Probing water structure and transport in proton exchange membranes
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CHAPTER 2
THEORETICAL BACKGROUND

2.1 Raman scattering

When light irradiates a material, its energy may be transmitted, absorbed or scattered. As shown in Figure 2.1 [31], absorption of an incident photon whose frequency is the same as the molecular vibrational frequency results in a transition between two energy levels – the ground state and excited state (Figure 2.1a). Scattering, on the other hand, is stimulated by an incident photon with a frequency that is not matched with a molecular vibrational frequency and leads to Rayleigh (elastic) scattering and Raman (inelastic) scattering.

Figure 2.1 Energy diagram of: a) absorption; b) Rayleigh scattering; c) Stokes Raman scattering with scattered photon energy of \( \hbar \omega_0 - \hbar \omega_1 \); d) anti-Stokes Raman scattering with scattered photon energy of \( \hbar \omega_0 + \hbar \omega_1 \). \( \hbar \omega_0 \) is the energy of an incident photon. \( \hbar \omega_1 \) is the energy difference between the ground level and the first level.
In Rayleigh scattering, a molecule is excited to a virtual state and “instantaneously” returns to the ground state. The scattered photon has the same energy as the incident photon (Figure 2.1b); while in Raman scattering, the scattered photon has less (Figure 2.1c, Stokes Raman scattering) or more (Figure 2.1d, anti-Stokes Raman scattering) energy compared to the incident photon. The scattered photon energy in Raman scattering contains unique vibrational information of the molecule.

From a classical physics perspective, molecular vibrations are Raman active when there is a change in the molecular polarizability with nuclear coordinate for the bound nuclei. The molecular polarizability is the deformability of the electrical environment of a molecule by an external electric field and is generally a function of the nuclear coordinates (and frequency, which is ignored for simplicity here). Variation of the polarizability ($\alpha$) for a small displacement with vibrations of the molecules with the nuclear coordinate can be expanded to the first order in Taylor series as:

$$\alpha(Q) = \alpha_0 + \left(\frac{\partial \alpha}{\partial Q}\right)_0 Q$$  \hspace{1cm} \text{Eq 2.1}

where $\alpha_0$ is equilibrium polarizability when the atoms of a molecule are at the equilibrium position with respect to vibrational motion, $Q$ is a normal vibrational coordinate and $\left(\frac{\partial \alpha}{\partial Q}\right)_0$ is vibrational modulation of molecular polarizability with respect to $Q$ around the equilibrium position. If we assume $Q$ varies sinusoidally with a nuclear vibration ($\omega_{vib}$), we can write $Q$ as:

$$Q = Q_0 \cos(\omega_{vib} t + \varphi)$$  \hspace{1cm} \text{Eq 2.2}

where $\varphi$ is a phase factor and $Q_0$ is the amplitude.

$$\mu = \alpha(Q)E(t)$$  \hspace{1cm} \text{Eq 2.3}

The induced dipole moment ($\mu$) represents the light-molecule interaction when looking at the charge in the local electrical environment caused by the incident radiation on the molecule. $\mu$ is the
product of the polarizability ($\alpha$) and external electric field $E(t)$ of the incident photons (Eq 2.3) to the first order and can be rewritten as:

$$\mu = \alpha_0 E(t) + \left( \frac{\partial \alpha}{\partial Q} \right)_0 Q_0 \cos(\omega_{\text{vib}} t + \varphi) E(t)$$

Eq 2.4

Substitution of $E(t) = E_0 \cos(\omega t)$ to Eq 2.4 yields

$$\mu = \alpha_0 E_0 \cos(\omega t) + \left( \frac{\partial \alpha}{\partial Q} \right)_0 Q_0 \cos(\omega_{\text{vib}} t) E_0 \cos(\omega t)$$

