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CO_2 Capture

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Capture of Carbon Dioxide at the Gas–Liquid Interface Elucidated by Surface Science Approaches

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In autumn 2010, with the goal of combating global climate change, the German government and parliament voted in the new "Energiekonzept 2050 (Energy Concept 2050)" and, thus, the search for new strategies for the reduction of greenhouse gases. As a consequence, the decision was made to extend the lifetime of German nuclear power plants beyond the limits imposed by the previous governing parties. Then, about five months later, in March 2011, the catastrophic earthquake off the coast of Japan and the concomitant tsunami destroyed Fukushima Daiichi, and, within a couple of weeks, the German government's nuclear energy policy crumbled. In June 2011, Chancellor Angela Merkel officially declared that Germany will cease using nuclear energy beyond the year 2022.

From a pessimistic but probably realistic point of view, this hurried and to some extent emotionally driven decision will most likely imply a considerable increase in global CO_2 emission originating from newly built conventional combustion plants. In this context, the development of new, emission-poor or emission-free energy resources as a long-term goal becomes more urgent. Even more important for the near future is the development of highly efficient CO_2 capture and storage/recycling (CCS) methods as transitory technologies. The storage problem is completely unsolved; this feature also holds true for the long-term disposal of nuclear waste and is one more reason for the departure from nuclear energy. Moreover, today's CO_2 capture techniques are far from full-scale application because of several extremely difficult requirements. This was described explicitly in the "Report of the Basic Energy Sciences Workshop for Carbon Capture: Beyond 2020" published by the U.S. Department of Energy in March 2010: "*The carbon capture problem is a true grand challenge for today's scientists. Postcombustion CO_2 capture requires major new developments in disciplines spanning fundamental theoretical and experimental physical chemistry, materials design and synthesis, and chemical engineering. […] A typical 550 MW coal-fired electrical plant produces about two million cubic feet of flue gas per minute (i.e. about 1000 $m^3 s^{-1}$), containing a mixture of CO_2, H_2O, N_2, O_2, NO_x, SO_x, and ash; however, the CO_2 is present at very low concentrations (< 15 % after conventional combustion). The sheer quantity of CO_2 that must be captured ultimately dictates that the capture medium must be recycled over and over. Hence the CO_2 once bound, must be released with relatively little energy input. […] Further, the CO_2 must be rapidly and selectively pulled out of a mixture that contains many other gaseous components. […] It is this nexus of high-speed capture with high selectivity and minimal energy loss that makes this a true grand challenge problem, far beyond any of today's artificial molecular manipulation technologies, and one whose solution will drive the advancement of molecular science to a new level of sophistication.*"[1]

For CO_2 capture from flue gas, concepts based on liquid absorption, solid adsorption, and membrane separation are already available at various levels of realization. One of the most common and best-established methods is the absorption by aqueous monoethanolamine (MEA) solutions.[2] In this approach CO_2 is first removed from the input gas stream in an adsorber unit at low temperatures/high pressure, and is then removed from the adsorber in a second step in the so-called stripper unit at elevated temperatures/reduced pressure for further processing (e.g. pressurizing for transport and storage). In both steps, gases have to pass the liquid/gas interface; detailed information on this interface is crucial for the understanding of the whole process. Despite its importance, the liquid/gas interface is still far from being well-understood. This is mainly related to the fact that—apart from surface-sensitive optical as well as X-ray- and neutron-scattering methods and computer simulations—most surface-sensitive techniques such as photoelectron spectroscopy (PES) require ultrahigh-vacuum (UHV) conditions incompatible with common liquids having high vapor pressure. However, sophisticated and advanced experimental PES methods have been developed recently that cope with the vapor pressure of water in aqueous systems. In recent work, Lewis et al. used synchrotron-based soft X-ray photoelectron spectroscopy combined with vacuum liquid microjets (this technique was established by M. Faubel and B. Winter around 2000[3]). By investigating the near-surface region of aqueous MEA solutions with and without CO_2 loading, the authors were able to demonstrate the non-isotropic distribution of molecules within the first 1–2 nm. Whereas non-reacted MEA exhibits a preferential enrichment at the surface, the reacted

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species are preferentially dissolved in the bulk.[4] The results from this very elegant and convincing study are an important contribution to the general understanding of relevant adsorption/dissolution processes of CO_2 that have to be taken into account for modeling (e.g., mass-transport characteristics) and further developments of highly efficient CO_2 capture systems.

Finally, in this context one should also mention an interesting new class of compounds, namely the ionic liquids (ILs). Several research groups have been able to apply "standard" surface science techniques in studies with ILs under UHV conditions, in particular PES (see overviews in Refs. [5,6]). This is possible because of the extremely low vapor pressure of ILs at room temperature. Angle-resolved X-ray photoelectron spectroscopy (ARXPS) was used, and preferential surface enrichment and depletion effects of dissolved metal ions or catalysts in ILs could be demonstrated,[7] similar to the case of aqueous MEA solutions discussed above. Hence, ILs provide a new opportunity to study the properties of liquid surfaces and interfaces on a molecular level and in unprecedented detail by means of UHV-based techniques. Recently, it was even possible to prove by means of ARXPS that pronounced molecular orientation effects occur within the surface layer of an amine-functionalized model IL for CO_2 adsorption (see Figure 1).[8] As related ILs are very promising candidates for CO_2 capture,[9] PES on IL systems is expected to also provide important contributions to the field of CCS research in the near future.

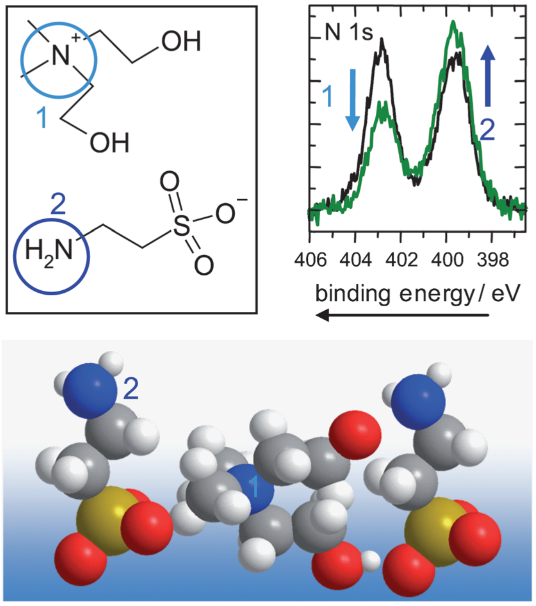

Figure 1. At the outermost surface of a model IL for CO_2 capture (top, left) the anions are oriented preferentially with the amine groups (2) pointing towards the vacuum and the SO_3^- tails towards the bulk phase (bottom structure). The surface enrichment of the amine groups is directly reflected by the signal increase with increasing surface sensitivity of the ARXP spectra (top right, N 1s region; more bulk-sensitive: black, more surface-sensitive: green).[8]

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