

# **An assessment of structure-activity relationship performance in predicting the gas-phase rate coefficients of organic compounds with hydroxyl, ozone, nitrate and chlorine**

Max McGillen, Bernard Aumont, Wahid Mellouki, John Orlando, Bénédicte Picquet-Varrault, Tim Wallington, Bill Carter

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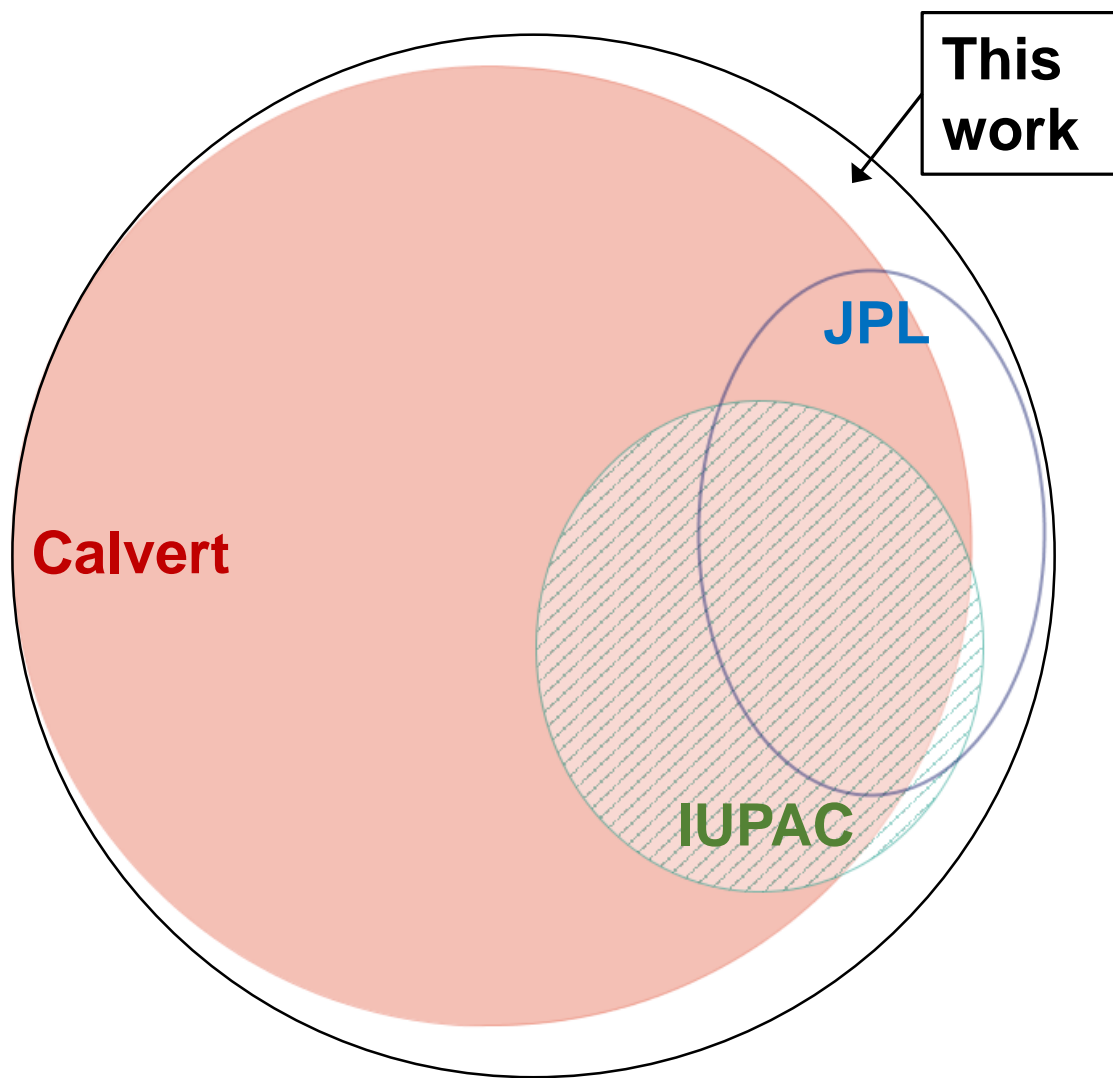
# Outline

- What do we want from SARs?
- The dataset
- Performance of SARs for several OH systems:
  - Jenkin et al. (2018a,b)
  - Carter SAPRC mechanism (2018?)
- A critical interpretation of current OH SARs
- Future outlook

# SARs, what are they good for?

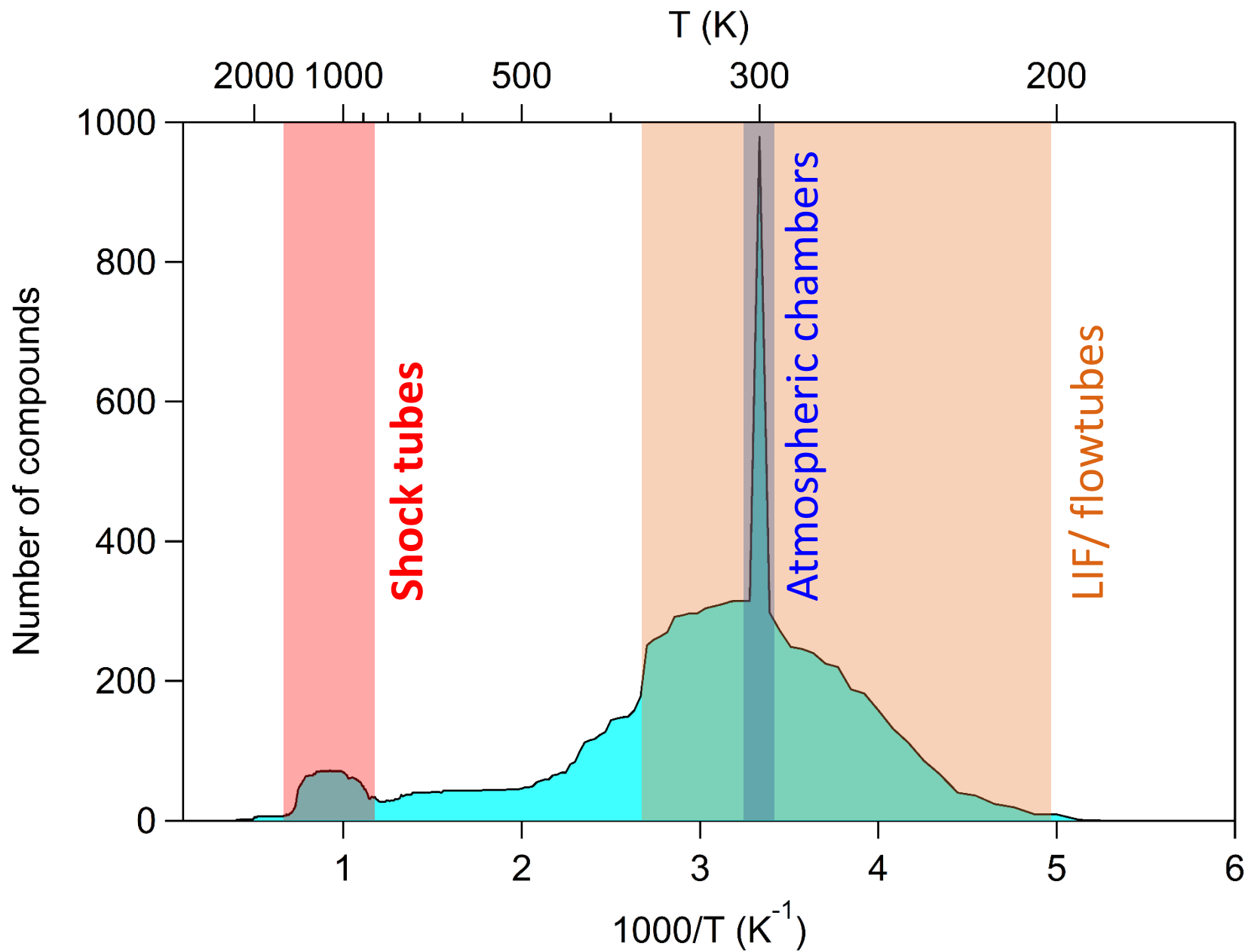
- The oxidation of VOCs in the atmosphere produces a huge number of compounds
  - For example, the Generator for Explicit Chemistry and Kinetics of Organics in the Atmosphere (GECKO-A) produces ~400,000 species for  $\alpha$ -pinene oxidation alone\*
- The next generation of detailed atmospheric chemical mechanisms will employ automated schemes such as GECKO-A and SAPRC
  - But the experimental dataset contains only ~1100 species
- So we have a potentially very large number of rate coefficients that require estimation

