

## Regular Article

## A set-up for simultaneous measurement of second harmonic generation and streaming potential and some test applications



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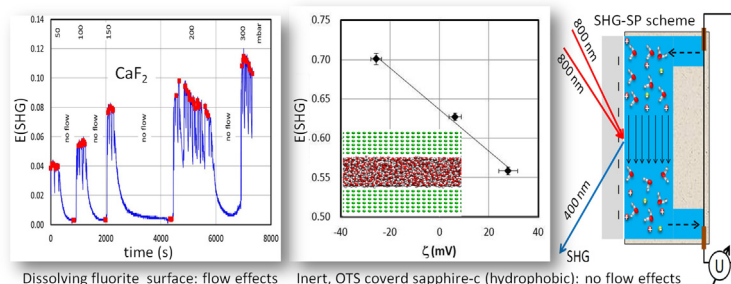
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## GRAPHICAL ABSTRACT



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## ABSTRACT

We present a measurement cell that allows simultaneous measurement of second harmonic generation (SHG) and streaming potential (SP) at mineral-water interfaces with flat specimen that are suitable for non-linear optical (NLO) studies. The set-up directly yields SHG data for the interface of interest and can also be used to obtain information concerning the influence of flow on NLO signals from that interface. The streaming potential is at present measured against a reference substrate (PTFE). The properties of this inert reference can be independently determined for the same conditions. With the new cell, for the first time the SHG signal and the SP for flat surfaces have been simultaneously measured on the same surface. This can in turn be used to unambiguously relate the two observations for identical solution composition. The SHG test of the cell with a fluorite sample confirmed previously observed differences in NLO signal under flow vs. no flow conditions in sum frequency generation (SFG) investigations. As a second test surface, an inert (“hydrophobic”) OTS covered sapphire-c electrolyte interface was studied to verify the zeta-potential measurements with the new cell. For this system we obtained combined zeta-potential/SHG data in the vicinity of the point of zero charge, which were found to be proportional to each other as expected. Furthermore, on the accessible time scales of the SHG measurements no effects of flow, flow velocity and stopped flow occurred on the interfacial water structure. This insensitivity to flow for the inert surface was corroborated by concomitant molecular dynamics simulations. Finally, the set-up was used for simultaneous measurements of the two properties as a function of pH in automated

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titrations with an oxidic surface. Different polarization combinations obtained in two separate titrations, yielded clearly different SHG data, while under identical conditions zeta-potentials were exactly reproduced. The polarization combination that is characteristic for dipoles perpendicular to the surface scaled with the zeta-potentials over the pH-range studied, while the other did not. The work provides an advanced approach for investigating liquid/surface interactions which play a major role in our environment. The set-up can be upgraded for SFG studies, which will allow more detailed studies on the chemistry and the water structure at a given interface, but also the combined study of specific adsorption including kinetics in combination with electrokinetics. Such investigations are crucial for the basic understanding of many environmental processes from aquatic to atmospheric systems.

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## 1. Introduction

Solid-liquid interfaces play a major role in many contexts from industry to aquatic and atmospheric environmental topics. At most interfaces protons and hydroxide ions are involved in the interfacial charging, frequently as potential/charge determining components.

