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Q-Sense

[Technology Note] 1

Quartz Crystal Microbalance with Dissipation (QCM-D)

Q-Sense has developed a patented technology for surface analysis called Quartz Crystal Microbalance with Dissipation monitoring (QCM-D). QCM-D enables real-time, label free measurements of molecular adsorption and/or interactions on various surfaces. In addition to adsorbed mass (ng/cm^2 sensitivity), measured as changes in frequency of the quartz crystal, the dissipation parameter (D) provides novel insights regarding structural (viscoelastic) properties of adsorbed layers.

History

Traditional Quartz Crystal Microbalance (QCM) has been used for more than 50 years to analyze mass changes on rigid surfaces, most effectively in air or vacuum. QCM relies on a voltage being applied to a quartz crystal causing it to oscillate at a specific frequency. Changes in mass on the quartz surface are related to changes in frequency of the oscillating crystal through the Sauerbrey relationship:

$\Delta m = -C \cdot \Delta f$ (Sauerbrey relation)

The Sauerbrey relation is valid for rigid, evenly distributed, and sufficiently thin adsorbed layers. However, for soft or viscoelastic films that do not fully couple to the oscillating crystal, the Sauerbrey relationship underestimates the mass and thus another method of analysis is needed to fully characterize such materials.

Dissipation

QCM-D measures both frequency and dissipation of the quartz crystal. Dissipation occurs when the driving voltage to the crystal is shut off and the energy from the oscillating crystal dissipates from the system. D is defined as:

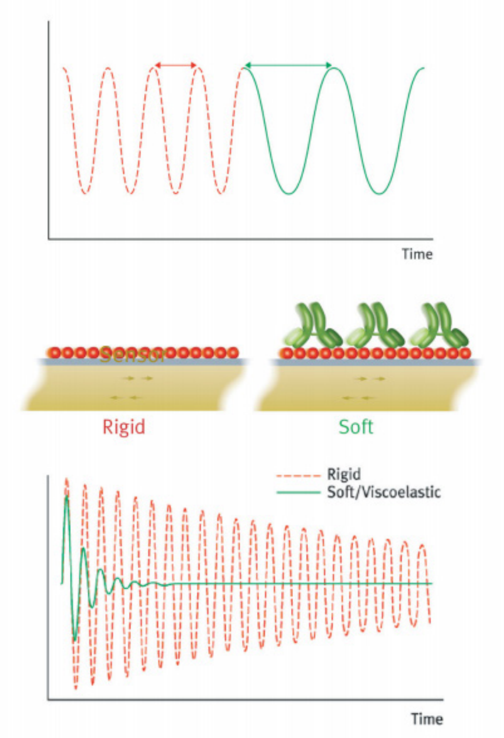
$D = E_{lost} / 2\pi E_{stored}$

where E_{lost} is the energy lost during one oscillation cycle and E_{stored} is the total energy stored in the oscillator. Figure 1 shows how the frequency of the oscillating quartz crystal changes with the mass on the sensor. Figure 2 shows the dissipation for a soft (green) and rigid (red) film when the driving voltage is turned off. This procedure can be repeated over 200 times per second, which gives QCM-D great sensitivity and high resolution.

Coupled water

When molecules adsorb to an oscillating quartz crystal, water (or other liquid) couples to the adsorbed material as an additional dynamic mass via direct hydration and/or entrapment within the adsorbed film. Thus, the layer is sensed as a viscoelastic "hydrogel" composed of the molecules and the coupled water. By measuring the dissipation, one can determine if the adsorbed film is rigid or viscoelastic (soft) which is not possible looking only

[Figure 1]: The top diagram illustrates how the frequency of the oscillating sensor crystal (gold) changes when the mass is increased by addition of a molecular layer. Here antibodies (green) are added to a layer of protein (red).