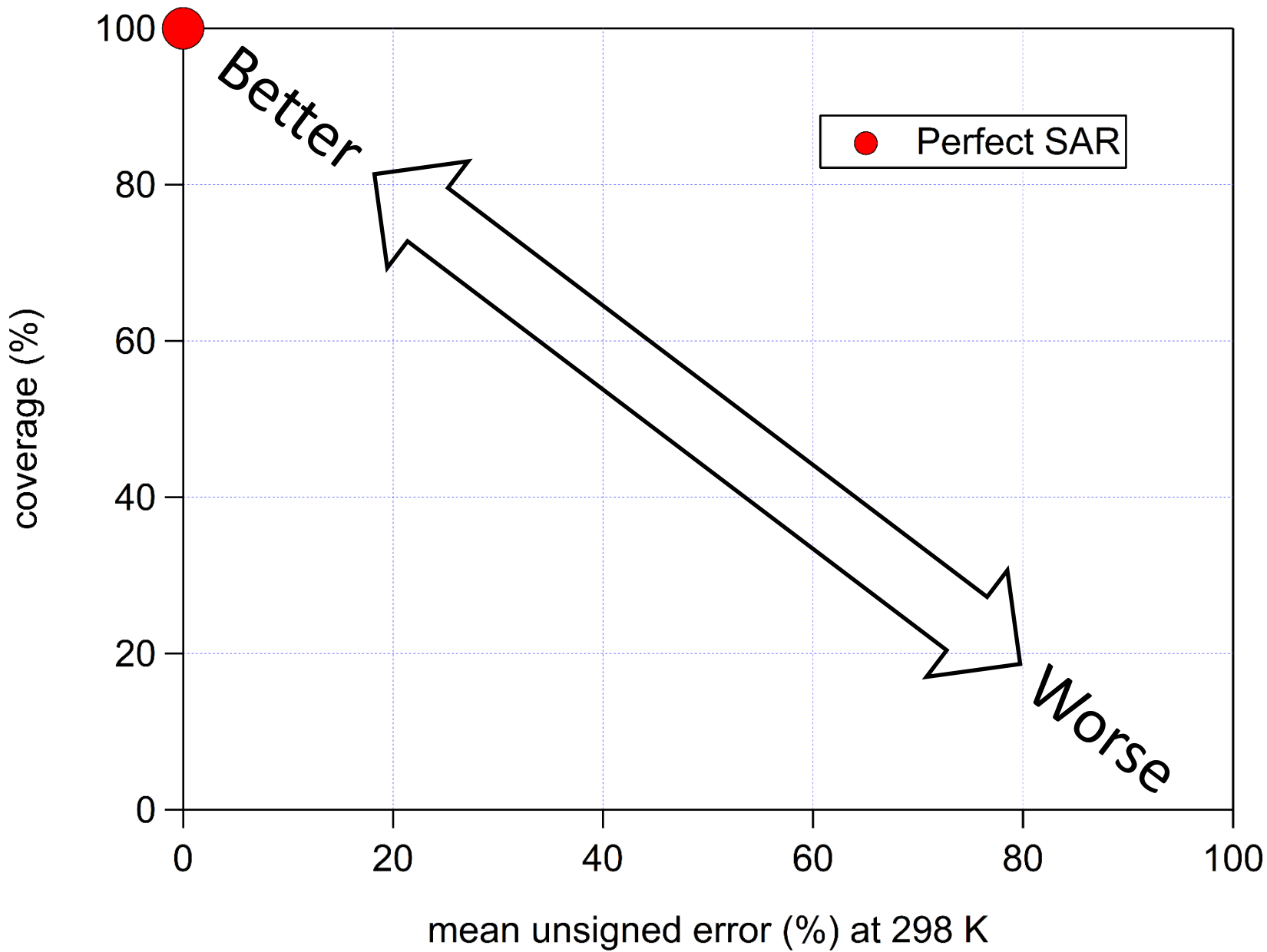
\*This is the number of species in the mechanism, and does not reflect the importance of individual species within the model that would come from a full simulation of this system

