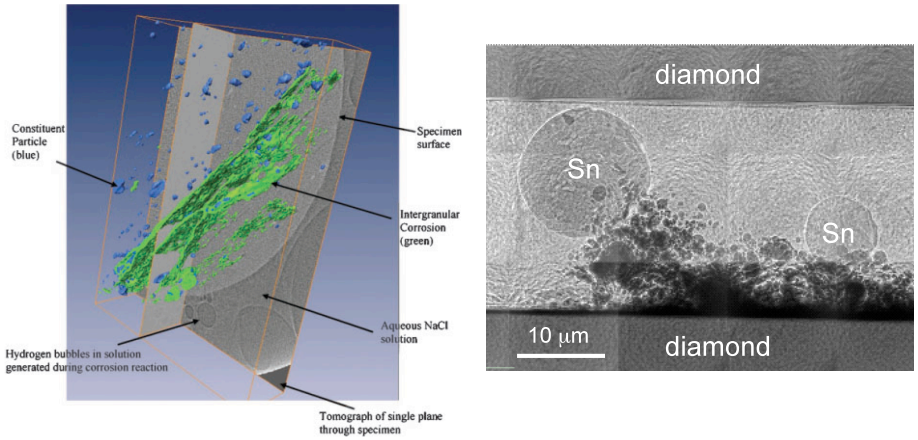

Left: Three-dimensional rendering of 200 synchrotron x-ray radiographs showing localized corrosion morphology within an Al specimen exposed *in situ* to a chloride environment. Rendering shows heat affected zone near weld in AA2024 after 40 hours exposure to 0.6M NaCl and highlights intergranular corrosion areas (green) and intermetallic particles (blue) [*Stock et al*, 2008]. Right: Synchrotron x-ray microradiograph of tin spheres of varying size compressed between diamond anvils. The sample chamber is composed of beryllium which allows transmission of x-rays and direct *in situ* viewing.

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Stock, S. R. (2008), Recent advances in X-ray microtomography applied to materials, *International Materials Reviews*, doi10.1179/174328008X277803

Develop characterization tools for the structure and dynamics of interfacial and thin films

Interfacial structure and molecular dynamics determines important transport and reaction kinetics for multiple-phase gas capture media. However it is difficult to characterize just a few atomic or molecular layers at an interface in the presence of the much larger bulk materials, especially when there is no simple crystalline order. To address this problem we need to advance and exploit interface-sensitive methods for structure determination and molecular dynamics in complex molecular systems and for characterization of unique properties of complex materials interfaces. Success in these analytical capabilities will enable design of complex multiphase gas capture materials such as membranes and complex fluids whose interfaces will enable breakthrough performance in high transport kinetics combined with low energy penalty for carbon dioxide separations cycles. Improved interfacial characterization methods for complex materials will also impact the ability to elucidate and design improved interfaces that are critical to many fields of

energy science, including catalysis, corrosion, electrical energy storage, and fuel cell energy conversion.

We need to develop and apply interface-sensitive methods for interfacial and thin film structure and dynamics at the atomic and molecular level in complex molecular systems. These advanced techniques for atomic structure and dynamics of interfaces may use x-rays, electron microscopy, and neutron scattering methods, exploiting capabilities of laboratory instruments and user facilities today and in the future. New methods are needed for complex liquid interface structure, transport and reactivity measurement—with possible approaches including new molecular beam scattering methods for liquid interfaces. We must also master methods and understanding of interface specific spectroscopies (nonlinear optical, photoemission) and existing surface-compatible spectroscopies, such as IR, Raman, X-ray Photoelectron Spectroscopy (XPS), for complex, poorly ordered interfaces.

We must develop tools to measure the mechanical, thermodynamic and transport properties in ultra-thin films (<100nm). As outlined in XXXXXX, ultra-thin membranes are highly desirable for isolating gases, such as CO_2 and O_2, from complex mixtures because of their high permeance; however, the challenge is that they must be mechanically, thermally and chemically robust. While this is challenging in its own right even for a uniform membrane, highly functional membranes of the future will likely be nanostructured, with structure in three dimensions. These nanostructures will require characterization with unprecedented high spatial resolution.

