Designing experiments for an application in laser and surface Chemistry

Ralph Mansson♠, Alan Welsh♠, Jeremy Frey♣ and Lefteris Danos♣
♠ Faculty of Mathematical Studies, ♣ Department of Chemistry, University of Southampton, Southampton, SO17 1BJ, United Kingdom

Introduction to Second Harmonic Generation Experiments

The investigation of the behaviour of interfaces between two phases, for example the surface of a liquid or the interface between a solid and a liquid is an important part of modern chemistry with implications in surfactants, catalysis, membranes, and electrochemistry. Interfacial second harmonic generation (SHG) experiments provide a convenient and effective method of investigating the structure and dynamics of these interfaces even in the presence of overlying bulk phases.

When an intense laser beam impinges on a surface a small fraction of the radiation is converted to the second harmonic. Only at the surface where there is no local centre-of-symmetry can the harmonic generation take place. The intensity of the harmonic signal and its polarisation characteristics can be related to the concentration and orientation of molecules adsorbed at the interface. The interfacial selectivity enables the SHG technique to be used to investigate solid/liquid or liquid/liquid interfaces in situ.

The ultimate objective of many SHG experiments is to obtain the components of $\boldsymbol{\chi}$, the surface second order susceptibility tensor, and to interpret them in terms of molecular behaviour. This process requires several stages of model building. The first step for experiments at an interface can be achieved within a phenomological model with unknown parameters A, B, and C.

Figure 1: Second harmonic generation experimental rig.

Statistical Analysis of SHG Experiments

In a SHG experiment pulsed laser radiation at 532nm is focused to and reflected from the liquid interface and the intensity of the small fraction of the harmonic radiation generated at 266nm is recorded as a function of the polarisation angles of the fundamental and harmonic beams. For each pair of polarisation angles γ_j and Γ_k, the laser is fired 2000 times and the intensity of the reflected light is recorded after each shot. The background intensity is subtracted from the measurements which are then averaged and normalised to produce the response Y_{kj}, referred to as the observed intensity. The observed intensity Y_{kj} is an observation on the theoretical intensity $|E_{kj}|^2$, where, for the molecules considered by the experimenters, we can write E_{kj} as

$$E_{kj} = E_{s,j}\sin(\Gamma_k) + E_{p,j}\cos(\Gamma_k)$$

with

$$E_{p,j} = A\cos^2(\gamma_j) + B\sin^2(\gamma_j) \qquad \text{and} \qquad E_{s,j} = C\sin(2\gamma_j).$$

The unknown parameters A, B, and C are complex, and conveniently parametrised as 3 pairs of real coefficients. We use the Euler parametrisation of complex numbers in which we express the complex coefficients in terms of their magnitudes and phase angles as $A = r_a\exp(i\phi_a)$, $B = r_b\exp(i\phi_b)$, and $C = r_c\exp(i\phi_c)$. The model is overparametrised ($\boldsymbol{\theta} = (r_a, r_b, r_c, \phi_a, \phi_b, \phi_c)^T$) because the overall phase of the experiment is not determined. There are 5 independent parameters in the model, and we introduce the constraint $\phi_a = 0$ so that A is real.

Choice of Design Points

In the current experimental setup the output polarisation angle, Γ_k, is restricted to three settings $0°$, $45°$, and $90°$ while the input polarisation angle, γ_j, can be set to angles at one degree increments between $0°$ and $90°$. The design used for a SHG experiment measures the intensity at fourteen equally spaced points (approximately $7°$ apart) for each of the three output polarisation angles. We are interested in whether fewer than 42 points can be used in the experiment (because experiments need to run rapidly before the sample degrades), and if there are a better set of combinations of polarisation angles to use.

To investigate these questions we use a set of parameter estimates from a model fitted to SHG data for the molecule Phenylalanine. For this data set, parameter estimates are $\hat{\boldsymbol{\theta}} = (0.889, 0.317, 0.588, 0, 1.142, 0.301)$. Locally optimal designs for this set of parameter estimates can be identified using a criterion based on the determinant of the variance covariance matrix for different sized designs. The determinant is adjusted for the number of parameters (p) and design points (n), i.e. $det^{(1/p)}/n$.

Number of Points	Variances (σ^2) $\hat{r}_a$	$\hat{r}_b$	$\hat{r}_c$	$\hat{\phi}_b$	$\hat{\phi}_c$	Determinant measure
42(current)	0.08	0.74	0.11	19.87	39.26	0.023
42	0.04	0.31	0.09	10.80	19.21	0.014
32	0.05	0.41	0.11	14.05	24.95	0.023
21	0.08	0.62	0.18	21.46	37.83	0.054
14	0.11	0.83	0.28	35.03	57.86	0.123

The table shows variances for the five parameter estimates and an adjusted determinant. The precision of the parameter estimates is based on $\hat{\sigma}^2$, and if this does not increase substantially, the variances of parameter estimates will not be greatly increased with the removal of ten design points. These locally optimal designs also suggest that the two angles ϕ_b and ϕ_c are poorly estimated in comparison to the three magnitudes.