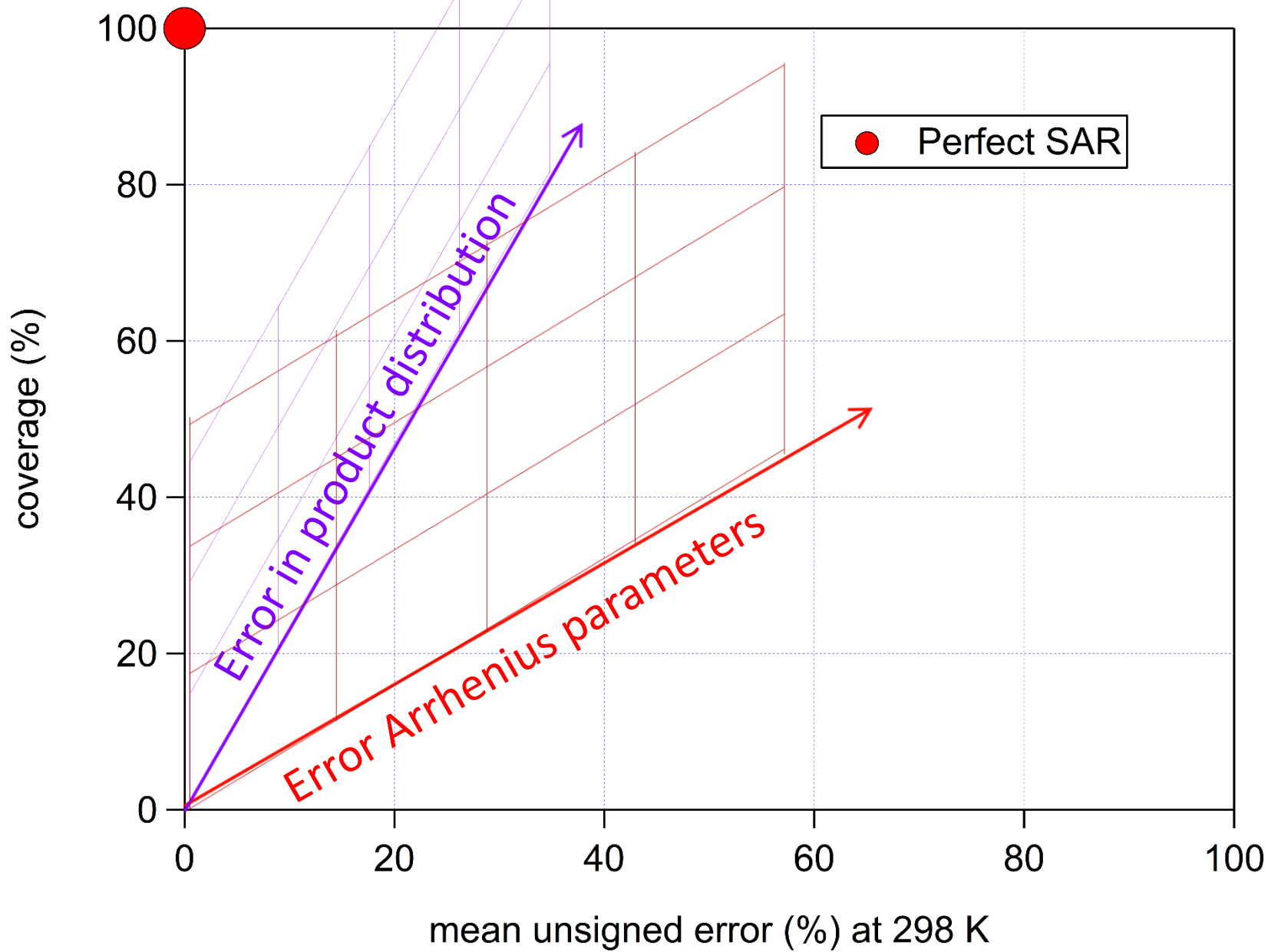


## Number of OH radical rate coefficients within datasets

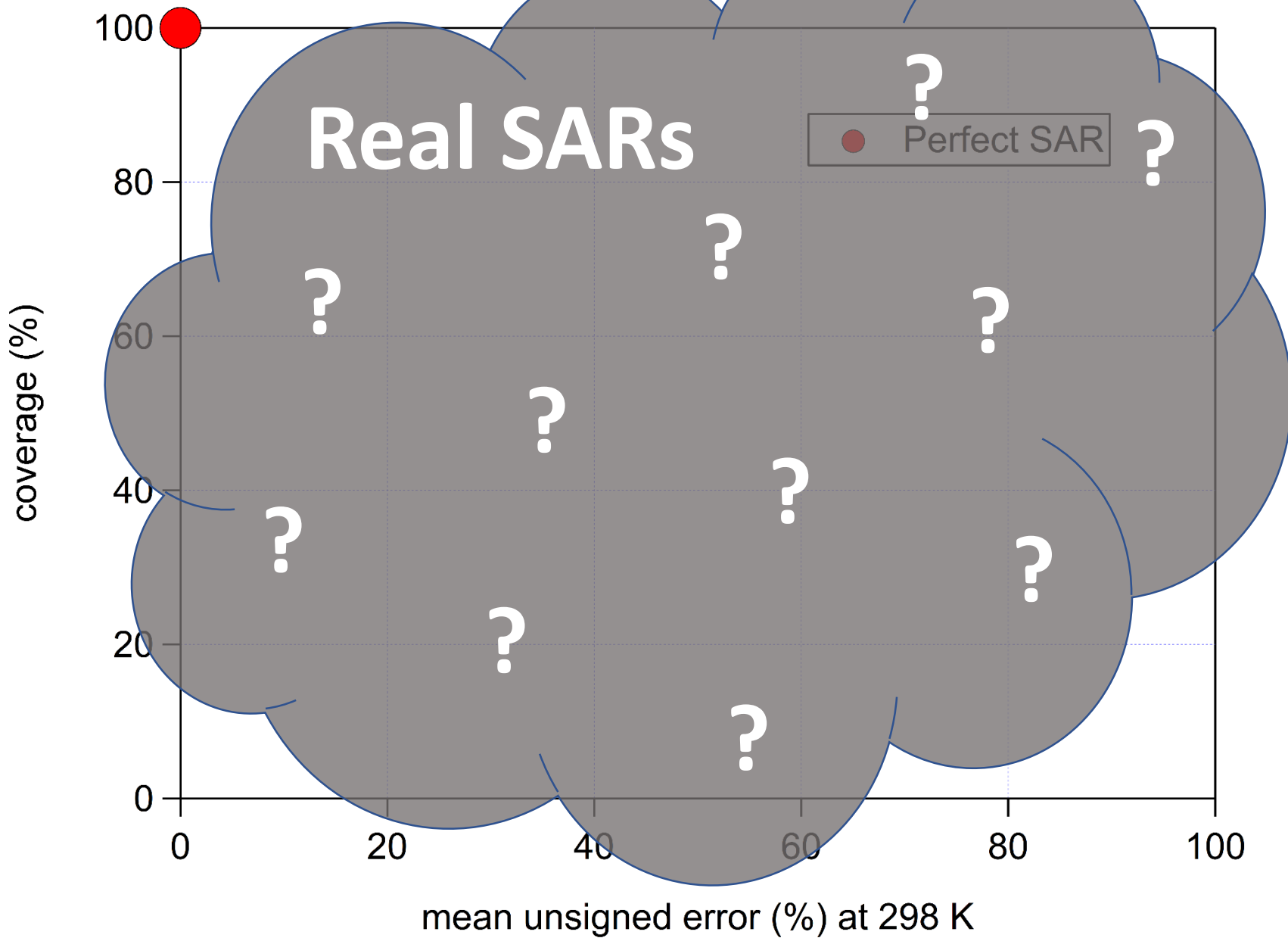
- >1100 species
- Present dataset is more comprehensive than the JPL, IUPAC and Calvert et al. reviews
- Cannot quantify overlap with the NIST database presently







