

# Revisiting the gas-phase rate coefficient of the $\text{OH} + \text{SO}_2 + \text{M} \rightarrow \text{HSO}_3 + \text{M}$ reaction

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PIVOTS

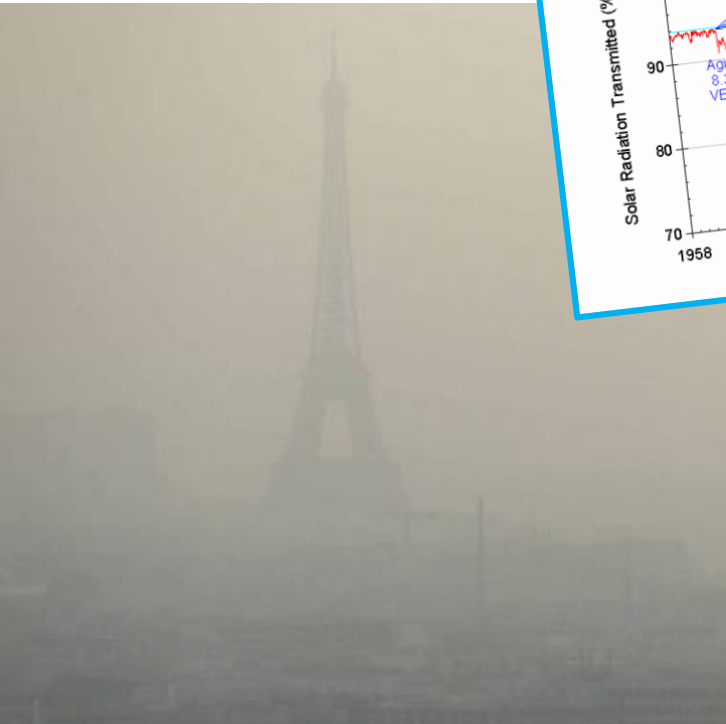
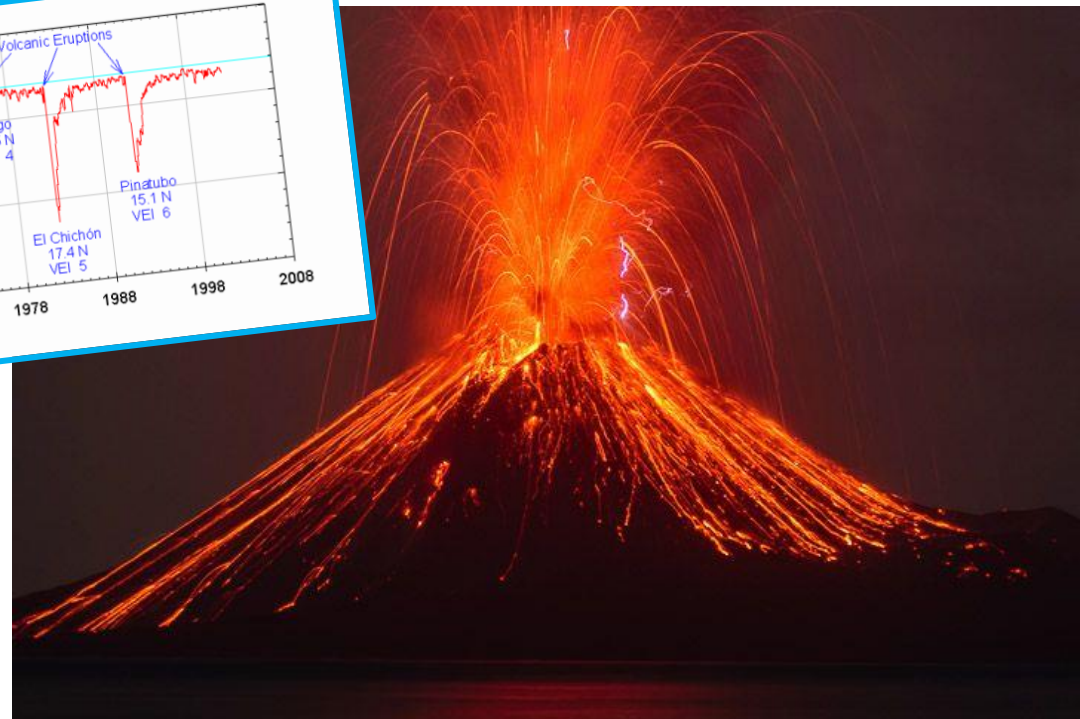
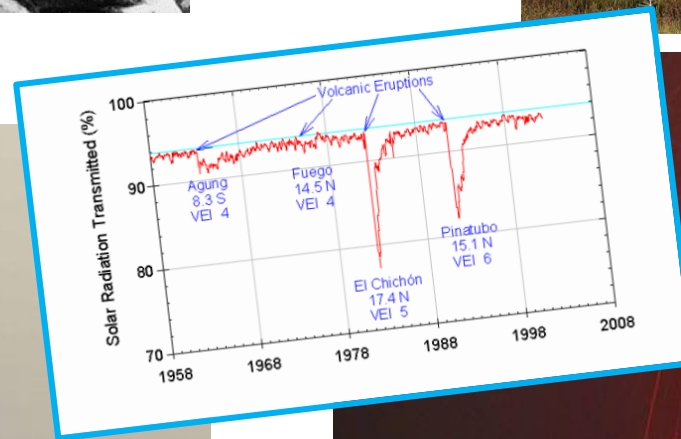
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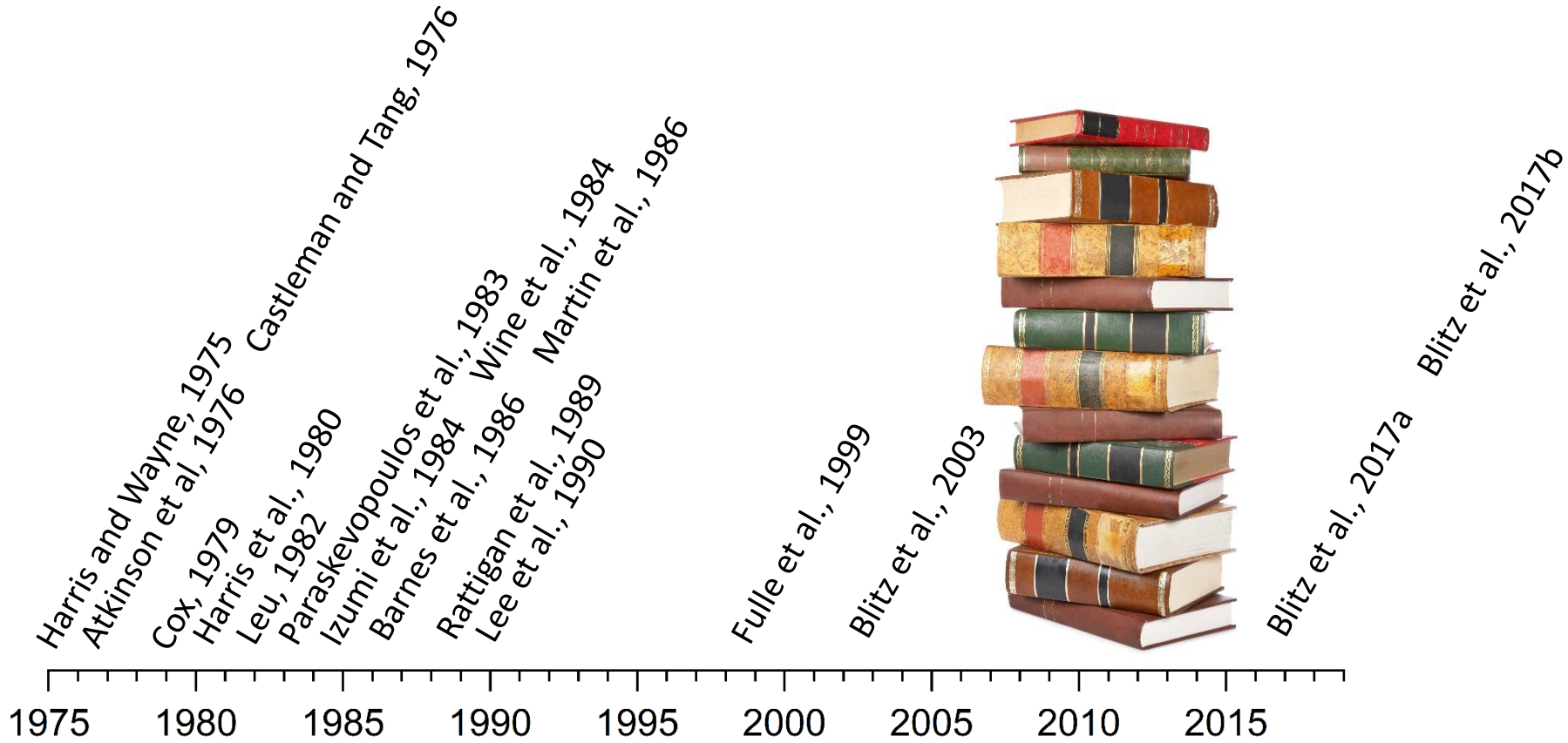