Eq 2.5

where I have dropped the phase factor ($\varphi$) for convenience. Using a trigonometric identity, Eq 2.5 can be reformatted to as

$$\mu = \alpha_0 E_0 \cos(\omega_0 t)$$

$$+ \frac{1}{2} \left( \frac{\partial \alpha}{\partial Q} \right)_0 Q_0 E_0 [\cos(\omega_0 - \omega_{\text{vib}}) t + \cos(\omega_0$$

$$+ \omega_{\text{vib}}) t]$$

Eq 2.6

Rayleigh scattering arises from the dipole oscillating at $\omega_0$ induced by field with the finite equilibrium polarizability of the molecular while the Raman scattering arises from the dipole oscillating at $\omega_0 \pm \omega_{\text{vib}}$. Note, the necessary condition for Raman scattering is that the term

$$\left( \frac{\partial \alpha}{\partial Q} \right)_0 \neq 0.$$

The intensity is linearly dependent on the number of scattering molecules ($N$) and can be used to quantify the abundance of the corresponding molecules. Increasing the laser flux power density ($I_0$) or using an incident laser with a shorter wavelength (due to the overall reduced Rayleigh scattering) can also increase the Raman intensity. The intensity of the spontaneous Raman intensity for a given molecular vibration is given as [68]:

$$I_{\text{Raman}} \propto \omega_0^4 N I_0 \left( \frac{\partial \alpha}{\partial Q} \right)^2$$

Eq 2.7

where $N$ is the number of the scattering molecules.

Practically, a molecular vibration excited by an incident laser at a frequency of $\omega_0$ produces a Raman scattering intensity as given by Eq 2.8. [69]
where $N$ is the number of scattering molecule, $A$, $\Omega$, and $\Gamma$ are the amplitude, frequency and line width of the vibration mode of the molecule.

## 2.2 Coherent anti-Stokes Raman scattering (CARS) spectroscopy

As the Raman cross-section for spontaneous Raman is very low and only $\sim 1$ out of $10^7$ incident photons are inelastically scattered [69], long acquisition times are typically required to obtain a spectrum with a high signal-to-noise ratio. Moreover, the Stokes Raman signal is often overwhelmed by single-photon fluorescence (also Stokes shifted relative to incident light) that can be orders of magnitude more prominent. [69] One solution to the low Stokes Raman signal is to use nonlinear excitation such as coherent anti-Stokes Raman scattering (CARS) spectroscopy, which provides a signal enhancement of up to 6 orders of magnitude compared to conventional Raman, and has many other advantages over the spontaneous Raman spectroscopy as outlined below. The nonlinear excitation allows one to acquire a spectrum much more quickly than conventional Raman for a given signal-to-noise ratio, on the order of milliseconds rather than seconds per spectrum – when processed appropriately (as described in section 2.3). The CARS technique is intrinsically optically sectioned (due to the nonlinear nature), and CARS emission is directional. Moreover, the contamination of fluorescence is minimized in CARS, since the detected signal is blue-shifted.

Generating a CARS signal involves interaction of three photons – 1) pump beam at a frequency of $\omega_{pu}$, 2) the Stokes beam at a frequency of $\omega_s$, and 3) probe beam $\omega_{pr}$ – with the sample (Figure
Coherent anti-Stokes Raman scattering (CARS) spectroscopy

The frequency of the generated CARS signal ($\omega_{as}$) is dependent on the pump, Stokes and probe beams as described below:

$$\omega_{as} = \omega_{pu} - \omega_{s} + \omega_{pr}$$  \hspace{1cm} \text{Eq 2.9}

The CARS setup in this work used a degenerate configuration with the pump and probe at the same frequency, thus the relationship of $\omega_{as}$ with the frequencies of incident photons is simplified to the equation below:

$$\omega_{as} = 2\omega_{pu} - \omega_{s}$$  \hspace{1cm} \text{Eq 2.10}

Figure 2.2 CARS energy diagram: a) vibrational resonant scheme for single-line CARS; b) nonresonant electronic contribution; c) vibrational resonant scheme for multiplex CARS (also called broadband CARS), where multiple transitions are addressed simultaneously.

The anti-Stokes process is resonantly enhanced when the frequency difference, $\omega_{pu} - \omega_{s}$, matches the frequency of a vibrational resonance ($\omega_{vib}$) of a molecule, thereby giving a strong signal corresponding to the vibrational modes in the sample. However, the CARS signal does not directly provide quantitative composition information. [70] Additional data processing for the CARS signal.
CHAPTER 2  Coherent anti-Stokes Raman scattering (CARS) spectroscopy must be conducted for extracting the quantitative chemical information. The CARS signal \( I_{\text{CARS}} \) is proportional to the squared modulus of the third-order induced polarizability \( P^{(3)} \) as shown below:

\[
I_{\text{CARS}} \propto |P^{(3)}|^2 \quad \text{Eq 2.11}
\]

and \( P^{(3)} \) is proportional to the squared modulus of the complex third-order susceptibility \( \chi^{(3)} \) as:

\[
|P^{(3)}|^2 = |E_{pr}|^2 |E_{pu}|^2 |E_s|^2 |\chi^{(3)}|^2 \quad \text{Eq 2.12}
\]

where \( E_{pu} \) and \( E_{pr} \) are the pump and probe electric fields, \( E_s \) is the Stokes electric field.