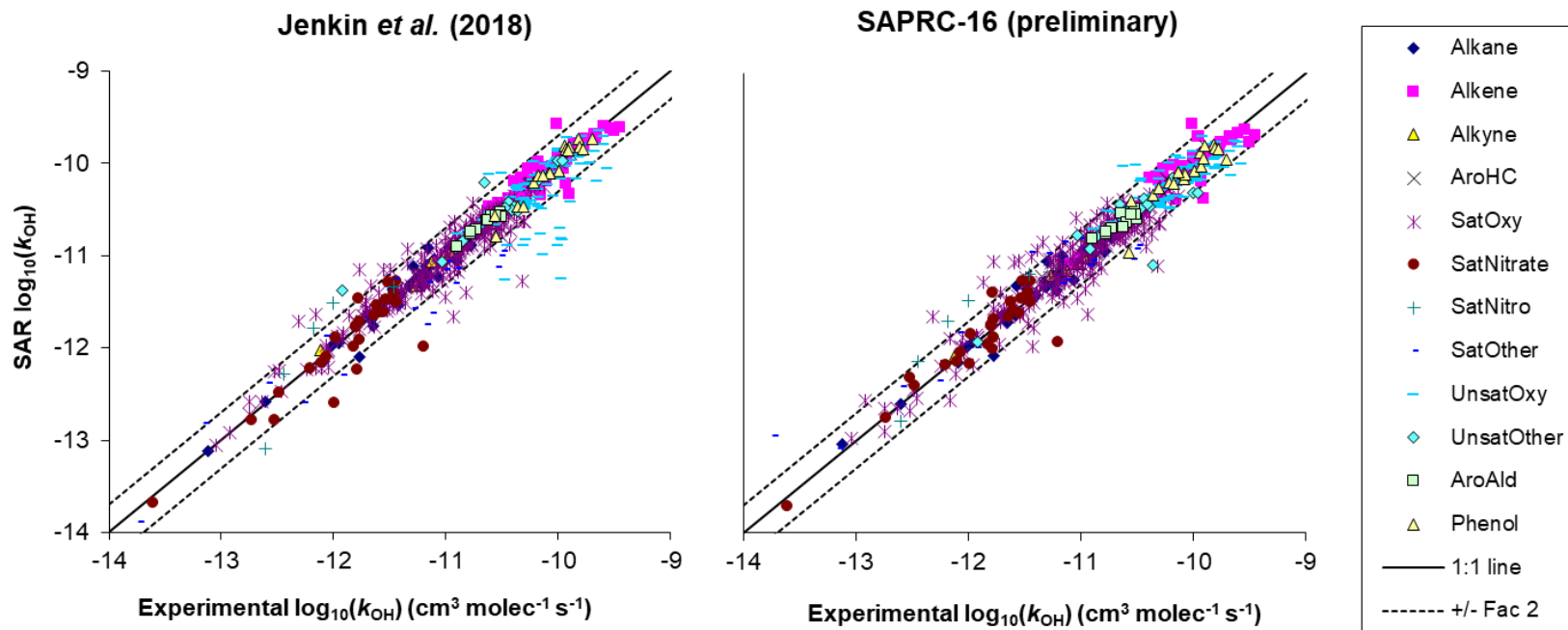




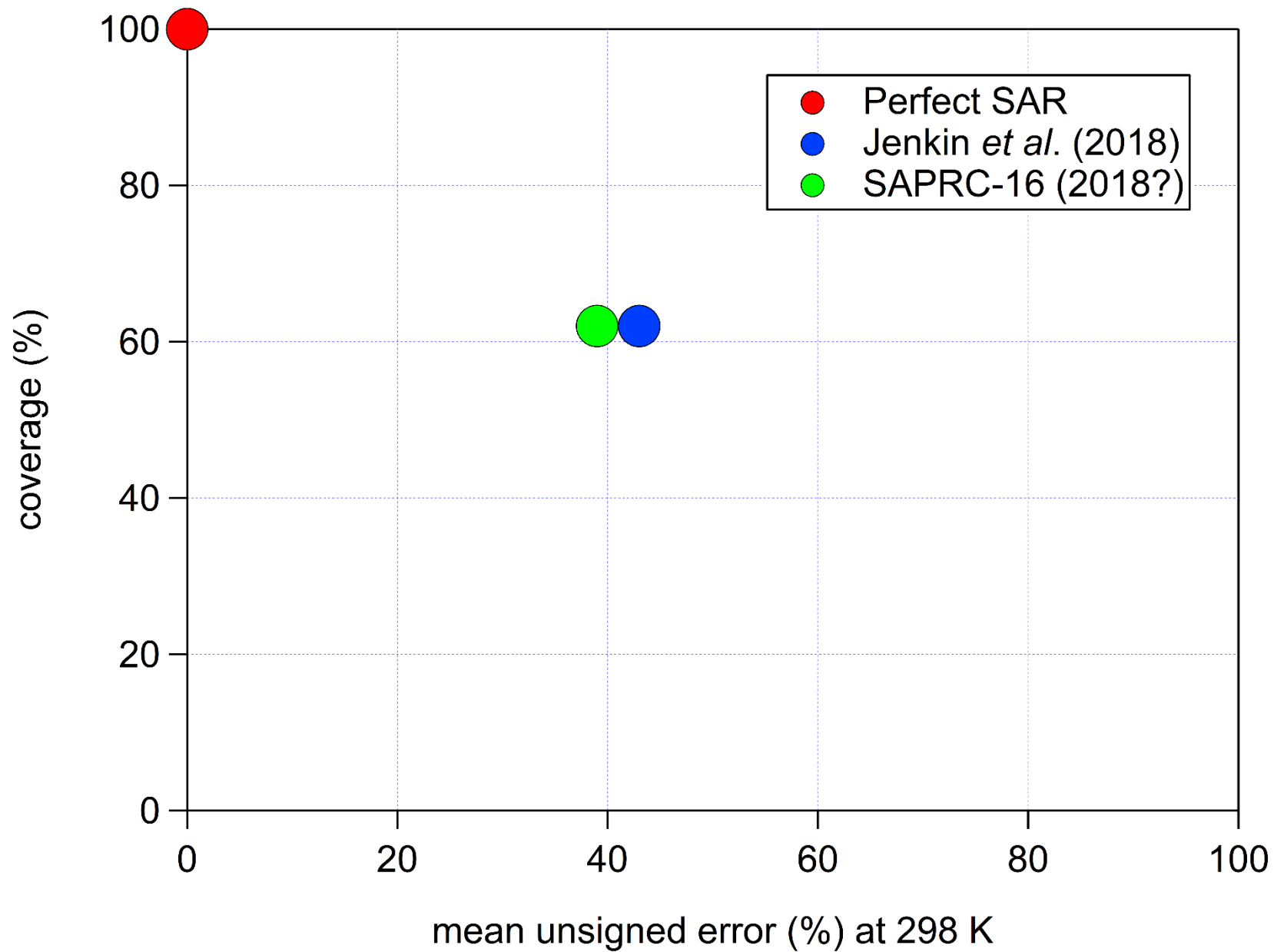
# The SARs

- Jenkin et al. (2018a,b)
  - Alkanes: Similar to Kwok and Atkinson (1995)
  - Alkenes: isolated and conjugated (Peeters *et al.* 2007)
  - Aromatics: specific to this work
- SAPRC-16, Carter et al. (2018?)
  - Alkanes: Similar to Kwok and Atkinson (1995)
  - Alkenes: Similar to Kwok and Atkinson (1995)
  - Aromatics: specific to this work

