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Estimating Rate Constants for the Reactions of Ethers + OH: A New Application of the Electropological State

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The E-state method

- The electropological state (E-state) is a new method for estimating T-dependent, site-specific OH rate coefficients [1]:



- It is based on a fundamental property of sites within molecules
- So far, it has been applied to the alkanes and haloalkanes
- Can it be applied to the more complex oxygenated molecules?
- Here, we will test with etheric compounds: ethers and halogenated ethers with one or more ether linkages ($N = 93$ molecules)

vdW complexes

- Pre-reactive complexes may explain the reactivity and negative/ non-Arrhenius temperature dependence of ethers at lower temperatures
- We consider 5- and 6-membered cyclic complexes
- Larger rings are possible, but entropy may limit size
- Ultimately, this leads to a multiplicative correction to the original E-states algorithm that we define as kappa, κ , the effective tunnelling parameter:

$$k_{total}(T) = \sum_i \kappa_i A_i \exp(-B_i/T) (T/300)^{n_i}$$

Multi-ring systems?

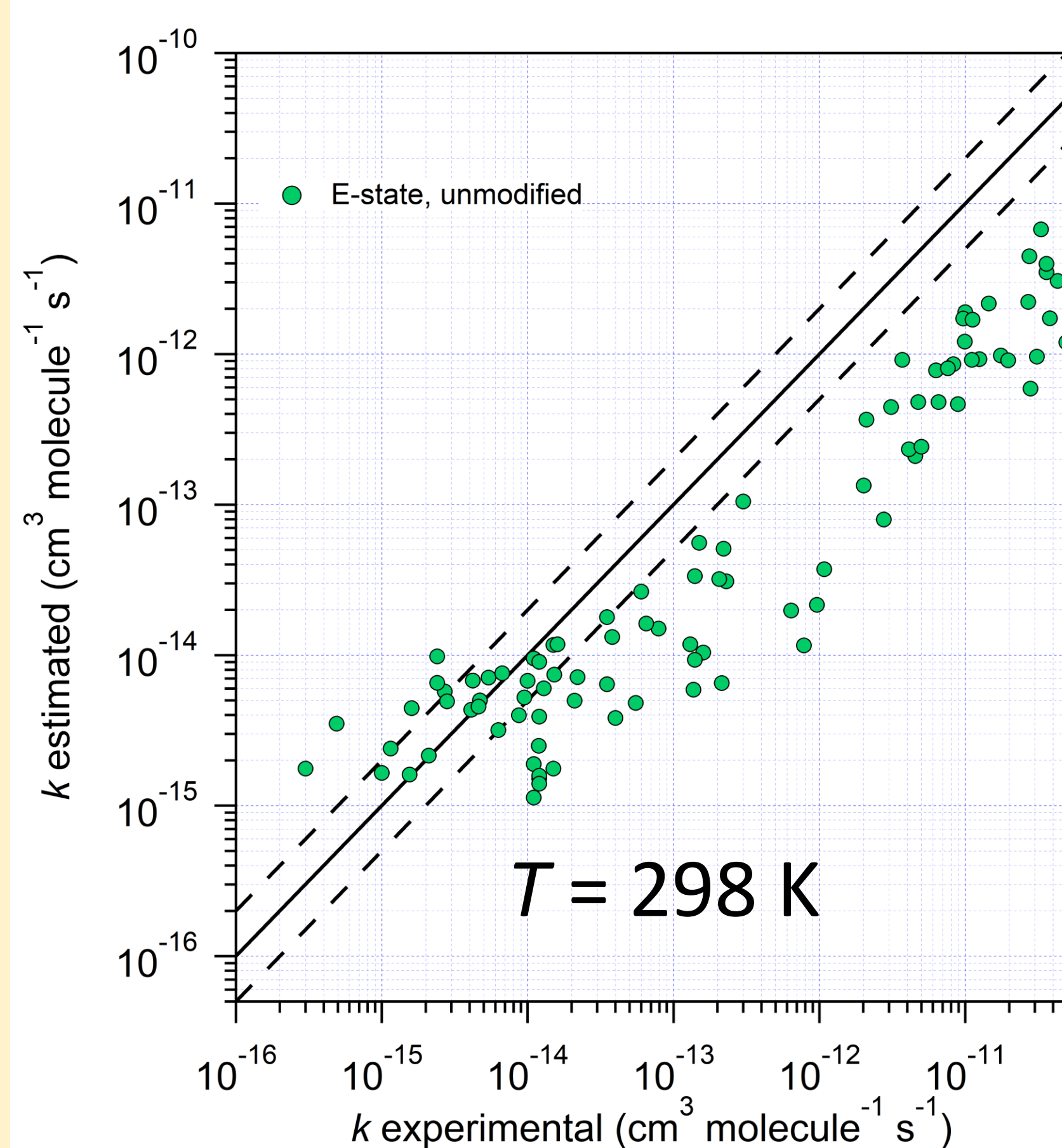
- Multiple ring parameterizations may apply where several ether linkages are present
- This concept is parameterized to improve the predictions for these compounds

