Electronic Supplementary Material (ESI) for Analyst.


Supporting Information

# Utility of Polarization Modulation Infrared Reflection Absorption Spectroscopy (PM-IRRAS) in Surface and *In-situ* Studies: New Data Processing and Presentation Approach

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**PM-IRRAS Spectrometer components and working principle**

This is a Brukers' Tensor 37 FTIR spectrometer equipped with PMA 50 chamber for spectroelectrochemical experiments.

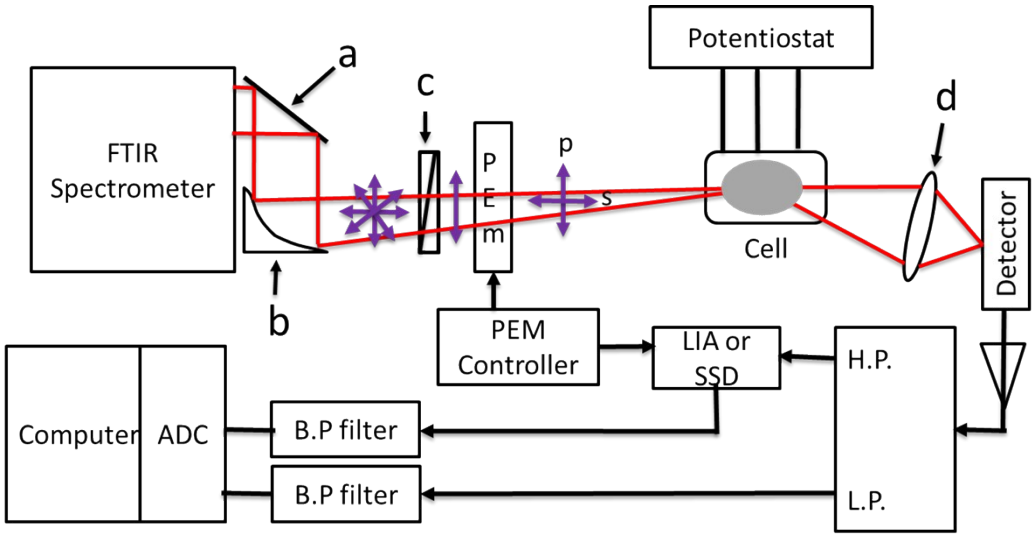


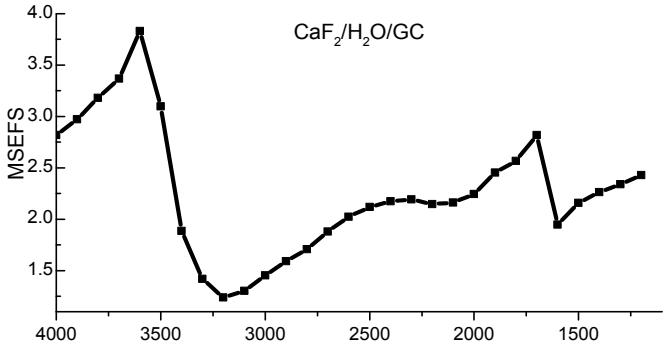

**Figure S1**: PM-IRRAS instrumentation schematic showing IR radiation optical path (red color) the positions for the mirrors (flat (a) and parabolic (b)), static polarizer (c), photoelastic modulator (PEM), spectroelectrochemical cell, focusing lens (d), detector, and data processing electronics, i.e., High Pass (H.P.) and Low Pass (L.P.) filters, Band Pass (B.P) filters, and Analog to Digital Converters (ADC). The non-polarized IR radiation from the spectrometer is reflected by a flat mirror (a) to a parabolic mirror (b) which converges the radiation to its focal point at the cell electrode via the static polarizer (c) and PEM. The static polarizer generates p-polarized light which is modulated by the PEM controller at 100 kHz to generate s-polarization with respect to the electrode surface. The p- and s-radiation go through the cell, and then are focused with the lens (d) to the detector at a pre-determined optimum angle. The detected signal is amplified and split into two channels (see text for details).

