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The composition of aqueous interfaces as foundation for multiphase chemistry

The investigation and comprehension of physico-chemical processes in the atmosphere can be conceptualized as a three-legged stool, with atmospheric modeling, field observations, and molecular-level laboratory experiments acting as its mainstays [1]. Our research contributes specifically to the molecular-level understanding of the liquid-vapor interface. Among the most critical processes in atmospheric chemistry are phase transitions and chemical reactions. Radical species such as OH, O₃, and NO₂ play pivotal roles in atmospheric reactions, which ultimately influence crucial molecular reservoirs such as stratospheric ozone, while the concentration of cloud condensation nuclei (CCN) governs cloud and haze formation. Beside the known formation pathways for radical species and CCN in the gas and liquid phase, the impact of multiphase reactions on the budget of such key molecules is debated. This includes for example the oxidation of halides by ozone and the conversion of S(IV) and NO₂ to sulfate, which is essential for CCN formation [2, 3]. It has been suggested that the enhanced kinetics at the liquid-vapor interface cause haze events in polluted environments [2–4]. The reaction of S(IV) and NO₂ also leads to the formation of nitrous acid (HONO), which in turn yields to HO and NO radicals through photolysis, thus initiating extensive radical-driven reaction chains.

For multiphase processes involving gas and aqueous phases (Fig. 1), the initial step is the adsorption of the gas-phase reactant at the liquid-vapor interface. Subsequently, reactions may occur directly at the interface with a solute (heterogeneous reaction), or following diffusion into the bulk liquid. Reaction kinetics at the interface can differ markedly from those in the bulk [5, 6]. Due to the broken symmetry, the properties of the interface can differ from those in the bulk solution. Ions, for instance, typically avoid the interface due to image charge repulsion [7], whereas surface-active organic molecules – ubiquitous in atmospheric systems – accumulate at the liquid-vapor interface. However, such simplified descriptions fail to capture the full complexity of the interfacial composition, as they neglect solute-solute interactions. These interactions include: (1) Salting-out effects, where increased ionic strength promotes the organic molecules to the interface due to the competition for solvent molecules; [8, 9] (2) Electrostatic interactions, whereby ions are either repelled or attracted depending on the surfactant charge; [8, 10] (3) Surfactant-surfactant interactions, which can enhance surface accumulation; [11] and (4), shifts of the pH at the interface or differences in the surface activity of neutral and charged species can lead to apparently shifted acid-base equilibria [12].

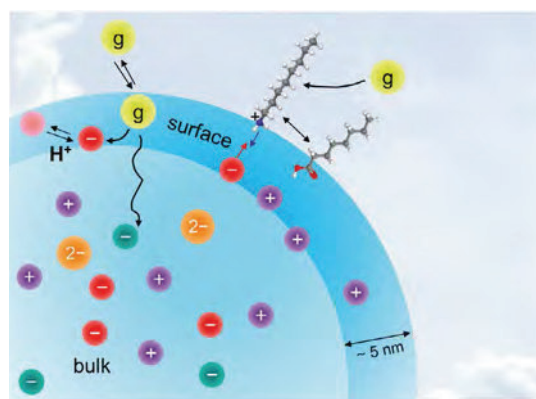


Fig. 1: The knowledge about the composition of the liquid-vapor interface is important for multiphase reactions.

The composition of the liquid-vapor interface defines the availability of potential reaction partners from the aqueous phase and might impact the adsorption rate of gases. In order to probe the composition of complex liquid-vapor interfaces (e.g., in seawater), chemically specific and surface-sensitive analytical techniques are required. This is the strength of X-Ray photoelectron spectroscopy (XPS), which in some cases also allows to quantify and obtain depth information with chemical specificity with sub-Ångström spatial resolution [13].

We have investigated the surface composition of various complex aqueous solutions with liquid microjet XPS [14]. One of these studies focused on the composition of S(IV) solutions at the liquid-vapor interface and compared it to the bulk composition (Raman spectroscopy) across a broad pH range. The acid-base chemistry of aqueous S(IV) is complex due to tautomerism (Fig. 2, bottom). From these data, we extracted both tautomer ratios (bisulfite/sulfonate) and individual pK_a values. While the interfacial and bulk compositions were largely consistent at pH > 4, we observed significant interfacial depletion of bisulfite under acidic conditions. At very low pH, only sulfonate and dissolved SO₂(aq.) were detected at the interface (Fig. 2, top). Molecular dynamics simulations attribute this behavior to ion pairing and an elevated deprotonation barrier of the sulfonic acid at the interface [15]. The detection of dissolved SO₂(aq.), enabled by removing the gas-phase signal using an electric field [16], marks a major advance in the in-situ observation of multiphase processes via XPS.