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We must develop advanced characterization methods, such as transmission electron microscopy, grazing incidence x-ray scattering, and neutron reflectometry, for this purpose. Advances in vibrational and optical spectroscopies and NMR will also be needed to provide new insight into these advanced separation media. A particular challenge is to combine these structural and dynamic techniques with simultaneous measurement of mechanical and other properties. An attractive approach to determining mechanical and transport properties is indirectly from interaction-potential sensitive techniques (IR, Raman, NMR) which are less invasive than, for example, direct mechanical measurements.

Measuring transport through innovative nanoscale geometries that are envisaged for tomorrow's membranes and adsorbents is a particular challenge for which no suitable technique exists today. Carbon capture science shares with all the basic energy sciences the need to develop revolutionary new tools for characterization of structure and properties down to the atomic level. The grand challenge is to know more and more about less and less material, avoiding as much as possible the ensemble averaging of the past.

Understand near-surface fluid properties

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Comment: Near interface or near surface?

Near-surface properties govern wetting in ultra-small capillaries, and the kinetics of exchange and reaction at these interfaces are difficult to examine. non-destructively in bulk matter. New methods are needed for identifying the near-interface composition and activity, and to profile this critical region as a function of distance from the surface. Techniques such as neutron and x-ray reflectivity provide profiles of solute concentrations over sub-nanometer distances near interfaces. X-ray photoemission using intense and angle-tunable sources can give elemental distributions over nanometers at interfaces. Light scattering techniques may also be used during the growth of thin membranes to relate the time-dependent measurements to position in the growing membrane. Nonlinear optical methods can selectively study dynamics and vibrational and electronic structure at solid-liquid and liquid-liquid interfaces.

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It is also critically important to obtain more information about the dynamics and transport at interfaces and surfaces. Dynamic spectroscopies, including those that are based on neutron/photon scattering and vibrational spectroscopies, could provide new information about these properties. New approaches may include molecular beam methods for reactivity/transport at liquid surfaces.

Methods for generating an atomic scale view of gas-host structures and kinetics

To design better molecular "traps"—in adsorbant and absorbent systems—and more selective separation membranes, a greater atomic-level understanding is needed of gas-host interactions for adsorption sites, kinetics (diffusion, reaction) and dynamics (vibrations, rotation, libration, translation) of molecules in complex media (liquids, solids). Experimental measurements of these critical phenomena are needed to validate and improve simulation and theory. Design of materials at the nanoscale offers the promise of tailored properties optimized for greater separation efficiency, but will require guidance to reach desired configurations.

New characterization tools will provide key insight that will help a new generation of functional materials for gas adsorption and separation to be designed. The fruit of these studies are also critically important for advances in other energy technologies, including fuel cells, capacitors, batteries, catalysis, and high surface area materials.. Specifically, we need to develop methods to deal with gas molecules in confined environments in order to study the molecular specificity and mechanism of gas loading, both CO_2 and O_2, in materials to develop new separation schemes for CO_2 reduction. These challenges become even greater when dealing with complex separation media, where both thelocation and dynamics of guest molecules in highly functionalized, three dimensional environments must be examined. Techniques such as elastic and inelastic neutron scattering and X-ray scattering, magnetic resonance, electron microscopies and infrared spectroscopy can yield this type of information. We aim to characterize gas organization, kinetics and dynamics

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around adsorption sites, in order to understand the chemical structure and molecular forces that aid in CO_2 and O_2 loading and ultimately in the design of improved separation materials. New characterization methods are needed to distinguish gas from host dynamics and discriminate, for example, bound CO_2 from gaseous CO_2. The grand challenge is to examine individual guest molecules, or at least ensure a full understanding of the nature of inhomogeneities in an ensemble. The grand challenge may be addressed by next generation techniques with much higher sensitivity. Today individual guest molecules may be observed in special cases onsurfaces by probe microscopy techniques. A major limitation of this approach is the damage or interaction of the probe with an often loosely bound molecule. Thus new techniques with high temporal resolution are needed where it may be possible to observe the molecule before disturbing it.