The non-polarized IR beam from the spectrometer is reflected by a flat mirror (a) at 45º to a parabolic mirror (b) which converges the radiation to its focal point (f = 160 mm) at electrode in the cell via the static metal grid polarizer (1-inch diameter ZnSe substrate, Bruker) and photoelastic modulator (PEM). The static polarizer generates p-polarized light which is then modulated by the PEM controller at 100 kHz to generate both p- and s-polarizations with respect to the electrode surface. The p- and s-radiations go through the cell (sample) and are reflected at a pre-determined optimum angle (*vide infra*) by the electrode via a focusing lens (1-inch diameter ZnSe, (d)) to the detector. The detected signal is amplified

and split into two signals; the absolute difference signal $|J_2(R_p - R_s)|$ and the average signal $(R_p + R_s)/2$. The (absolute) difference signal goes through the H.P. filter into the demodulator (LIA or SSD) where a reference signal from the PEM controller is provided and then sent through the B.P. filter.[5] The average signal obtained at the L.P. and is passed directly into B.P. filter. The signals from the two channels are digitized and saved separately as interferograms for further processing by the user. The signal processing electronics, High Pass (H.P.) and (L.P.) filters, Band Pass (B.P.) filters, Analog to Digital Converter (ADC), and the computer are part of the Bruker setup. Electrode potential was controlled by a BioLogic VSP potentiostat equipped with the EC-Lab software (Bio-Logic Science Instruments SAS, Claix, France).

**Optimum experimental set up conditions**

Figure S2 demonstrates that setting the angle of incidence to the range between 60 and 64 degrees and keeping the thin-cavity distance as small as possible should yield the best MSEFS at the surface. The obtained values of the MSEFS are about twice lower compared to highly reflective metal surfaces for which MSEFS reaches 4x enhancement. However, the values close to the magnitude of 2 indicate that there should be at least 2x enhancements with respect to the incident light.



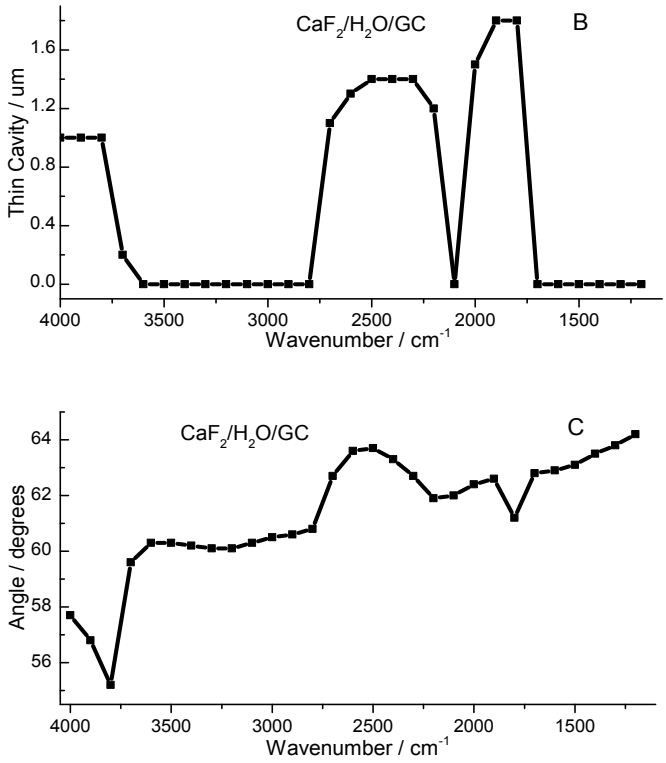



**Figure S2**: Coordinates of the global maximum in the MSEFS for $CaF_2/H_2O$/GC system calculated in the mid infrared region for the beam of ±3º convergence (Figures with values obtained with a convergence of 5 was used.) Panels A, B, and C show the optimum values of the MSEFS, the electrolyte thin cavity thickness and the angle of incidence, respectively.