The effect of temperature

- As would be expected, the effect of hydrogen-bonded vdW complexes decreases with temperature
- A simple exponential function is employed to describe this
- κ can enhance rate coefficients >100 times at lower T
- $\kappa \rightarrow 1$ as T approaches 1000 K

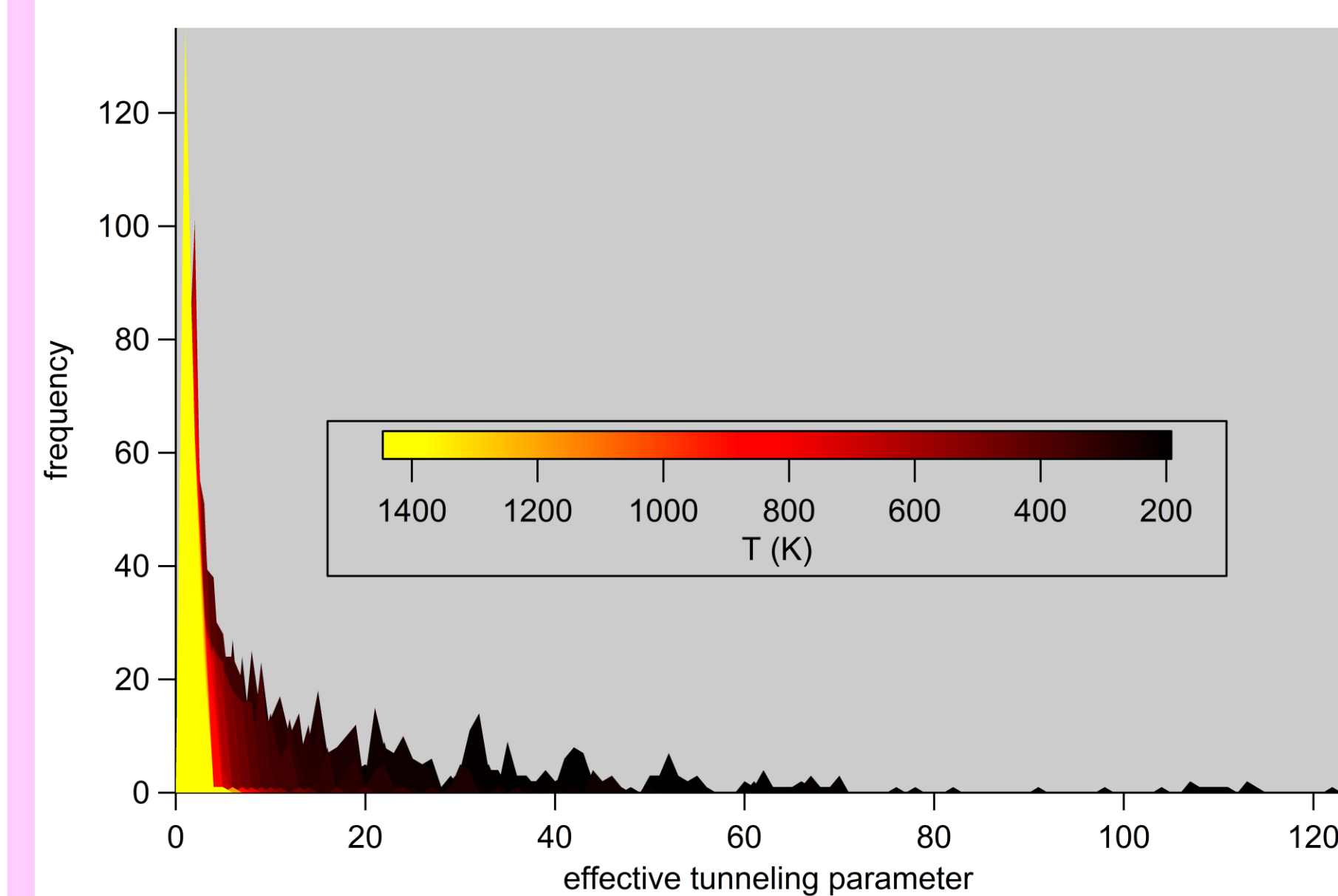
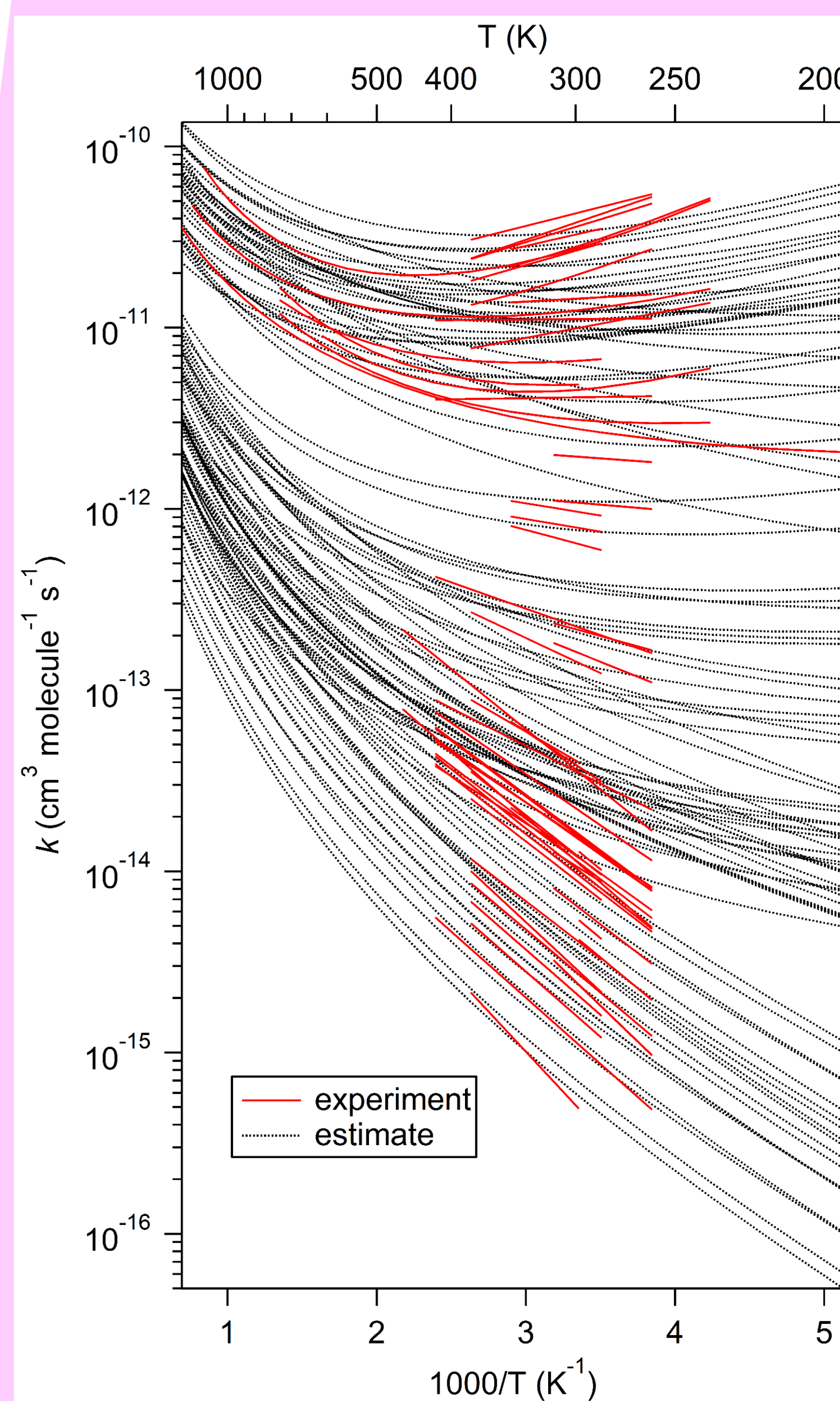