Beyond direct observation of guest molecules, there is often an associated disturbance in the host that is important to understand, since it plays a role in the energetics and dynamics of transport, capture and release. The host disturbance can also reveal the position of the guest. The disturbance includes matrix structural deformation around the guest. At high gas loadings effects should change and must be understood. In addition to matrix-guest interactions at high loading, guest-guest chemical interactions will grow and are important to understand.
Multidimensional infrared and optical spectroscopies might be well-suited for these tasks by measuring electronic and/or vibrational coupling between the host and guest in order to identify the binding site and associated structural changes. Well established pulse field gradient NMR methods [4] can be exploited to measure gas diffusion in complex media. Changes in the host structure with gas adsorption can be monitored with conventional multi-nuclear magic-angle spinning NMR.

[4] Peter Stilbs, "Fourier transform pulsed-gradient spin-echo studies of molecular diffusion." Progress in NMR Spectroscopy 19:1-45 (1987).

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Just as important as understanding the static guest-host configuration is measurement of the kinetics and dynamics. From infrared measurements we can spatially map the local interaction potentials and thus the energy landscape associated with binding. Where frustrated motion occurs this is important to study and control. Information can validate theoretical models and lead to more fundamental understanding of transport. The kinetics of transport are very difficult to measure today, especially in the lower-dimensional systems envisaged for nanostructured high-performance systems.

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Just as for the static case, cooperative effects (gas-gas, host-phonon) will be important and must be understood. A grand challenge for existing techniques lies in the need to make these measurements very locally in solid or liquid disordered systems. At very high loadings the strong gas-gas and gas-host interactions may lead to rapid changes in chemical or mechanical behavior. These interactions could

be useful if controlled. For example, mechanical changes could be used as a means to release an adsorbed gas with low energy penalty, but they may also be damaging e.g. causing materials cracking and failure.

(sidebar) Infrared spectroscopy and its application to nanoporous and disordered materials

Infrared absorption spectroscopy is particularly useful to probe the interaction between guest molecules and nanoporous materials for storage and separation applications because it complements other physical measurements. IR absorption measurements are sensitive to the local geometry (adsorption sites) and to the details of the interaction potential.[1] Typically, the internal stretch of guest molecules (e.g., H_2, CO_2, CH_4) is shifted from its unperturbed position. For molecules with a center of symmetry (e.g. H_2), the mode also becomes IR active because if the interaction potential is not symmetrical. Information can be derived from IR absorption measurements with theoretical calculations. Quantum calculations deal with weak interactions well, however they are expensive and slow for large unit cells found in MOFs. A relatively new theory developed to treat weak interactions within a Density Functional Theory (DFT) framework, call van der Waals-Density Functional (vdW-DF),[2] appears to be able to treat large systems well. It should also be possible to apply non-linear 2D IR spectroscopy to MOFs and other inorganic and/or disordered systems. 2D IR spectroscopy would improve the structural resolution by identifying the amount of symmetry breaking and resolve the inhomogeneous distribution of binding sites, for example.

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1. Vitillo, J. G.; Regli, L.; Chavan, S.; Ricchiardi, G.; Spoto, G.; Dietzel, P. D. C.; Bordiga, S.; Zecchina, A. *J. Am. Chem. Soc.* **2008**, *130*, 8386-8396
2. Dion, M.; Rydberg, H.; Schröder, E.; Langreth, D. C.; Lundqvist, B. I. *Phys. Rev. Lett.* **2004**, *92*, 246401; Kong, L.; Román-Pérez, G.; Soler, J. M.; Langreth, D. C. *Phys. Rev. Lett.* **2009**, *103*, 096103.

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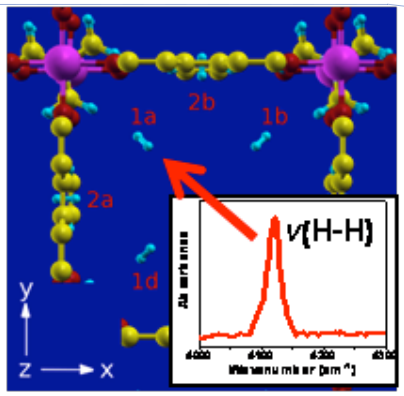
Figure Caption:

Schematic of use of IR spectroscopy and vdW-DF theory to determine the possible adsorption sites for H_2 in a Metal Organic Framework materials of the form **M(bdc)(ted)$_{0.5}$** [where M = Zn, Ni, Cu ; bdc = 1,4-benzenedicarboxylate, ted = triethylenediamine]. The associated IR absorption spectrum of the H-H stretch vibration is superposed on the structure. Of the two possible distinct sites 1 and 2, only site 1 has a detectable dipole moment, although both sites exhibit similar H-H stretch frequency shifts (from the frequency of the unperturbed H_2 molecule) [from ref. 1]



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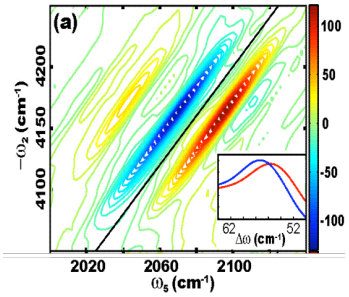
Ref 1: *Interaction of molecular hydrogen with Microporous Metal Organic Framework materials at room temperature,* Nour Nijem, Jean François Veyan, Lingzhu Kong, Kunhao Li, Sanhita Pramanik, Yonggang Zhao, Jing Li, David Langreth and Yves Chabal, J. Am. Chem. Soc. 132, 1654-1664 (2010).

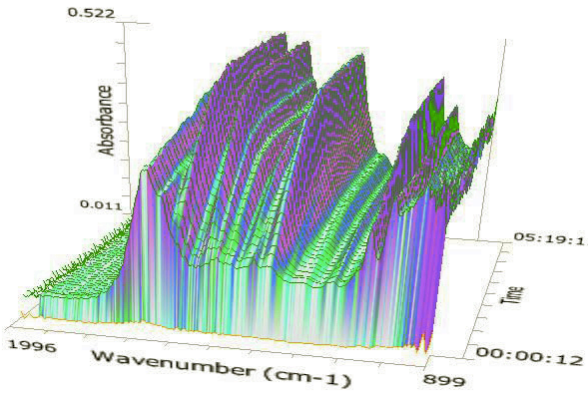
Figure Caption: A 2D IR spectrum of the azide ion in an ionic glass. The elongated peaks indicate that the azide ion is extremely inhomogeneously broadened. That is, the 2D lineshapes provide information on the distribution of vibrational frequencies, which are related to the disorder of the electrostatic environment around the azide ion. [Taken from Eric C. Fulmer, Feng Ding, Prabuddha Mukherjee, and Martin T. Zanni, Vibrational Dynamics of Ions in Glass from Fifth-Order Two-Dimensional Infrared Spectroscopy, Phys. Rev. Lett., 94, 067402 (2005)].



(sidebar) An example of CO_2 reaction kinetics measured with IR spectroscopy

There is a need for improved understanding of molecular level interactions in capture systems can be seen in recent studies of the molecular mechanisms in the well developed aqueous amine capture systems using monoethanolamine (MEA). While versions of this system have been used in industry for decades, its optimization with new capture materials requires further elucidation of the still poorly understood detailed reaction mechanisms. It is known that a key result of the process is the formation of an amine – carbon dioxide interaction called a carbamate, but only recently have time-resolved IR[1] and NMR[2] spectroscopy studies

elucidated the actual detailed reaction mechanism necessary to form this species in solution on the capture side.



IR spectral surface between 2000-900 cm^{-1} for the reaction between aqueous 30.00 % wt MEA and a gas stream containing 13.04 % CO_2. Several of the prominent growing peaks are identified as carbamate formed by amine-carbon dioxide interaction. In a carbon dioxide capture system, this carbamate is dissociated at higher temperature in a stripper column to release the captured carbon dioxide. [Ref 1].

1. P. Jackson, K. Robinson, G. Puxty and M. Attalla, ***In situ Fourier Transform-Infrared (FT-IR) analysis of carbon dioxide absorption and desorption in amine solutions,*** Energy Procedia **1**, 985-994 (2009). [Example of recent kinetic IR studies of classic amine systems.]

Methods for the characterization and control of nanoscale synthesis in 1- and 2 dimensions

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Comment: 1 and 2 only???