Surface charge and potential due to these ions are crucial in understanding and modelling environmental and industrial processes. The “inner” surface potential is maybe the most important but least accessible property of the electrical double layer and the origin of it. As a consequence its determination via spectroscopic methods some 25 years ago [1] continues to be of interest. Recent examples address for example how surface potential affects the ice nucleation properties of atmospheric minerals [2–5], which cannot be investigated by classical solid solution approaches. Charging at classical solid solution interfaces has been traditionally studied by electrokinetics and potentiometric methods [6–8]. Less frequently applied approaches involve non-linear optical (NLO) methods [9–11] that are non-invasive and can cover salt concentrations beyond those accessible to the classical methods [12]. The latter are appropriate either at the higher salt levels (potentiometric titrations, more salt means increased proton interaction) or lower salt concentrations (electrokinetics, less salt means reduced screening). A current discussion exists on the meaning of NLO signals from solid-liquid interfaces concerning amongst other issues the extent of various electrical double layer contributions [12–15]. The pioneering work of Ong et al. on fused silica/aqueous electrolyte interfaces [1] related second harmonic generation (SHG) data to “surface potential”. The SHG signal depends on the second order nonlinear susceptibility,  $\chi^{(2)}$ , of the interfacial molecules that are asymmetrically orientated at the interface, and the third order nonlinear susceptibility,  $\chi^{(3)}$ , of the bulk water molecules oriented due to the static electric field of a charged surface [1,12,16]. Attempts to quantify are available [12,14,15], but in particular the  $\chi^{(3)}$  contribution, which is related to the static electric field at the interface, will strongly depend on what kind of surface potential is involved. Concerning the salt dependence of the NLO signal, the strong effect of salt and the ability of a Gouy-Chapman approach to model it would rather point to the electrokinetic/DLVO potential (the diffuse layer potential) than to the “inner” surface potential. A more detailed discussion associated with typical experimental data from the literature can be found in [Supplementary Information](#).

In some of the available surface complexation models (single plane models) only one potential occurs, which then automatically is the surface potential. In multi-layer models, different distinct potentials occur and these have to be clearly distinguished. The most advanced models attempt to cover the complete double layer sometimes from a truly mechanistic point of view [17]. Besides the question which interfacial potential should be used to interpret NLO experiments (i.e. surface potential or diffuse layer potential

or both?), the comparison of a set of data on single crystal surfaces suggests that this might for example depend on how the experiment is carried out. SHG data on sapphire-c (the basal, i.e. (0 0 0 1), plane of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>) obtained through the liquid by Fitts et al. [18] produced a point of zero charge identical to independently measured isoelectric points [19–21]. Thus the data by Fitts et al. would mimic the zeta-potential vs. pH curves obtained by others [20], whereas SHG measurements through the crystal [21] instead produced data that are clearly reminiscent of the expected “inner” surface potential vs pH curve [20,22], see SI. Unfortunately, such seemingly contradictory results can be conveniently explained by differences in sample origin or preparation [21]. Thus ambiguity will remain if one attempts to compare data from different laboratories. The solution to this is to measure the data of interest simultaneously on one sample and under the same conditions to avoid this ambiguity.

While previous modeling work reporting NLO data has been involving purely diffuse layer models mainly (sometimes in exchange with a constant capacitance model, i.e. another single plane model, at higher salt levels), recent work [23] has used, in the case of a charged water interface, an electrical double layer model that involves separation of the NLO signal contributions originating from the “bonded interface layer (BIL)” from those due to the diffuse layer. The former was attributed to the  $\chi^{(2)}$  contribution to the total resonant susceptibility and might be associated with the Stern layer, while the latter was associated to the diffuse layer. The  $\chi^{(3)}$  contribution in this model continues to be related to the electric field and most of the available attempts to quantification finally resort to a Gouy-Chapman type equation. This usually concerns data at constant pH, with variation of salt level, and although exceptions exist [24,25], most modelling studies involve erroneous assumptions, namely that proton related surface charge density does not change with the concentration of background electrolyte concentration [14] or the concentration of specifically adsorbing ions [25], see also SI for examples of typical experimental behavior.

The dependence of NLO signals on salt level is surprisingly well described by Gouy-Chapman type approaches, while it is known from classical work on oxide interfaces that this approach fails to correctly describe the protonation/deprotonation behaviour even at low salt levels. As a consequence the purely diffuse layer approach can hardly yield accurate values for the “inner” surface potential. From this point of view NLO signals should rather scale with DLVO (diffuse layer) potentials as obtained from Stern-Gouy-Chapman models.

To come to a more profound understanding of for example the relation between the NLO and the classical (electrokinetic) data simultaneous measurements of electrical double layer properties and NLO signals under identical conditions and for the same sample are required. The aim of the present work was therefore to design a cell capable of measuring SHG and streaming potential (SP) for flat surfaces. Although flat surfaces may have the

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