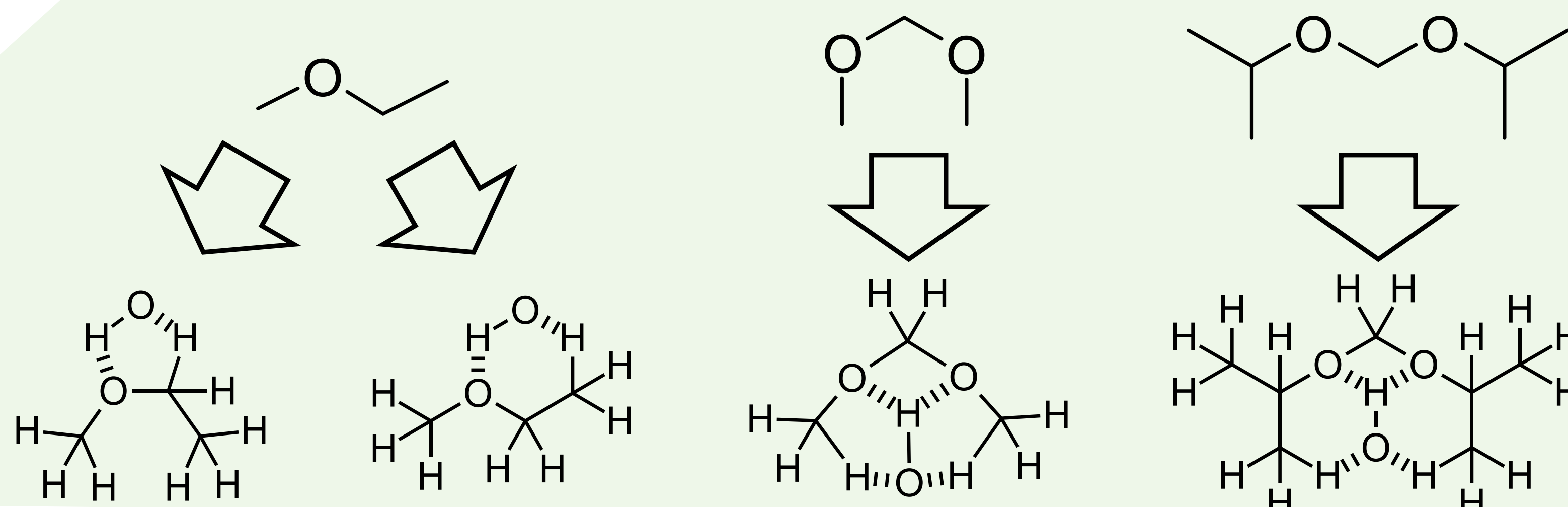
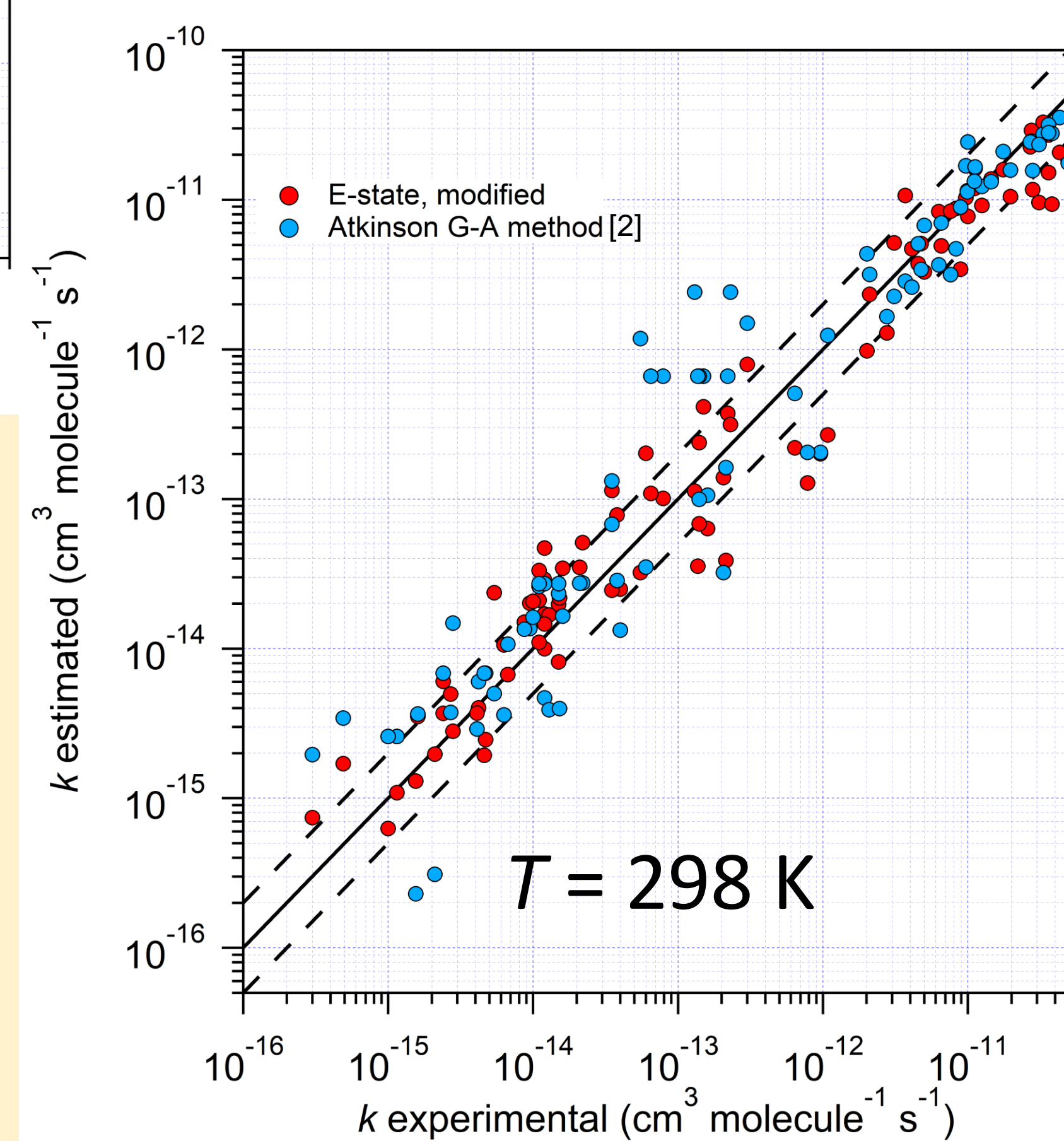
Conclusions and next steps

- The initial E-state parameterization was trained on alkanes and haloalkanes
- This parameterization was retained and augmented with a multiplicative correction to describe vdW
- The results are convincing for etheric molecules, and will be extended to other oxygenates
- Open, Python-based software will be upgraded to include these new aspects



- Without modification, the E-state underestimates k_{OH} for alkyl ethers and overestimates k_{OH} for halogenated ethers

- By parameterizing the capacity of a molecule to form van der Waals complexes, we obtain a much better performance



- Frequency distributions of κ for different values of T

- Experimental and estimated $k(T)$ for each etheric molecule considered in this study. Clear non-Arrhenius behaviour is observed in many cases

References

- [1] M.R. McGillen, L. Michelat, J.J. Orlando, W.P.L. Carter, Environ. Sci.: Atmos., 4 18–34 (2024)
 [2] E.S.C. Kwok, R. Atkinson, Atmos. Environ., 29 1685–1695 (1995)