New separation media will require design and synthesis of tailored structures with external and internal surfaces optimized with respect to geometry and functionality. Methods to probe nanoscale structures, including imaging (electron and probe microscopy), diffraction (x-ray, electron, neutron), and spectroscopy (vibrational, optical, electron, neutron, etc…) will be needed to visualize the structures. We need to develop methods to aid imaging nano- and meso-scale two-dimensional structures using "tags" that could illuminate chemical or other activity (e.g. quantum dots or nanoparticles).

One dimensional structures such as nanotubes or pipes offer a route to tailored membranes. We must develop methods to functionalize the openings of 1-dimensional structures (e.g. channels), such as aligned carbon nanotubes (membranes) or external surfaces of nanoporous channels in crystalline and amorphous materials. We will also need characterization methods to probe chemical functionalization at spatially restricted areas such as openings of channels.

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Comment: This section is kind of weak. Wonder if it might be rolled into one of the above sections?

Michelle – We thought that a section like this would be good to tie in theory and experimental cross cut sections.

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Comment: Good! This also overlaps with the section above?

(BROAD CROSS CUT ON) Characterization for guided synthesis & processing

A very broad and important cross-cutting theme emerged from the workshop. It involves characterization, but equally computation and materials synthesis. It is clear that all of the strategies for carbon capture are limited today by the lack of high performance materials. Optimally performing membranes for separation, higher performance solid and liquid adsorbents and many other critical components of an energy-efficient carbon capture system are not performing at the theoretical limits of what is possible, and so today they are not energy and resource efficient which impacts the cost and dispersal of these critical technologies. It is clear from the BESAC report on the "Grand Challenges" that the solution to this materials problem and that of almost all energy technologies, involves the development of new materials with radically improved performance. The route to this has been regularly identified as a "control" as opposed to a "trial-and-error" empirical approach to materials development. To achieve this revolution will require a very close coordination of novel materials synthesis and processing, combined with state-of-the-art characterization techniques of the kind we have described, and theory and computation. Not only do the instruments and techniques need to be closely located, but also the expertise to fully utilize and develop them. We expect to use routine, high-throughput techniques, e.g. powder x-ray diffraction, together with innovative methods e.g. *in situ* observation of phase nucleation and kinetics.
Characterization plays the ultimate role of validating the theory and simulation that will ultimately allow us to "inverse engineer" the best possible material based on a list of its needed properties. But we are a long way from that today, and the most important step will be the concerted and integrated attack of the synthesis, characterization and simulation triumvirate on specific use-inspired problems – especially carbon capture.

We can also learn a lot from biology in our design of biomimetic structures, and fully develop nanoengineering to control materials on functional length scales. We can expect the outcome to be tunable materials with localized dynamics ideally suited for capture, release and transport control, and materials with hierarchical textures optimized for carbon capture, release and separation.

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(sidebar) Connecting theory and experiment: Polymeric CO_2 under extreme environments

CO_2 has a very complicated phase diagram, forming a number of extended solids at high pressure and variable temperature. These materials were studied *in situ* using synchrotron x-ray diffraction and Raman spectroscopy [*Iota et al.*, 2007]. The existence of these structures are useful constraints for theory and computations,

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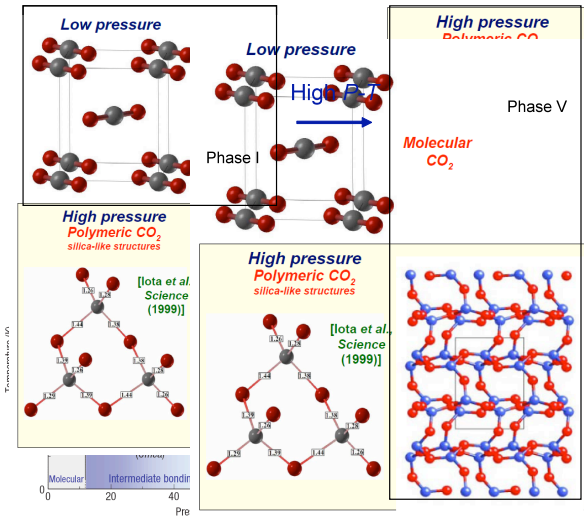
and may provide guidance for designing novel materials based on tetrahedrally coordinated carbon structures.



Iota, V., et al. (2007), Six-fold coordinated carbon dioxide VI, *Nat. Mater.*, *6*, 34-38.