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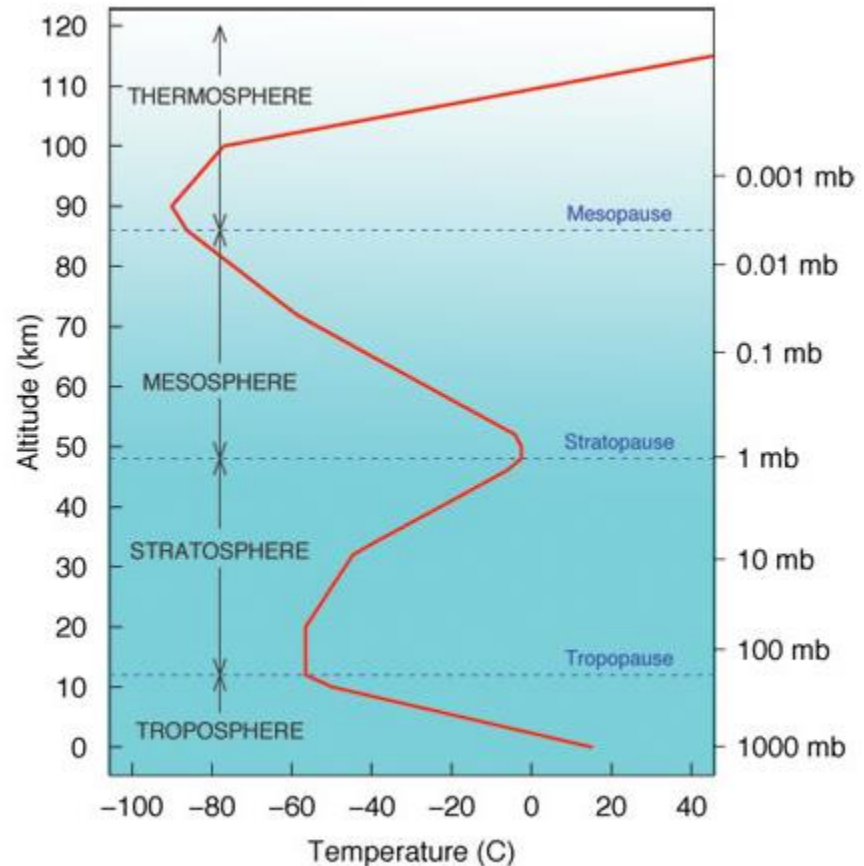