The complex third-order susceptibility \( \chi^{(3)} \) contains two terms (Eq 2.13): 1) the resonant part containing the quantitative and chemically specific information about the sample including a real component and an imaginary component, and 2) the nonresonant \( \chi^{(3)}_{NR} \) part depending solely on the electronic properties of the sample. The \( \chi^{(3)}_{NR} \) can be assumed to be strictly real and is generally considered to be frequency-independent.

\[
\chi^{(3)} = \chi^{(3)}_{NR} + \chi^{(3)}_R \quad \text{Eq 2.13}
\]

Because of the squared dependence on \( \chi^{(3)} \), the resonant and nonresonant responses interfere as described below:

\[
|\chi^{(3)}|^2 = |\chi^{(3)}_{NR}|^2 + |\chi^{(3)}_R|^2 + 2\chi^{(3)}_{NR} Re[\chi^{(3)}_R] \quad \text{Eq 2.14}
\]

Thus, the nonresonant term cannot be removed by a simple background correction method. The presence of nonresonant contribution to the overall susceptibility means that there is no simple linear correlation between the CARS intensity ( \( I_{\text{CARS}} \) ) and concentration; it strongly depends on the ratio \( \chi^{(3)}_R / \chi^{(3)}_{NR} \).

For a given vibrational resonance, \( \chi^{(3)}_R \) describes the vibrational response of the sample and is given by the equation below: [69]
Coherent anti-Stokes Raman scattering (CARS) spectroscopy

\[ \chi_R^{(3)} = \frac{NA}{\Omega - (\omega_{pu} - \omega_s) - i\Gamma} \quad \text{Eq 2.15} \]

where, \( N \) is the number of scattered photons per unit volume; \( A, \Omega, \) and \( \Gamma \) are the amplitude, frequency and line width of the vibration mode.

The imaginary part of \( \chi_R^{(3)} \), given by Eq 2.16 can be compared directly to \( I_{Raman} \) (Eq 2.8). [71] In other words, \( \text{Im}\left[ \chi_R^{(3)} \right] \) is chemically specific and depends linearly on concentration.

\[ \text{Im}\left[ \chi_R^{(3)} \right] = \frac{NA\Gamma}{\left[\Omega - (\omega_{pu} - \omega_s)\right]^2 - \Gamma^2} \quad \text{Eq 2.16} \]

Hence, for obtaining corresponding quantitative information, it is crucial to extract \( \text{Im}\left[ \chi_R^{(3)} \right] \) from the CARS signal is crucial for obtaining corresponding quantitative information. In the following section, we describe one approach to extract \( \text{Im}\left[ \chi_R^{(3)} \right] \) from the CARS signal, which is the time-domain Kramers-Kronig transform (TD-KK) for spectral phase retrieval. [72] The \( \text{Im}\left[ \chi_R^{(3)} \right] \) of all CARS spectra in this work were extracted using TD-KK.

\section*{2.3 Time-domain Kramers-Kronig transform}

The phase \( \varphi(\omega) \) of a complex function \( \chi(\omega) \) can be expressed by a Kramers-Kronig (KK) transform as:

\[ \varphi(\omega) = -\frac{P}{\pi} \int_{-\infty}^{+\infty} \frac{\ln|\chi(\omega'')|}{\omega'' - \omega} \, d\omega'' \quad \text{Eq 2.17} \]

where \( P \) is the Cauchy principal value, and \( \chi(\omega) = |\chi(\omega)|e^{i\varphi(\omega)} \) when \( \chi(\omega) \) is causal.
To ensure causality, an operator $\psi(f(\omega))$ can be defined as:

$$\psi(f(\omega)) = F[u(t)F^{-1}[f(\omega)]] \quad \text{Eq 2.18}$$

where $F$ and $F^{-1}$ denote the Fourier and inverse Fourier transforms, respectively, and $u(t)$ is the Heaviside Function, and Fourier transform of $u(t)$ can be expressed as:

$$F[u(t)] = \frac{1}{i} \sqrt{2\pi} \omega + \frac{\sqrt{\pi}}{2} \delta(\omega) \quad \text{Eq 2.19}$$