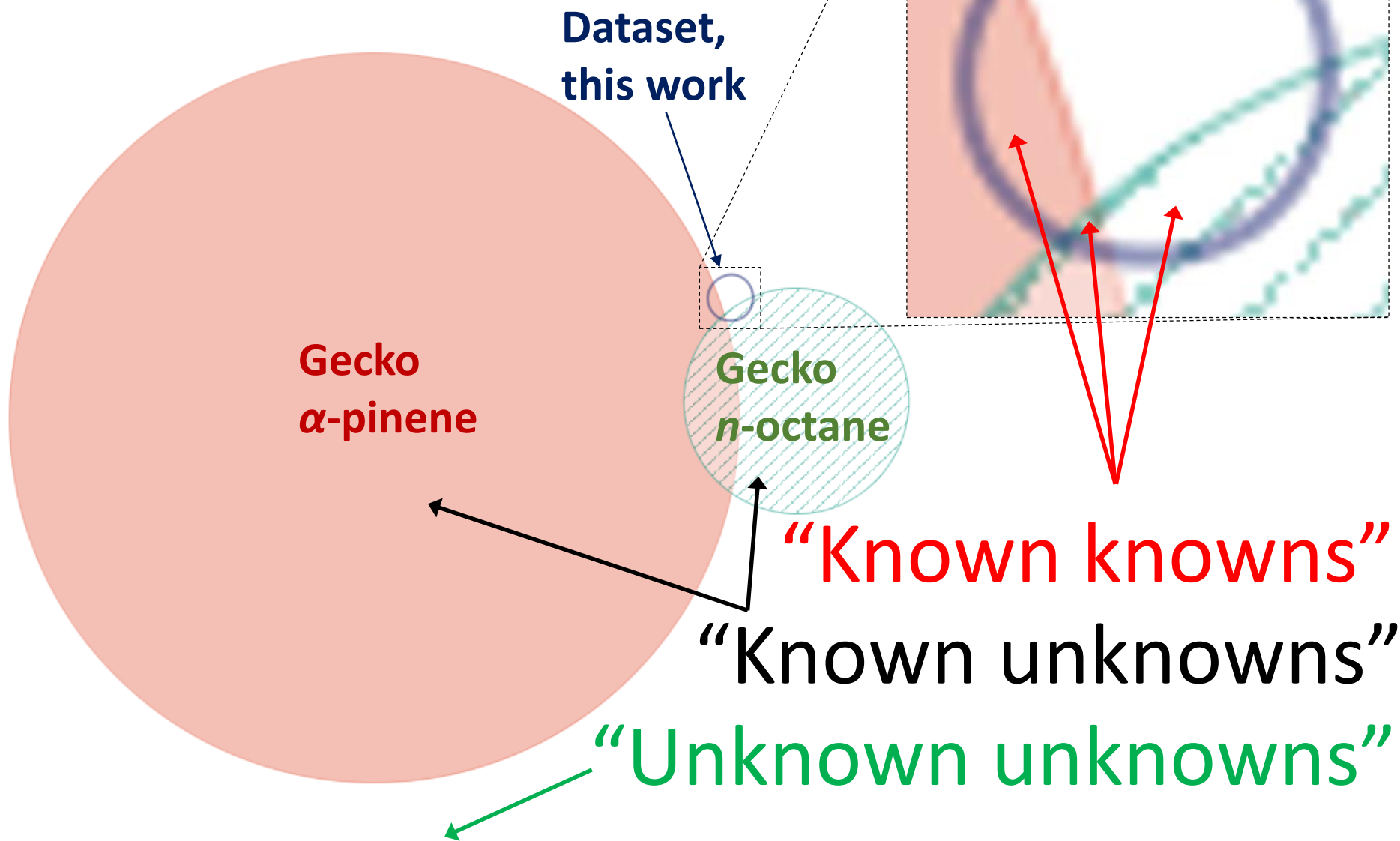
# Results



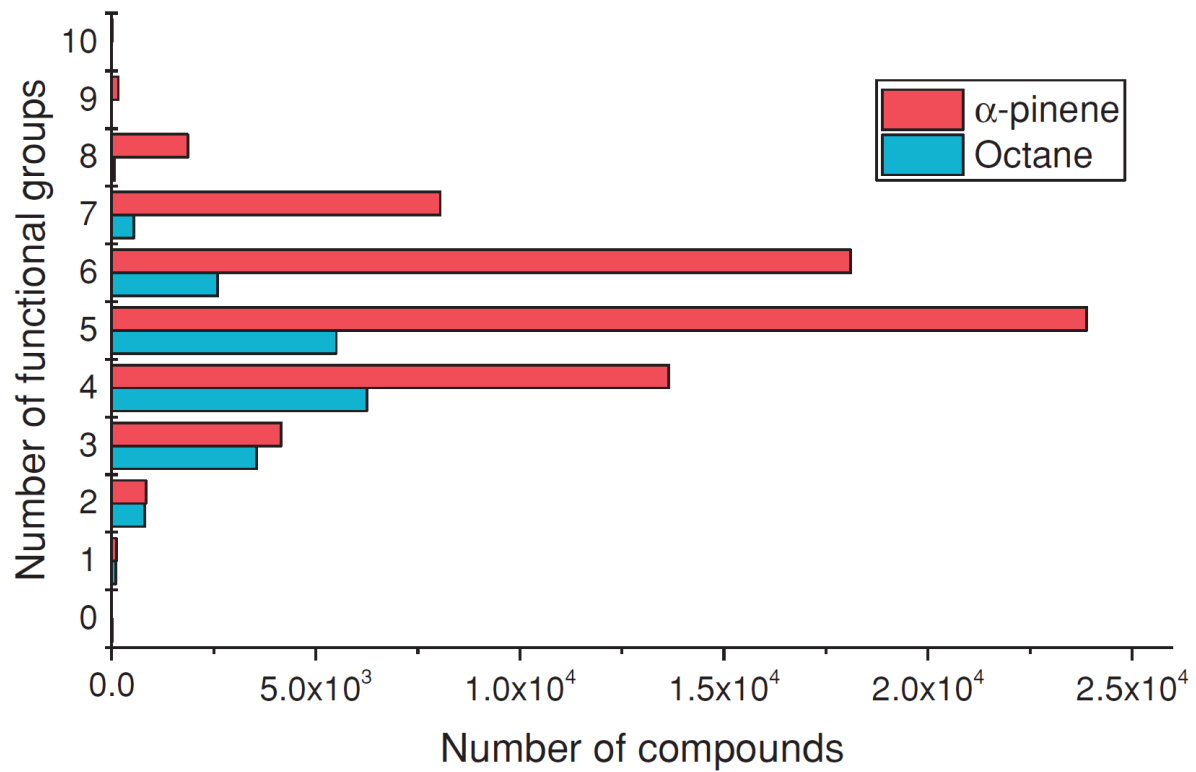
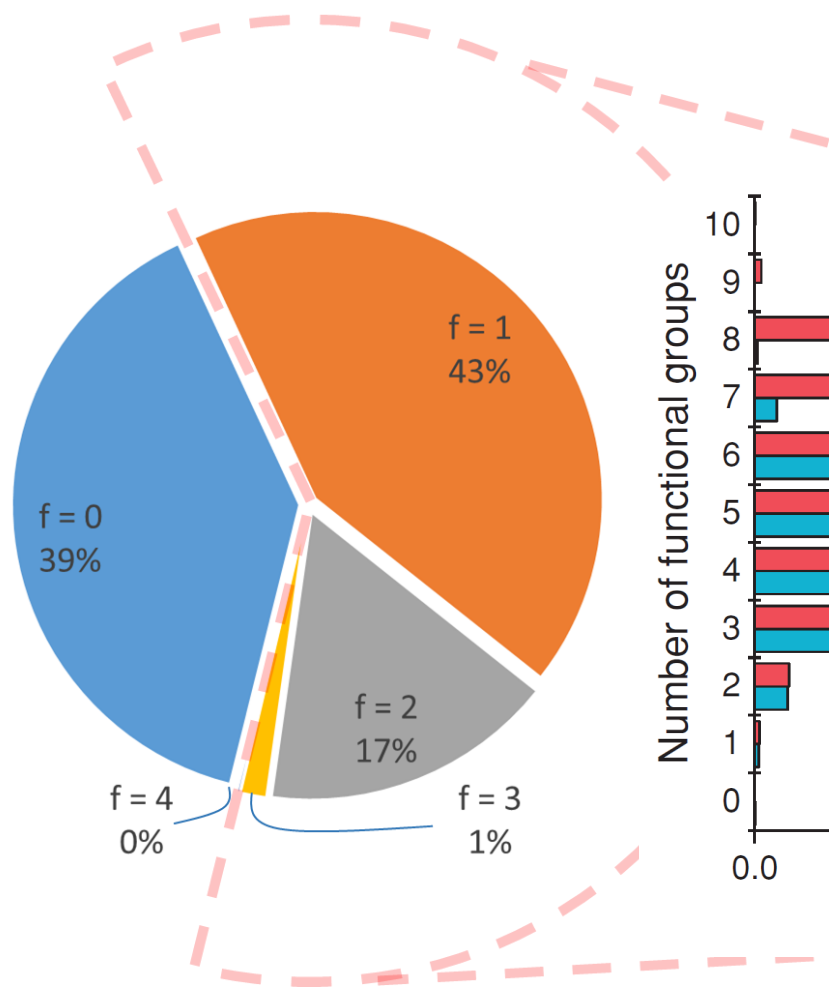
- Despite differences in estimation methods, results are very similar, with