Title of the Abstract for ISCRE 28 [Max. two lines. Bold Times New Roman 12].

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Highlights

- The potential of quantitative analysis using MES-PSD is investigated.
- Higher modulation frequency is required to acquire lower parameter estimation uncertainty.
- The stimulation species should be chosen to ensure that the forward rate parameter is larger than the backward rate parameter in the specific reaction step

1. Introduction

Heterogeneous catalysis plays a key role in various chemical industries. It is paramount to have a thorough understanding of the catalytic reaction mechanisms to facilitate the design and optimization of catalytic processes, which requires identifying crucial reaction intermediates experimentally[1]. Modulation excitation spectroscopy - Phase sensitive detection (MES-PSD) is a transient response spectroscopic technique with high sensitivity and selectivity applied for the qualitative identification of reaction intermediates[2]. Nevertheless, the analysis in quantitative aspect using MES-PSD has not been fully explored. In our study, we analyze the *quantitative* potential and limitations of the MES-PSD technique. The methodology of quantifying rate parameters of chemical reactions using MES-PSD results are derived and relevant analysis are provided to provide detailed insights into the methodology and assess its robustness.

2. Methods

Relevant simulations are performed in Matlab2021b software. Ode15s is chosen as the ODE solver for stiffness problem. Fast Fourier transform is used for phase lag φ estimation from time domain results. We propose a scheme to estimate rate parameters from the phase-lags of reaction surface species, as illustrated in Figure 1.

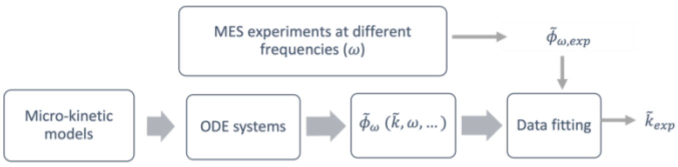

Figure 1. Scheme of rate parameter estimation.

3. Results and discussion

Models for a few representing fundamental steps in catalytic mechanisms are proposed to demonstrate the implementation of the estimation scheme: Model 1: $A(g) \leftrightarrow A^*$ Model 2: $A(g) \leftrightarrow A^* \leftrightarrow C^* \leftrightarrow C(g)$.

Figure 2 illustrates the impact of modulation frequency on the estimation uncertainty in Model 1. It shows that **higher modulation frequencies result in reduced uncertainty**.

An estimation uncertainty analysis is conducted on the phase-lags of the four species in Model 2. Figure 3 shows that the equilibrium constant K_2 has a significant impact on the estimation uncertainty. This observation is particularly relevant in the context of **determining the optimal species to stimulate to minimize estimation uncertainty.** When choosing a species to stimulate, one should ensure that the forward rate parameter is larger than the backward rate parameter in the specific reaction step, and choose the species that will result in the smallest estimation uncertainty.

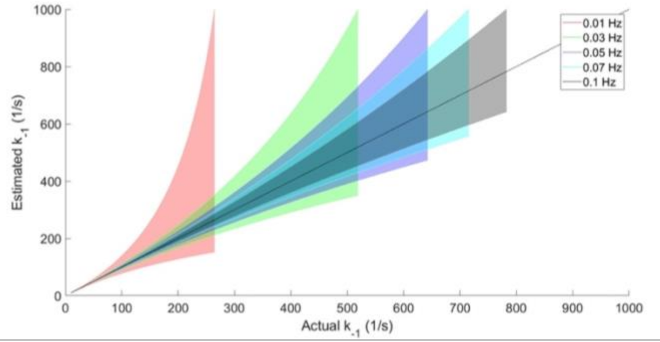

Figure 2. The estimation bound of rate parameter k_{-1} under different modulation frequency. The estimation is based on the phase-lag between A^* and the stimulation. The lower and upper bound is calculated under the phase angle measurement uncertainty at 0.01°.

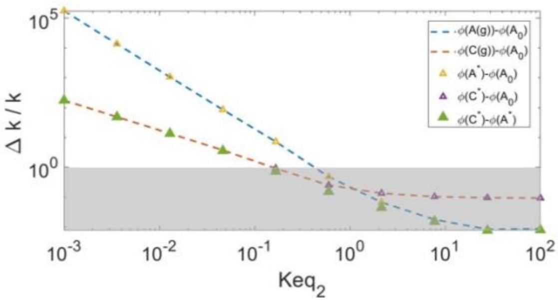

Figure 3. Relative uncertainty analysis on rate parameter estimating from different species phase-lags: $\Delta k/k$ with respect to K_2. The grey area marks the (acceptable) relative uncertainty lower than 1.

4. Conclusions

The discussions of quantitative analysis scheme for MES-PSD results can open a novel way in quantifying kinetic parameters which is based on reaction intermediates results This can provide better insights of the catalytic process.

References

The reference format is provided below [1 – 3]. [Times New Roman 10].

[1] Müller, P. & Hermans, I. *Ind. Eng. Chem. Res.* **56**, 1123–1136 (2017).
[2] Baurecht, D. & Fringeli *Rev. Sci. Instrum.* **72**, 3782–3792 (2001).

Keywords
Modulation excitation spectroscopy; Phase sensitive detection; Rate parameter estimation