[Figure 2]: The bottom diagram illustrates the difference in dissipation signal generated by a rigid (red) and soft (green) molecular layer on the sensor crystal.

at the frequency response. The amount of water in an adsorbed film can be as high as 95% depending on the type of material and the surface you are studying. For instance, picture elongated molecules - if they adsorb flat on the surface, little water would couple to the molecules and the film would have a low Dissipation value. However, if they adsorb standing up at the surface, lots of water will couple to the film and it would be highly dissipative. In addition to such structural analysis, QCM-D also allows real-time, kinetic analysis of both mass and viscoelastic changes.

Analysis using modeling

Dissipation measurements enable qualitative analysis of the structural properties of adsorbed molecular layers. Different materials can easily be compared and one can ascertain if the Sauerbrey relation will accurately approximate the adsorbed mass or not. Furthermore, the QCM-D technology allows quantitative analysis of the thickness, shear elastic modulus, and viscosity of the adsorbed films whereas these measurements are well beyond the Sauerbrey regime. This is achieved by combining frequency (f) and dissipation (D) measurements from multiple harmonics (overtones) and applying simulations using a Voigt-based viscoelastic model included in Q-Sense software (figure 3). If the adsorbed film is assumed to have a uniform thickness and density, f and

D can be described as functions of:

n – overtone number

d – thickness

ρ – density

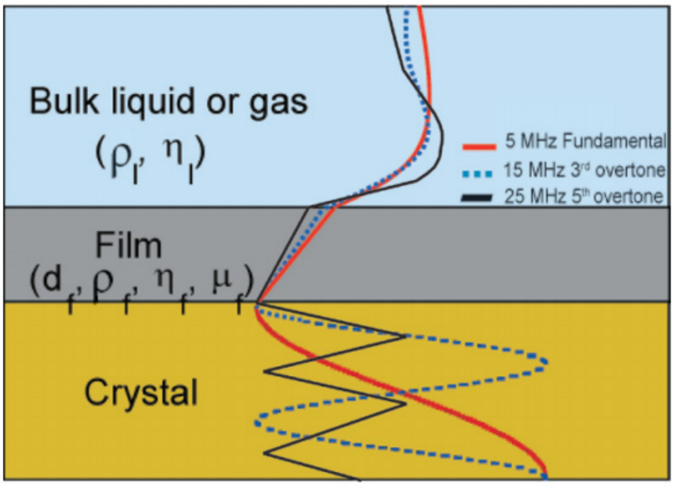
η – viscosity

μ – elasticity

By fitting experimental frequency and dissipation data from 2 or more harmonics, the unknown parameters can be extracted. This model has been successfully used in many publications studying a variety of experimental systems; however, it is important to note that it is a model with certain assumptions being made.

Conclusions

QCM-D enables real-time measurements of both mass and structural properties of molecular layers. Measuring the dissipation parameter allows accurate analysis of soft films that do not obey the linear relation between change in frequency and change in mass.



[Figure 3]: The Voigt based viscoelastic film model, describing the propagation and the damping of acoustic waves in a single uniform viscoelastic adsorbed film in contact with a Newtonian bulk liquid.

References:

Hundreds of publications illustrate the use of QCM-D for different applications; below are some references for further reading about QCM-D and data modeling.

A basic explanation of the QCM-D technology is found in Energy Dissipation Kinetics for Protein and AntibodyAntigen Adsorption under Shear Oscillation on a Quartz Crystal Microbalance in Langmuir 1998, 14, 729-734 by Hook et al. Interpretation of QCM-D data and applying the viscoelastic model is well described in:

Variations in Coupled Water, Viscoelastic Properties, and Film Thickness of a Mefp-1 Protein Film during Adsorption and Cross-Linking: A Quartz Crystal Microbalance with Dissipation Monitoring, Ellipsometry, and Surface Plasmon Resonance Study in Anal. Chem. 2001, 73, 5796-5804 by Hook et al.

Analysis of Interpenetrating Polymer Networks via Quartz Crystal Microbalance with Dissipation monitoring in Langmuir. 2005 Jun 7;21(12):5529-36 by Irwin et al.

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