the vast majority of estimates within a factor of 2
- Unsaturated oxygenates appear to be better estimated by SAPRC

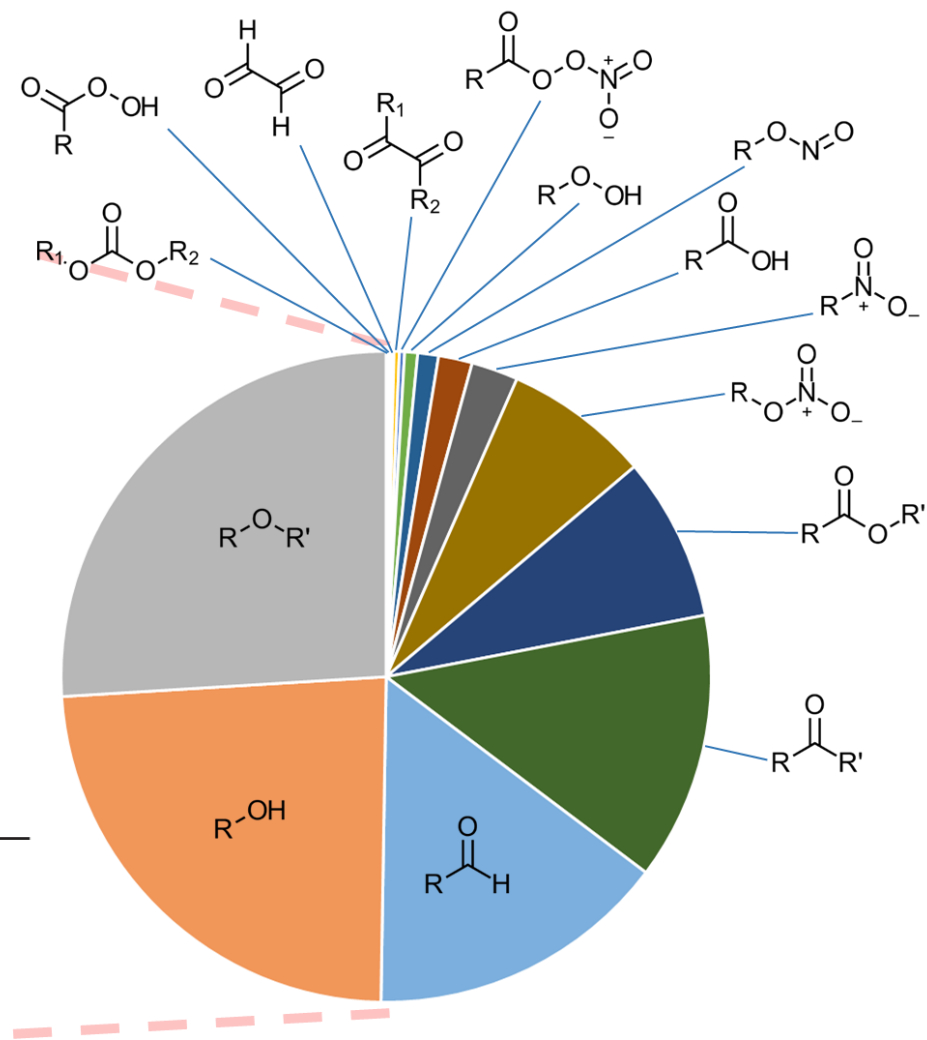
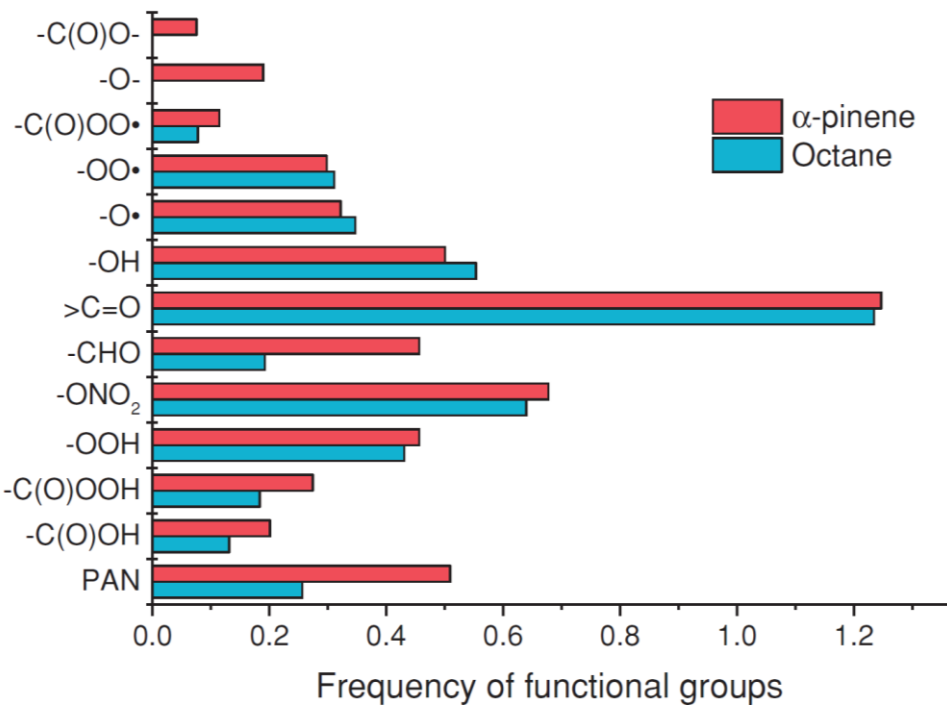