Using convolution theorem and substituting Eq 2.19 to Eq 2.18, one obtains:

$$\psi(f(\omega)) = \frac{1}{2} \left[ -\frac{i}{\pi} P \int_{-\infty}^{+\infty} \frac{f(\omega')}{\omega' - \omega} d\omega + f(\omega) \right] \quad \text{Eq 2.20}$$

Combining Eq 2.17 and Eq 2.20, the phase is expressed as

$$\varphi(\omega) = 2Im \left[ \psi(ln|\chi(\omega)|) - \frac{ln|\chi(\omega)|}{2} \right] \quad \text{Eq 2.21}$$

where the CARS signal is proportional to $|\chi(\omega)|^2$. $u(t)F^{-1}[f(\omega)]$ is replaced with Eq 2.22 and the Fourier transform of the nonresonant background signal is used at negative time.

$$\eta(t:f(\omega)) = \begin{cases} F^{-1}[f(\omega)], & t \geq 0 \\ F^{-1}[f_{NR}(\omega)], & t < 0 \end{cases} \quad \text{Eq 2.22}$$

Thus, the spectral phase is given as:

$$\varphi(\omega) = 2Im[F(\eta(t:ln|\chi(\omega)|) - \frac{ln|\chi(\omega)|}{2}] \quad \text{Eq 2.23}$$

An example of this process is shown below (Figure 2.3). Here, we used the CARS signal of a dry Nafion® 212 membrane as a representative spectrum, and the nonresonant background (NRB) was taken from a membrane on top of a glass coverslip (Figure 2.3a).
Inverse Fourier transformation of both the square root of the CARS spectrum and that of the NRB, $F^{-1}[f(\omega)]$ and $F^{-1}[f_{NR}(\omega)]$ is the initial step (Figure 2.3b). Then $\eta(t: f(\omega))$ was obtained by replacing $F^{-1}[f(\omega)]$ at negative time with the negative-time $F^{-1}[f_{NR}(\omega)]$. Then, the time-domain signal $(\eta(t: f(\omega)))$ was Fourier-transformed back into the frequency domain and substituted the results to Eq 2.23; such the phase was reconstructed (Figure 2.3c). Slight errors or noise in the measured NRB result in a non-constant error phase, which has to be removed. [73] The Raman-like spectrum $\text{Im}[\chi_R^{(3)}]$ is produced after subtracting the error phase from the reconstructed phase as $\text{Im}[\chi_R^{(3)}] = \sin(|\chi(\omega)|e^{i\varphi(\omega)})$, where $\varphi'$ is the retrieved phase after error phase subtraction.

The Raman-like spectrum was compared with a spectrum taken from the dry Nafion® 212 membrane via a spontaneous Raman spectroscopy (the excitation laser is 633 nm with a laser power of 21 mW). The spontaneous Raman spectrum after background subtraction (with an iterative moving window of 293 cm$^{-1}$ wide) is shown in Figure 2.3d.
Figure 2.3 a) the CARS spectrum from the dry Nafion® 212 membrane (red) and the nonresonant background (NRB) from glass coverslip (black); b) the imaginary part of $F^{-1}[f(\omega)]$ and $F^{-1}[f_{NR}(\omega)]$; c) the phase given by Eq 2.23, and a third-order polynomial accompanied by a fit mask (gray) was used to fit a slowly varying error phase, as shown in red; d) red, the Raman-like (RL) spectrum (red) produced after subtracting the error phase, and black, the spectrum of Nafion membrane measured by spontaneous Raman spectroscopy (excitation laser: 633 nm, 21 mW, integration time 10s).
2.4 Constrained non-negative least squares algorithm

2.4.1 Multivariate curve resolution–alternating least squares (MCR-ALS)

In linear systems, a spectral data matrix can be reconstructed with a linear combination of spectral shapes of “pure” components weighted by their scaling factors as:

\[ M = \sum_{i=1}^{n} c_i s_i + E \]  

where \( M \) is a measured spectrum of the mixture of \( s_i \) components in that are weighted by \( c_i \) the scaling factors (or concentrations) where \( j \) is the index for \( n \) total components; \( E \) is the experimental error. If one knows the spectral shape of all pure components, the corresponding set of \( c_i \) can be readily extracted by the fit the of the spectral data matrix to Eq 2.24.