In a separate study, we examined ion-surfactant interactions in artificial seawater (including Na⁺, Cl[−], SO₄^{2−}, Mg²⁺, and Ca²⁺) with model surfactants with positive (octylammonium) and negative (octanoate) charge [8]. The salting out of the surfactants was directly observable by the increased carbon signal compared to a solution with a low ionic strength. Moreover, the surfactants significantly altered the interfacial concentration of

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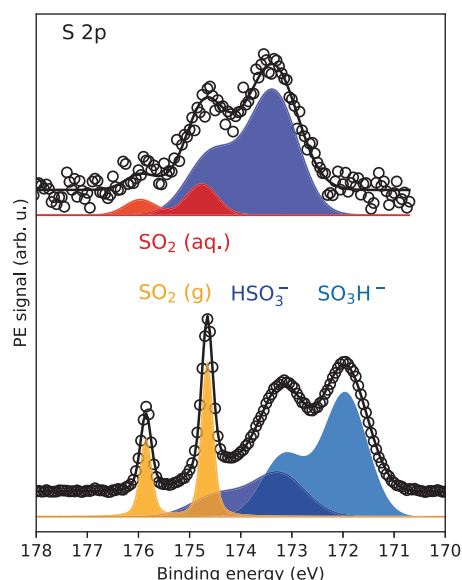


Fig. 2: Photoelectron spectra of aqueous S(IV) solutions (400 mM) at pH 0.4 (top) and 1.8 (bottom) [13].

ions, as illustrated in Cl 2p and S 2p spectra (Fig. 3). In principle, the increase or decrease of ion concentration can be justified by attractive or repulsive Coulomb interactions. Moreover, the enhancement of the signal strongly depends on the bulk concentration of the ion. Surprisingly, negatively charged sulfate ions were also enriched at the interface in the presence of negatively charged octanoate. Cooperative interactions involving divalent cations (e.g., Mg^{2+} , Ca^{2+}) may account for this unexpected behavior, which is subject to further studies.

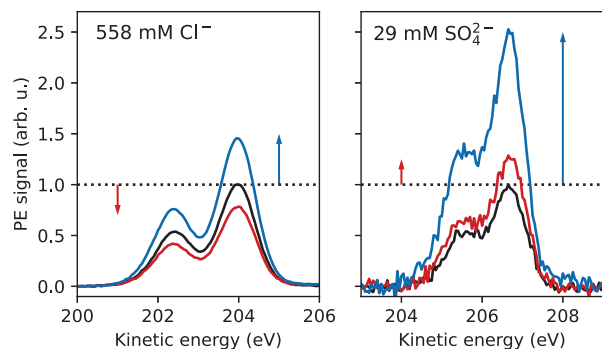


Fig. 3: Cl 2p and S 2p XPS spectra of artificial seawater (black), with additional octanoate (red), with additional octylammonium (blue). The arrows indicate the increase or decrease of the signal due to the presence of surfactant [7].

In summary, liquid microjet XPS is a powerful tool to investigate the composition of the liquid-vapor interface of complex solutions. It has revealed strong deviations of the interface properties from the bulk, which are important for the investigation of multiphase atmospheric reactions. However, the high flow rates of liquid jets limit the gas-liquid interaction time to ~0.1 milliseconds and consequently the in-situ observation of gas uptake and interfacial reaction dynamics to extremely fast reactions like the oxidation of bromide by ozone [17]. To overcome this limitation, ambient-pressure XPS [18] combined with advanced sample delivery methods is essential. One step forward was accomplished with the in-situ observation of the protonation of ammonia on ice surfaces by gaseous acetic acid [19]. Future research will focus on achieving

direct, time-resolved observations of multiphase reactions at the liquid-vapor interface under atmospherically relevant conditions.

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Tillmann Buttersack is a research associate at the Fritz Haber Institute since 2020. His work focuses on investigating the composition of complex aqueous interfaces and how these can be modified, particularly in the context of multiphase reactions, using photoelectron spectroscopy. He studied chemistry at the TU Braunschweig, where he also earned his doctorate in 2016 under the supervision of Prof. Sigurd Bauerecker. His doctoral research focused on the freezing behavior of supercooled water droplets. Thereafter, he was awarded a PostDoc scholarship by the Czech Academy of Sciences and joined the group of Prof. Pavel Jungwirth. During this time, he began studying the transition of aqueous and ammonia electrolyte solutions to metallic states using photoelectron spectroscopy. This line of research he continued in the group of Prof. Stephen Bradforth at the University of Southern California.