# Coverage of dataset



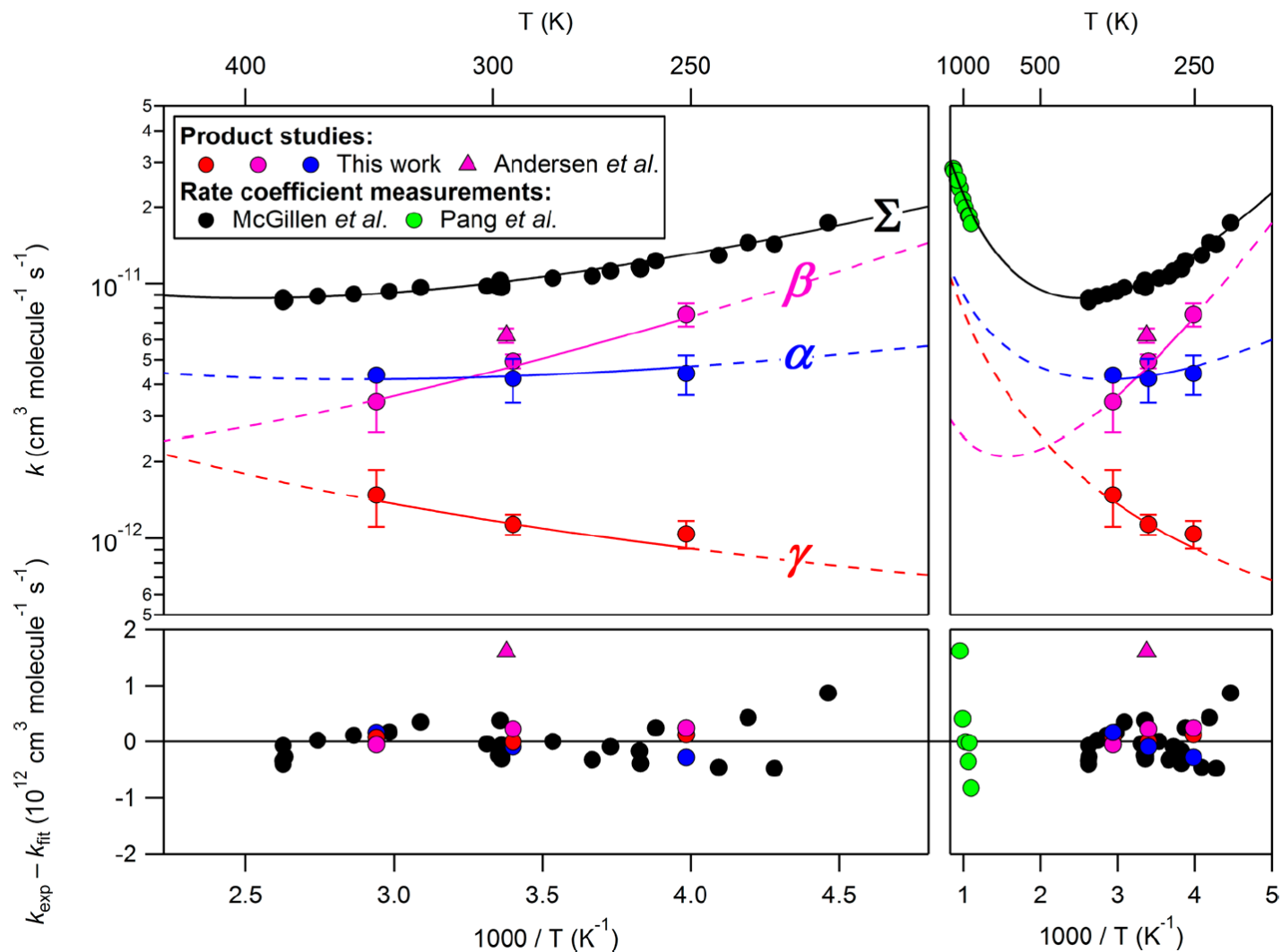






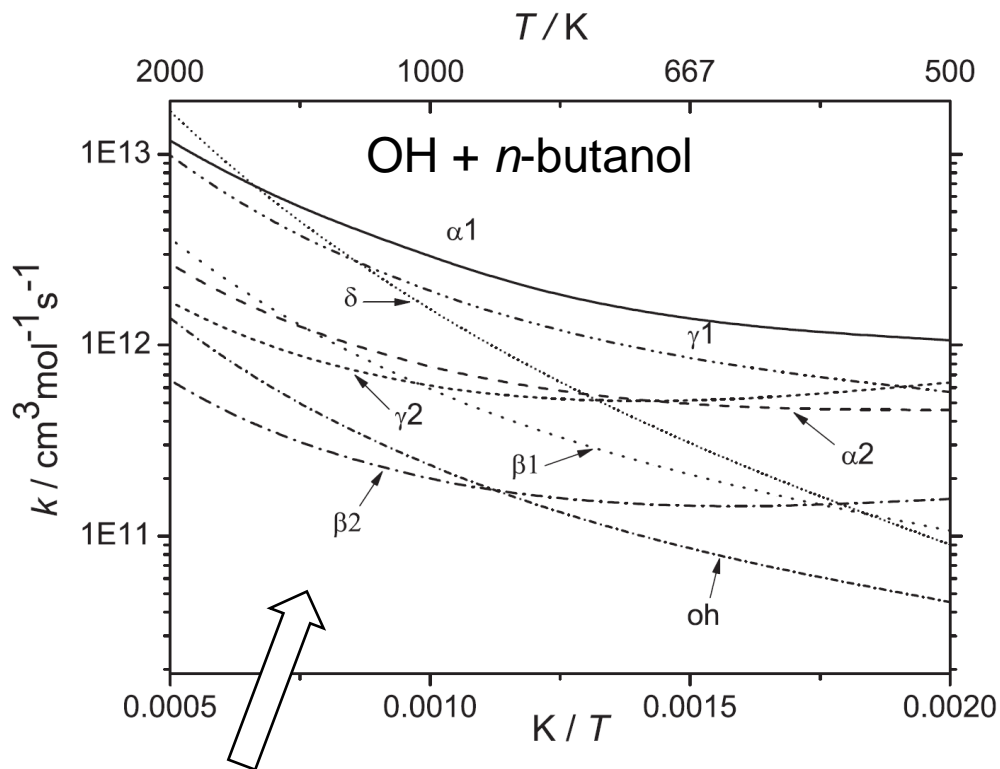


# Different reaction sites



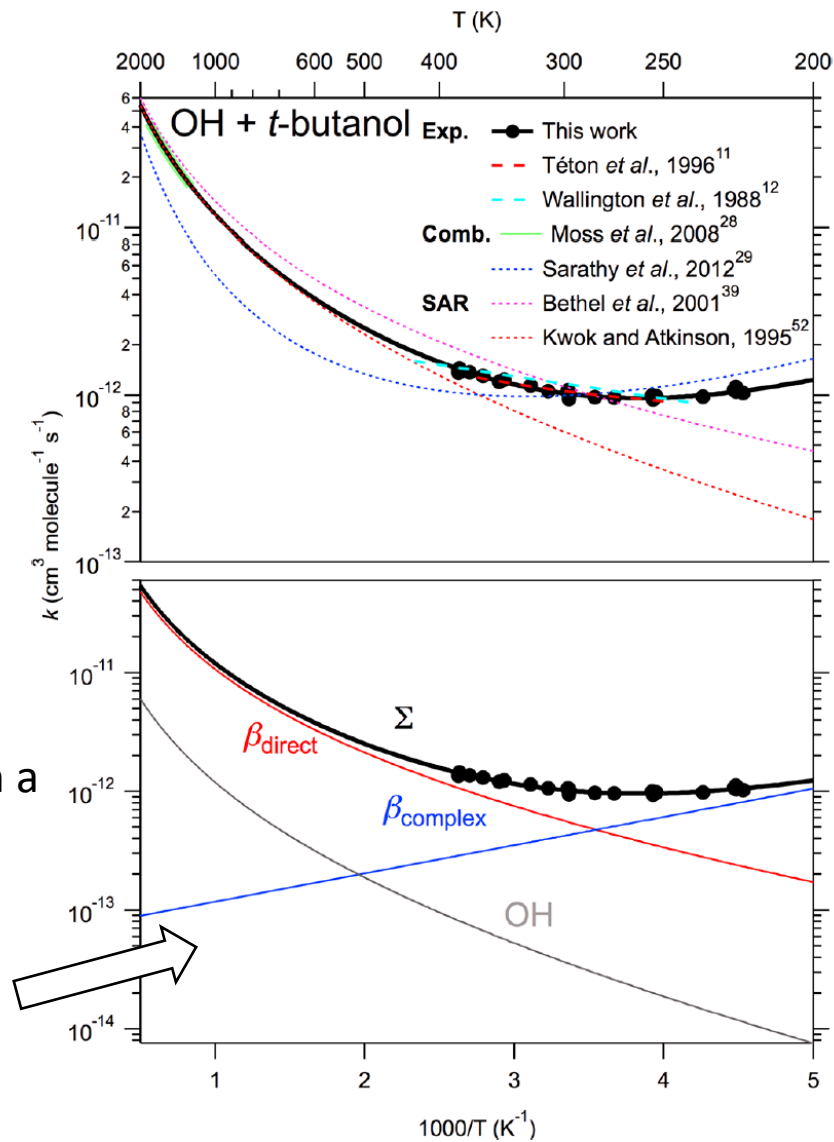
McGillen *et al.* (2016) experimental observations of competing, and complex T-dependent reaction channels in *i*-butanol

# Reaction channels within sites

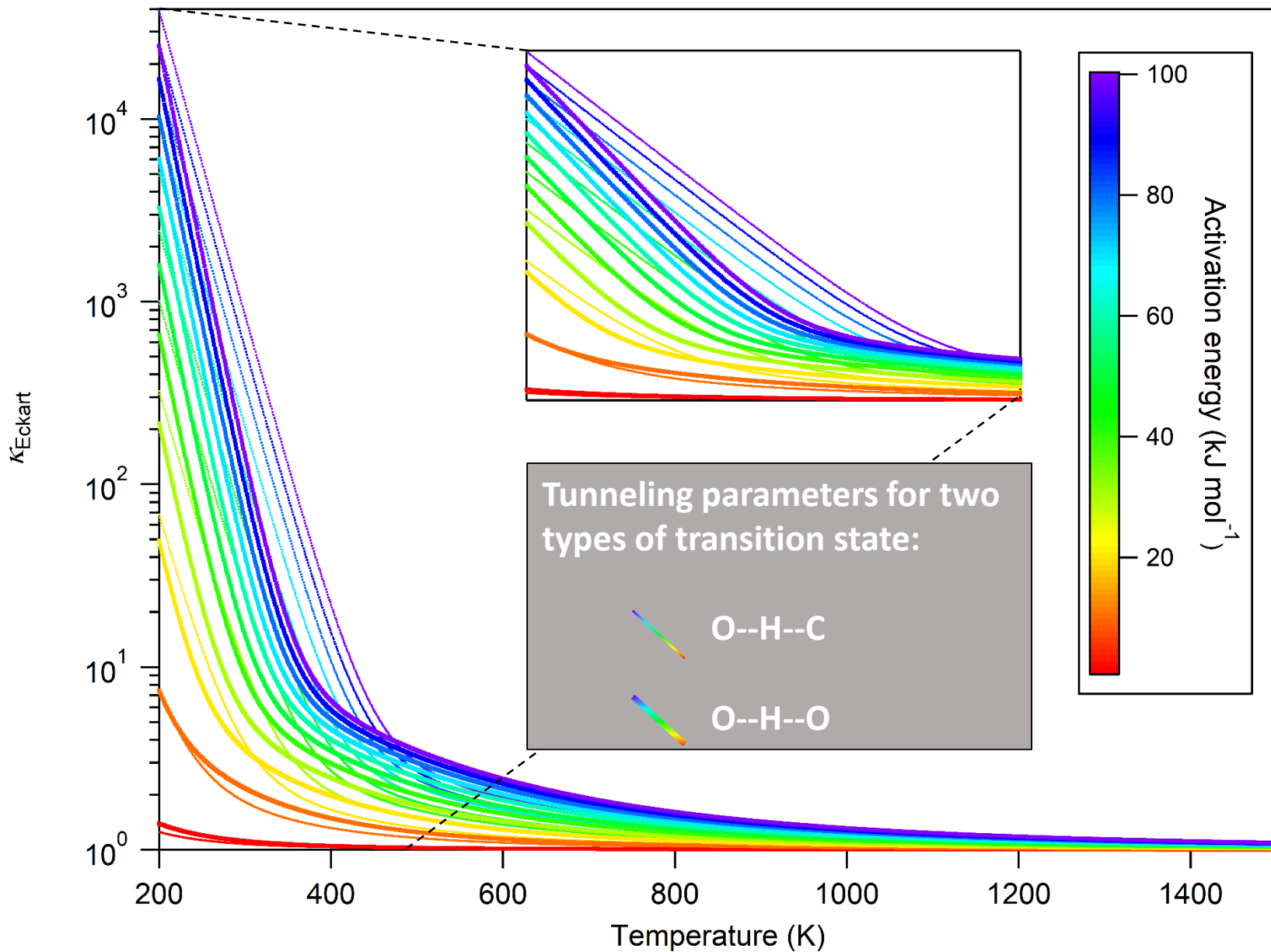


Zhou *et al.* (2011) identified 8 reaction channels in a reaction that possesses 5 reaction sites

