How Do We Know if Model and Data are really **Consistent**?

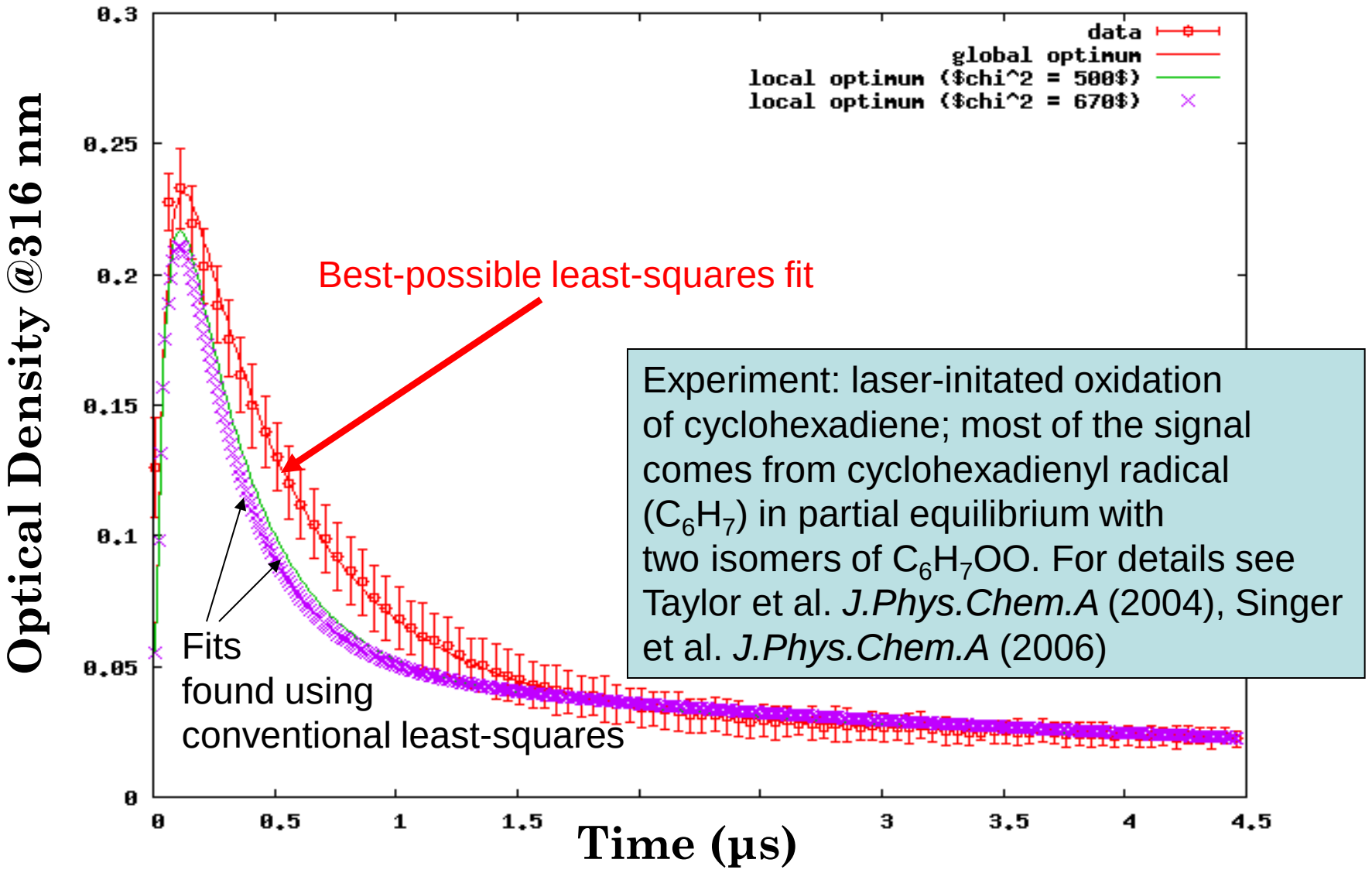
$$\chi^2(\theta) = \min_\theta \|(y_{expt}-y_{model}(\theta))/\sigma\|^2$$

θ are the parameters we are adjusting to fit the data

- Uncertainty $\sigma = \sigma_{model} + \sigma_{expt}$
- If $\min_\theta \chi^2 >$ tolerance it is very likely that the model is inconsistent with the data.
- USUALLY χ^2 HAS MANY LOCAL MINIMA
- Need ***globally*** optimal choice of adjustable parameters θ to be 100% sure model & data are inconsistent. *It just became possible* to guarantee global minimum in $\chi^2(p)$ for nonlinear ODE kinetic models:

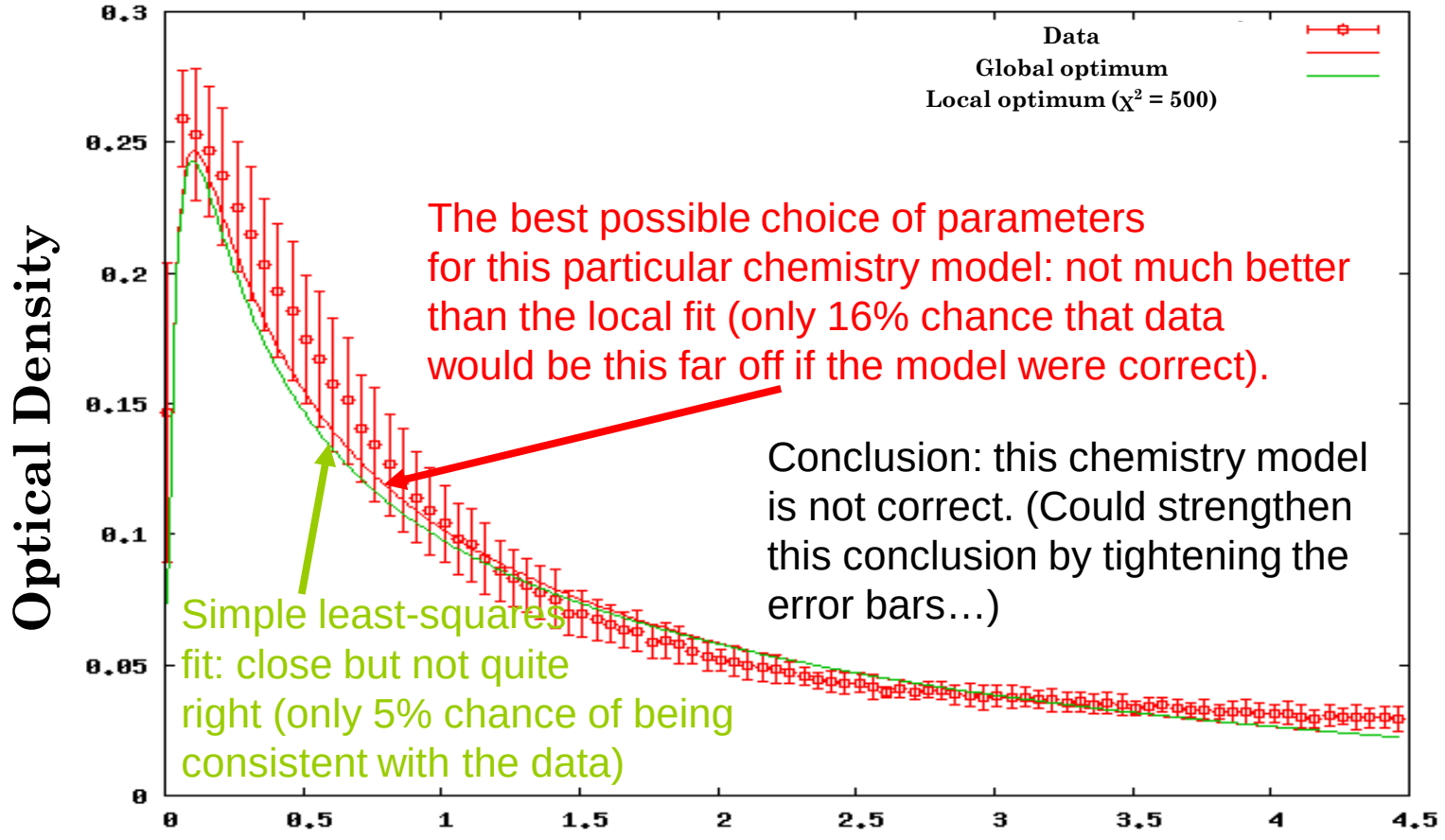
  Singer et al., *J. Phys. Chem. A* (2006).

Example 1: Local optimization suggested model is wrong, but global optimization finds good fit



Experiment: laser-initated oxidation of cyclohexadiene; most of the signal comes from cyclohexadienyl radical (C_6H_7) in partial equilibrium with two isomers of C_6H_7OO. For details see Taylor et al. *J.Phys.Chem.A* (2004), Singer et al. *J.Phys.Chem.A* (2006)

Example 2: Global Optimization Proves Model & Data Inconsistent



Singer et al.,
J. Phys. Chem. A (2006)

10.34 Numerical Methods Applied to Chemical Engineering

Fall 2015