Influence of Parameter Estimates on Design Points

We can identify a locally optimal design for a given set of parameter estimates. If we do not have accurate estimates of the parameters then it is sensible to select a design that performs well for reasonable choices of parameters rather than a design that is optimal only for a given set of parameters $\boldsymbol{\theta}$.

The locally optimal designs suggest that there are approximately six distinct design points of interest. We can investigate the effect of varying the parameter estimates on the location of these design points for the locally optimal designs. We can cover a sensible range of parameter values by choosing three values for each of the five parameters, which corresponds to $2^5 = 243$ distinct designs when the parameter values are considered together.

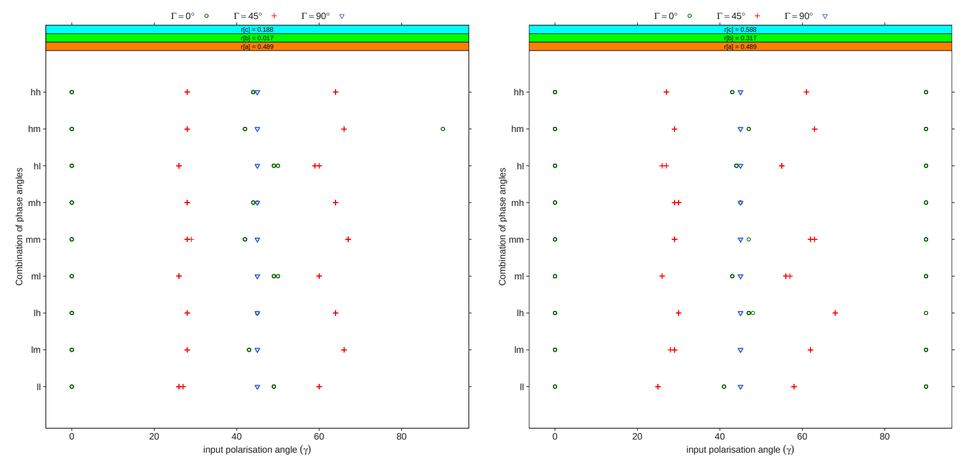

Figure 2: Examples of design points for locally optimal designs under different sets of parameter estimates - the strip at the top gives values for the magnitudes. The nine rows in each plot correspond to nine pairs of the three values of each phase angle.

We can identify important design points for all combinations of parameter estimates. Examples of these designs are given in Figure 2. Each row corresponds to a different set of parameters - the input polarisation angle of the design points is shown on the horizontal axis with different symbols identifying the three output polarisation angles. When r_b is small (0.017 in this example) there are five rather than six distinct design points that are identified. The graphs suggest that the input polarisation angle of three of the six points are affected by the parameter estimates.

Conclusions and Proposed Design

We recommend the following combinations of polarisation angles to investigate a molecule where there is no information on parameter estimates. The graph on the left in Figure 3 is the current factor settings for a SHG experiment, and the proposed new design is on the right. For $\Gamma = 0°$ and $\Gamma = 90°$ it is not necessary to collect data corresponding to input angles between $15°$ and $35°$ and between $60°$ and $80°$. Extra points are included to check that the data is close to zero for values of (γ_j, Γ_k) where the theoretical model is zero. The third output angle $\Gamma = 45°$ requires equally spaced points between $\gamma = 15°$ and $\gamma = 75°$.

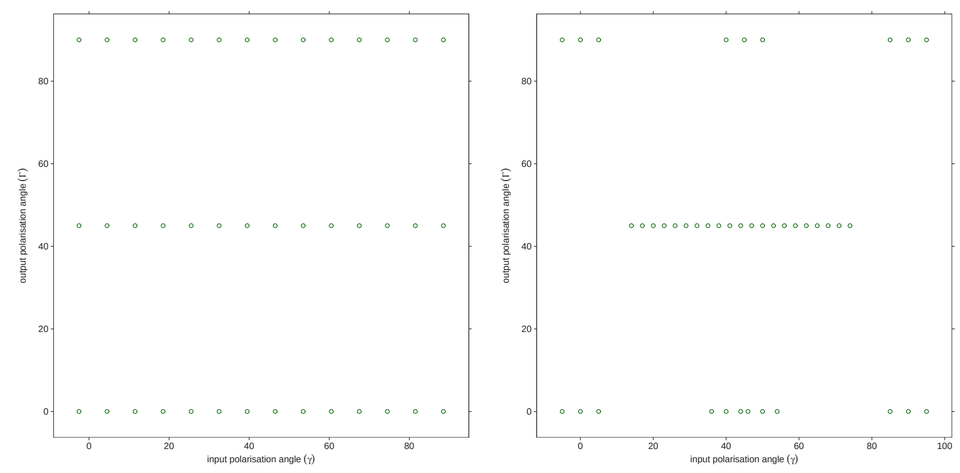

Figure 3: Current design and recommended choice of designs points for investigating a new molecule.

There is a locally optimal design for each of the 243 sets of parameter estimates, and we can compare how efficiently the current and new designs estimate the model parameters compared to the locally optimal design. Computing the ratio of determinants for the locally optimal and more general design gives a measure of the loss of efficiency in parameter estimation. For the proposed design, this loss is between 10% and 45% for all 243 situations. The current design used for a SHG experiment performs worse than this new design for the majority of the combinations of parameter estimates.

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