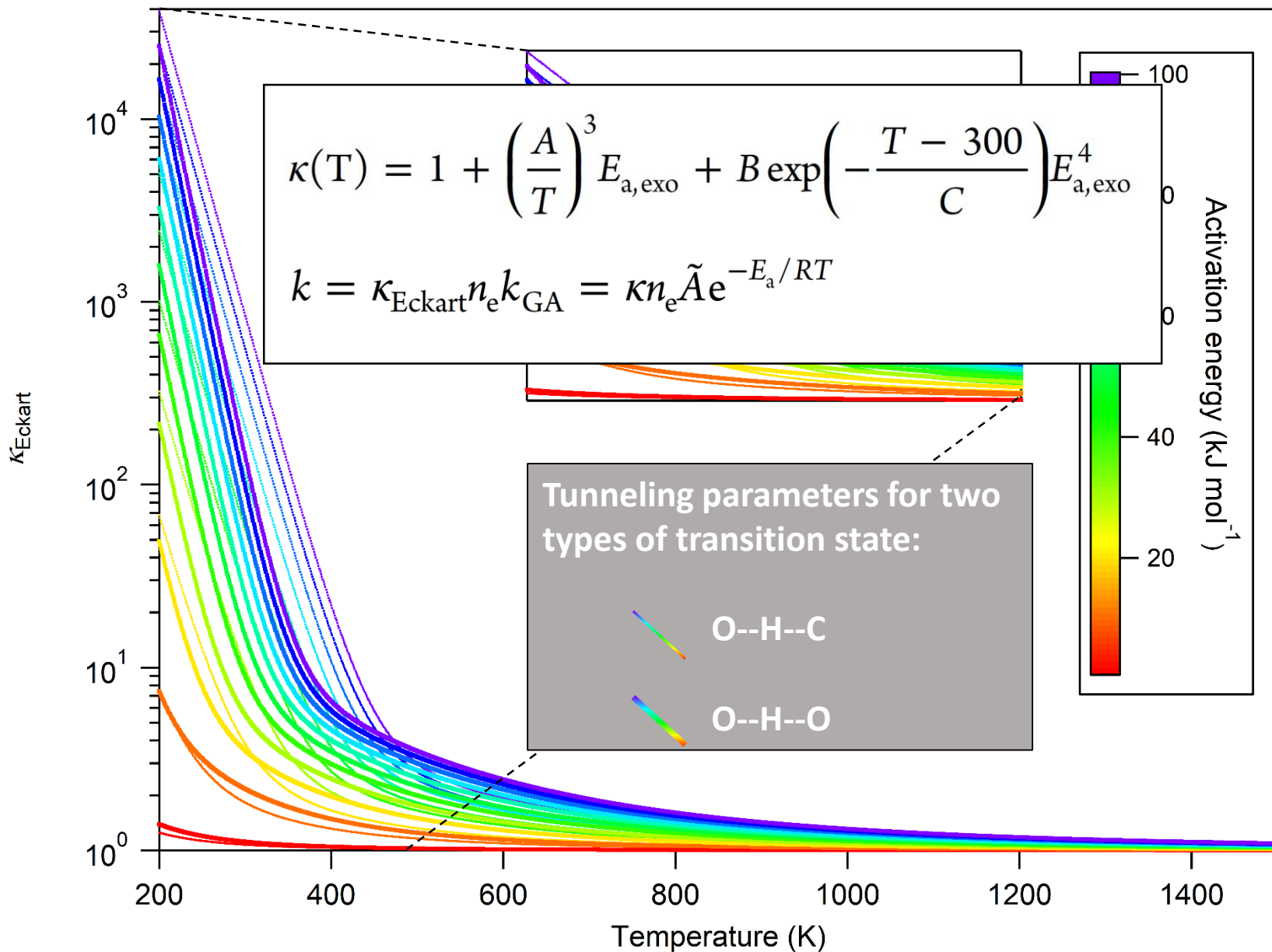
McGillen *et al.* (2013) used 3 reaction channels to describe a reaction that possesses 2 reaction sites



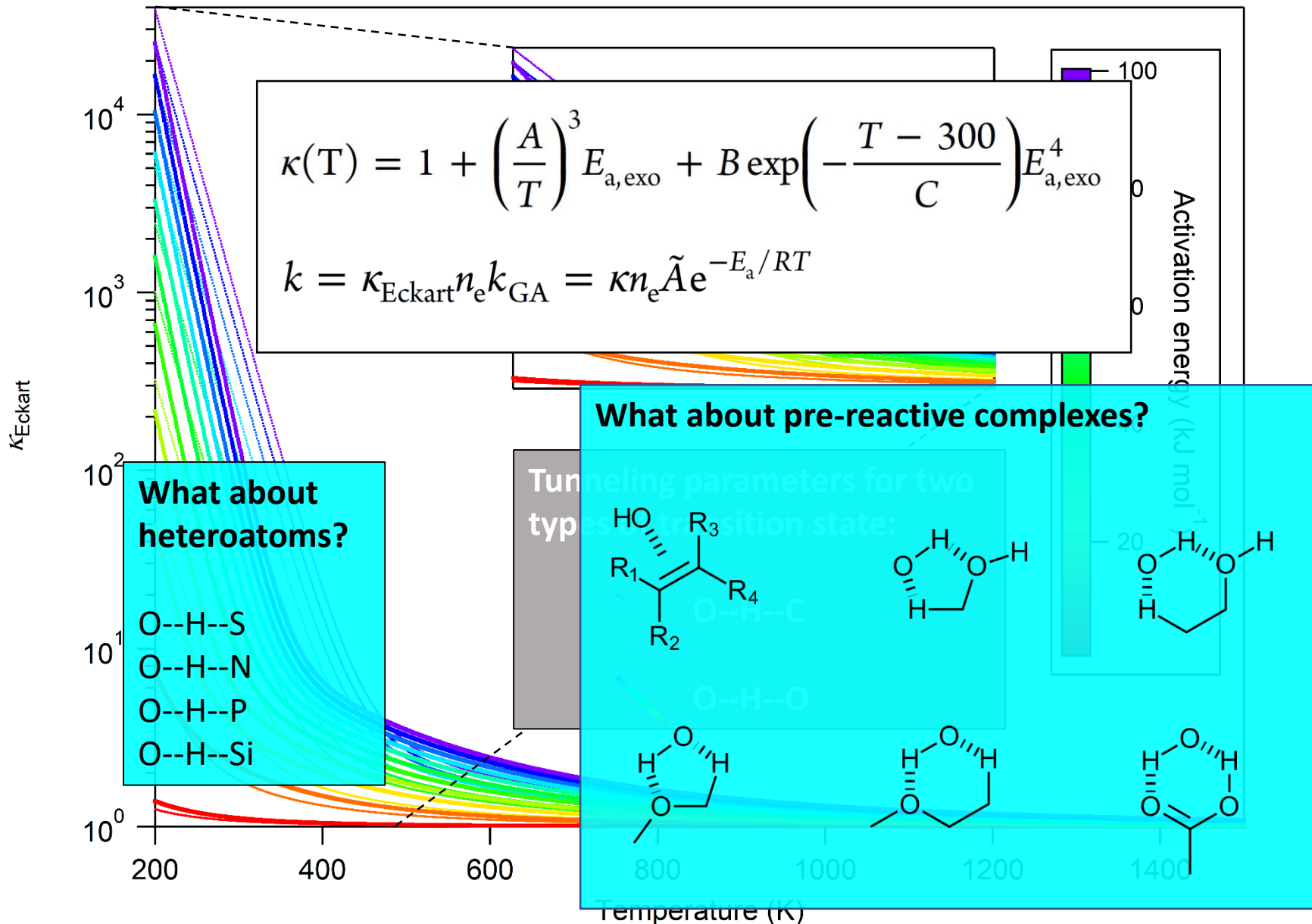
Estimated  $\kappa_{\text{Eckart}}(T)$ , Paraskevas *et al.* (2015)



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# Temperature dependence

$$k_{\text{total}}(T) = \sum_i \kappa_i A_i e^{-E_i/RT}$$

- For functionalized molecules,  $i$  probably larger than number of reaction sites
- $\kappa(T)$  is best described by a 4<sup>th</sup>-order polynomial
- For abstraction reactions, channels that involve hydrogen-bonded complexes show negative T dependence, whereas other channels are positive  $\rightarrow$  curvature
- Is Atkinson's group-additivity approach insufficiently parameterized to handle this kind of complexity?

$$k(\text{CH}_3\text{-X}) = k_{\text{prim}} F(\text{X}),$$

$$k(\text{X-CH}_2\text{-Y}) = k_{\text{sec}} F(\text{X}) F(\text{Y}),$$

$$k(\text{X-CH}(\text{-Y})\text{-Z}) = k_{\text{tert}} F(\text{X}) F(\text{Y}) F(\text{Z})$$

- Current SARs are restricted to mainly Arrhenius behavior (<400 K), or room temperature in the case of SAPRC (*cf.* earlier SARs such as Kwok and Atkinson (1995) which make quite accurate estimates at >1000 K)

# Current problems

- SARs are essentially untested for the vast majority of oxidation products expected in the atmosphere (mode  $f = 4-5$ , compared with only one  $f = 4$  compound in our dataset so far)
- T-dependence is generally much more complex than the algorithms of many current SARs afford
- As SARs learn to describe more data at and around room temperature, can we expect them to become less physical and possibly less general and predictive?

# Possible solutions

- Given that the dataset for the foreseeable future is not sufficiently functionalized, a range of estimation techniques may be best
- Targeted laboratory studies on more functionalized species
- Could we derive more physical SAR parameters from datasets outside of the atmospheric T range? i.e. away from tunneling, H-bonding, etc.
- Could we restructure SARs to make them more physical? e.g. describe tunneling, H-bonding and Arrhenius parameters separately



# Acknowledgements

- We acknowledge the Coordinating Research Council's Atmospheric Impacts Committee who gave the authors their support
- My co-authors
- Thank you to the organizers of GK2018
- Thank you for listening