# Haven't people measured this rate constant already?!



# The atmosphere: it's structure and composition

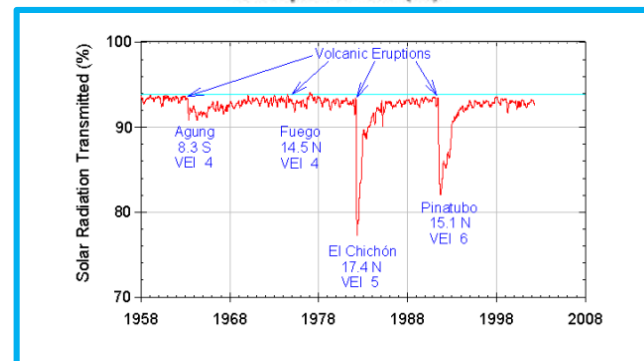
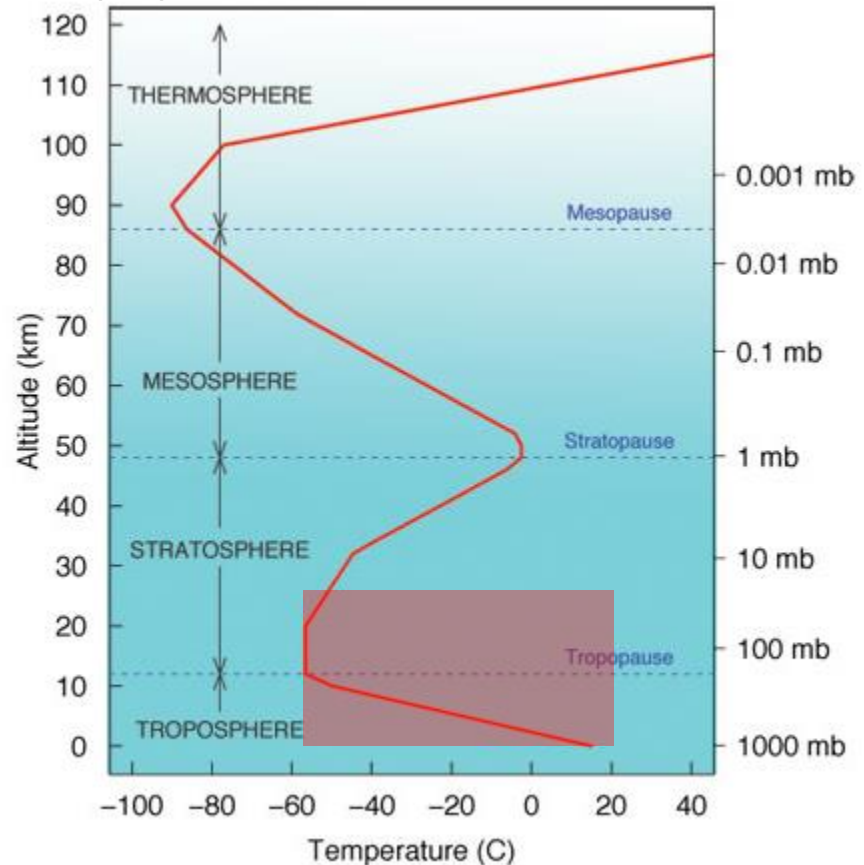
- The atmosphere is composed of a mixture of gases:  
N<sub>2</sub>: 78%, O<sub>2</sub>: 21%, Ar: 1%,  
and trace gases: <1%
- The atmosphere experiences a range of temperatures (-90–40°C)
- And pressures (0.0076–760 Torr)



Two approaches are possible...