However, the above concepts cannot be applied in a straightforward format to all systems because the number and the spectral shape of the pure components in many systems are unknown. For the systems with limited or even no prior knowledge for the pure components in terms of the number and the spectral shapes, one has to develop a method able to decide the number and spectral shape of the possible pure components. Multivariate Curve Resolution-Alternating Least Squares (MCR-ALS) reported by Anna de Juan and co-workers is a sophisticated way to work with such unknown systems. [75] In MCR-ALS, the spectral data matrix \( M \) is reconstructed by a linear combination of unknown components weighted by a scaling factor (the linear combination is an analogue to Eq 2.24; \( c_i \) and \( s_i \) are referred to as matrix instead of one spectrum). As applied in this thesis, the number of components for MCR-ALS was chosen by
assessing the singular values from a singular value decomposition (SVD) for $M$. In the SVD, $M$ is decomposed to three matrices as: \[ M = U\Sigma V^T \] where $M$ is a matrix of dimension $m \times p$; $U$ is an $m \times m$ unitary matrix (left singular vectors), $\Sigma$ is an $m \times m$ diagonal matrix relating to the average contributions of the singular vectors (singular values) and $V$ is a $p \times p$ unitary matrix (referred to the spatial distribution of the singular vectors of $M$). A larger singular value means a larger contribution to $M$ from the corresponding singular vector, which can be referred to as chemical contributions, while a small value generally implies that it involves a contribution from noise. In the graphical user interface (GUI) of MCR-ALS provided by Anna et al., the singular values of all singular vectors are shown in a decreasing sequence. Then, one can define the threshold singular value above which the singular values are retained. The number of components that have larger singular values is therefore chosen as the total number of components. Prior knowledge of the system can certainly help decide the number of pure components. After deciding the number of components, initial guesses for either $c_i$ or $s_i$ are obtained using various methods to start the iteration algorithm. The initial guesses are optimized until a convergence criterion is fulfilled. The MCR-ALS GUI provides two ways to set the criterion: 1) a pre-set number of iterations; 2) to set the threshold value of the difference between consecutive interactions.

MCR-ALS provides a reasonable way to decide the number of pure components for the unknown systems and to obtain the spectral shape as well as the fractional concentration for each pure component. However, MCR-ALS is not the best way for analysing multi-component system where the spectral shape of one or more pure components is known. For the system with known components, the spectral shape of the known components has to remain constant, meanwhile that of unknown components has to be deduced. With the MCR-ALS GUI implementation, it is impossible to fix the spectral shape of the known components because the concentration and the
CHAPTER 2  Constrained non-negative least squares algorithm

spectral shape for all components are optimized quasi-simultaneously. A different method is required to deal with systems consisting of known components and unknown components. We propose a related method called constrained classical least squares (CCLS) to deal with the systems with known components.

### 2.4.2 Constrained classical least squares (CCLS)

The idea behind CCLS is that data matrix $M$ is represented by a linear combination of known components ($a$) and unknown components ($b$) weighted by their scaling factors as described below:

$$ M = \sum_{a=1}^{A} c_a s_a + \sum_{b=1}^{B} c_b s_b + E $$

where $a$ and $b$ are the indices of the known and unknown components, respectively; $A$ and $B$ are the total numbers of the known and unknown components, respectively; $E$ is the deviation between the experimental data and model data and will be minimized to optimize the fit data to Eq 2.26. In CCLS, we want to obtain the spectral shape of $B$ ($s_b$) as well as the scaling factors ($c_a$ and $c_b$). It should be noted that with more known than unknown components the spectral shape of unknown component can be determined more precisely. Ideally, we need the number of data spectra in $M$ to be the same as, or larger than, the undetermined variables in Eq 2.26, such that we will obtain an unique solution to Eq 2.26 with the smallest error ($E$). Practically, CCLS works well to obtain one unknown component from a system with one or more known components and with a $M$ comprising less than 20 data spectra. However, using CCLS to deduce the more than one unknown component from a larger $M$ requires substantial amount of computational time.