# 1. The pragmatic approach

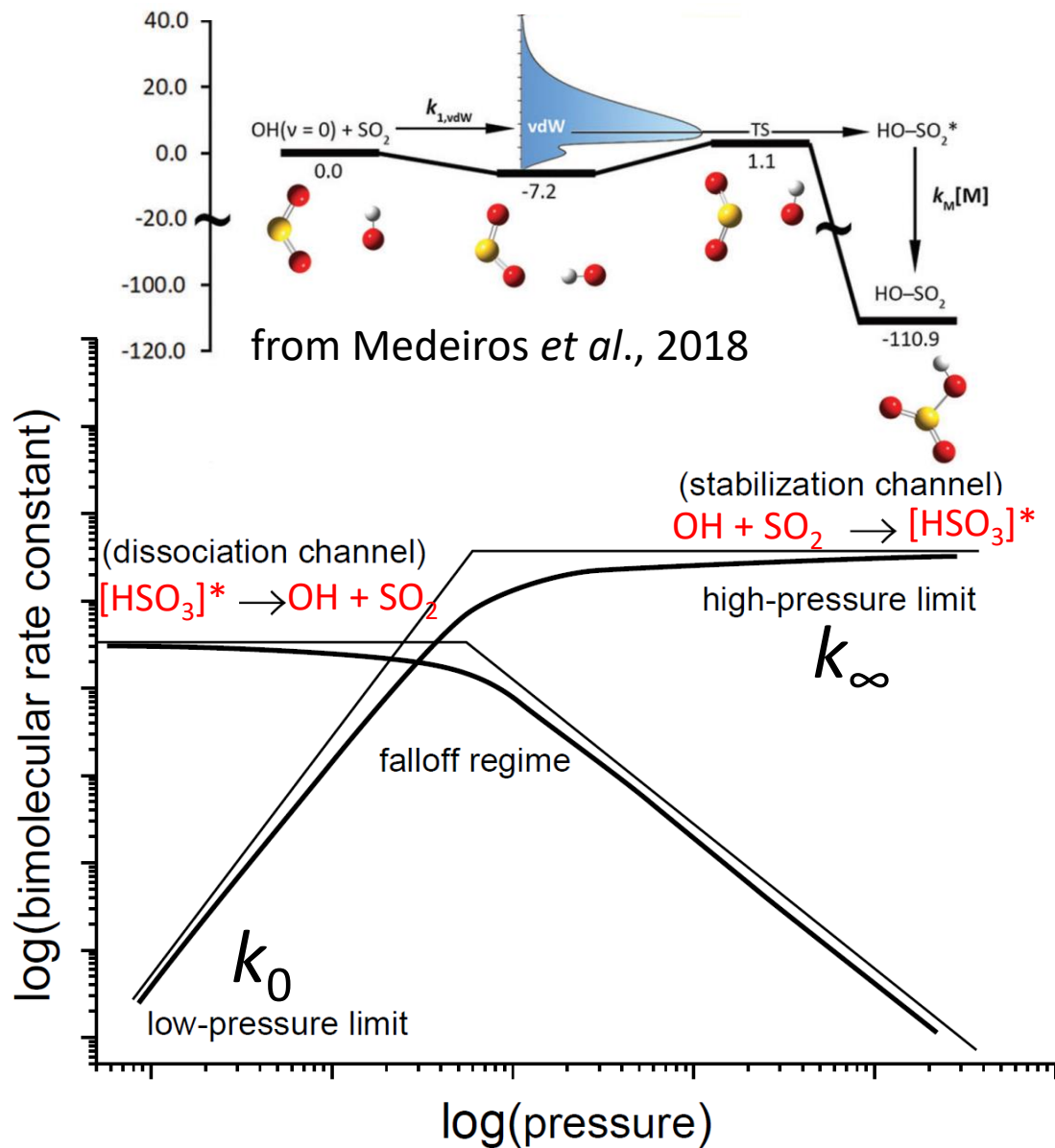
- Sources of  $\text{SO}_2$  are at ground level:  
Fuel burning/ volcanic eruptions/ DMS oxidation
- Lifetime of  $\text{SO}_2$  (and precursors) is short (days)
- Transport up to the stratosphere takes time (5–10 years)
- Large volcanic eruptions can inject  $\text{SO}_2$  <25 km
- So,  $\sim -50$ – $20^\circ\text{C}$  and 25–760 Torr (air)