To initiate CCLS, one needs to determine the total number ($n = A + B$) of the pure components in the system. We can use the SVD to yield an estimated value for $n$. The value of $B$ is given as ($n - A$). Then, we have to provide, as an input, an initial guess for the
CHAPTER 2  Constrained non-negative least squares algorithm

independent variables, \( c_a, c_b \) and \( s_b \). There are \(( n + B \times \nu v )\)
independent variables in total, given the frequency range of the
spectrum \( \nu v \). Given \( \beta_0 \) as the initial guess of the vector composed
with the independent variables, CCLS uses a global fit to find a
solution to \( \beta \) by minimizing the \( \phi^2 \) as defined below:

\[
\phi^2 = \| M - M' \|^2 \quad \text{Eq 2.27}
\]

where \( M' \) is the estimated data (from the fit) [77].

An iterative procedure, e.g. Levenberg-Marquardt algorithm (LM)
[77, 78], is used to find the solution. In the LM algorithm, \( \phi \) is
represented by a function \( F(x) \) as shown below:

\[
\phi^2 = \| F(x) \|^2 \quad \text{Eq 2.28}
\]

where \( x \) is an independent variable.

For a small \( \delta \), a Taylor expansion yields the approximation as:

\[
F(x + \delta) \approx F(x) + J\delta \quad \text{Eq 2.29}
\]

where \( J = \frac{\partial F(x)}{\partial x} \). [79]

Substitution of Eq 2.29 to Eq 2.28 yields:

\[
\phi^2 \approx \| F(x) + J\delta \|^2 = [F(x) + J\delta]^T [F(x) + J\delta] = [F(x)]^T [F(x)] + [F(x)]^T J\delta + \delta^T J^T F(x) + \delta^T J^T J \delta
\]

where \( T \) denotes transposition of the respective matrix

\[
\frac{\partial (\phi^2)}{\partial \delta} \approx \frac{\partial ([F(x)]^T [F(x)] + [F(x)]^T J\delta + \delta^T J^T F(x) + \delta^T J^T J \delta)}{\partial \delta}
\]

Taking the partial derivative with respect to \( \delta \) gives:

\[
\frac{\partial ([F(x)]^T [F(x)] + [F(x)]^T J\delta + \delta^T J^T F(x) + \delta^T J^T J \delta)}{\partial \delta} = 0 \quad \text{Eq 2.32}
\]

Simplifying Eq 2.32 gives:

\[
J^T J \delta = J^T F(x) \quad \text{Eq 2.33}
\]

It should be noted that a damping term \( \lambda \text{Diag}(J^T J) \), [77] is
appended to Eq 2.33 yielding Eq 2.34 as described below:
CHAPTER 2  Constrained non-negative least squares algorithm

\[
(J^T J + \lambda \text{Diag}(J^T J)) \delta = J^T F(x) \quad \text{Eq 2.34}
\]

where Diag(J^T J) is the diagonal element of J^T J.

The LM algorithm iteratively repeats 5 steps as described below:

1) at i-iteration, giving \( x = \beta_i, F_i(\beta_i) \) and J is updated;
2) \( \text{Diag}(J^T J) \) and the damping parameter at i-iteration \( \lambda_i \) is updated;
3) \( \delta_i \) is proposed and \( F_{i+1}(\beta_i + \delta_i) \) is evaluated;
4) if \( F_{i+1} < F_i \), accept, otherwise reject;
5) stop when the algorithm meets the desired convergence criteria or exceeds a specified number of iterations.

\( \lambda \) is adjusted at each iteration in LM to assure a reduction in \( F(x) \) and to determine the iterative step size \( (\delta) \) as \( \delta \) is a monotonically decreasing function of \( \lambda \).

\[
\delta = (J^T J + \lambda \text{Diag}(J^T J))^{-1} J^T F(x) \quad \text{Eq 2.35}
\]

If step 4 is rejected, \( \lambda \) is raised otherwise is reduced (Eq 2.35).

It is crucial to initiate LM with a sensible starting point, which requires one to choose an appropriate initial guess for both \( \beta \) and \( \delta \). An inappropriate initial guess \( \beta_0 \) may lead the value of \( \phi^2 \) to a local minimum (Figure 2.4). As shown in Figure 2.4, if \( \phi^2(\beta) \) is closer to the local minimum than to the global minimum, its minimization would direct the value to the local minimum.

![Figure 2.4 Schematic of local minimum and global minimum of \( \phi^2 \).](image)

APPENDIX I contains the source code for processing the CCLS global fit in Igor Pro 6.32 A.