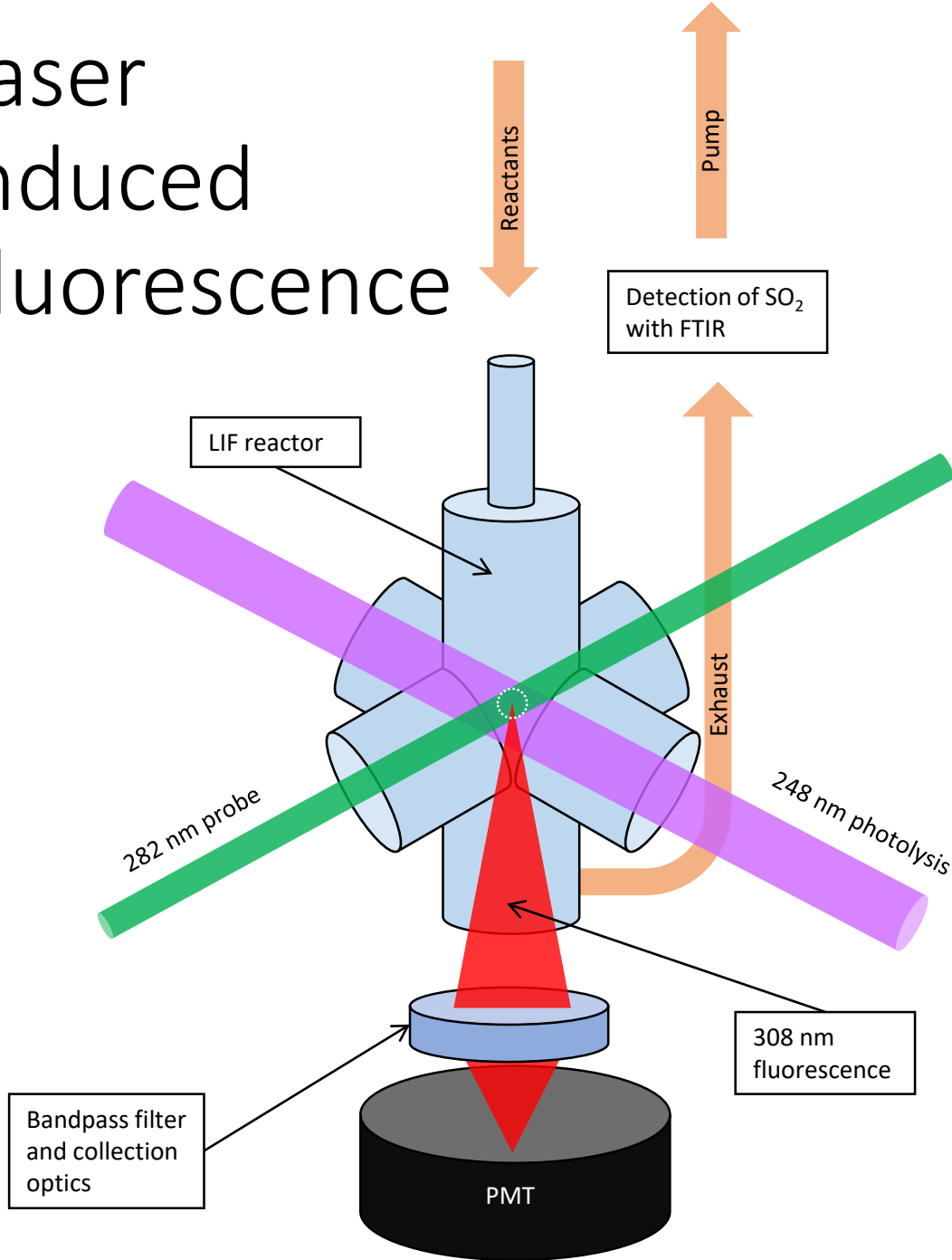


# 2. The fundamental approach

- Direct experimental measurements need to be performed at  $v.$  high and  $v.$  low  $P$
- Knowledge of  $k_{\infty}(T)$  and  $k_0(T)$  constrains fit to  $P$
- Observation of a positive temperature dependence to  $k_{\infty}$  indicates a barrier to this reaction
- Why is this reaction so slow?

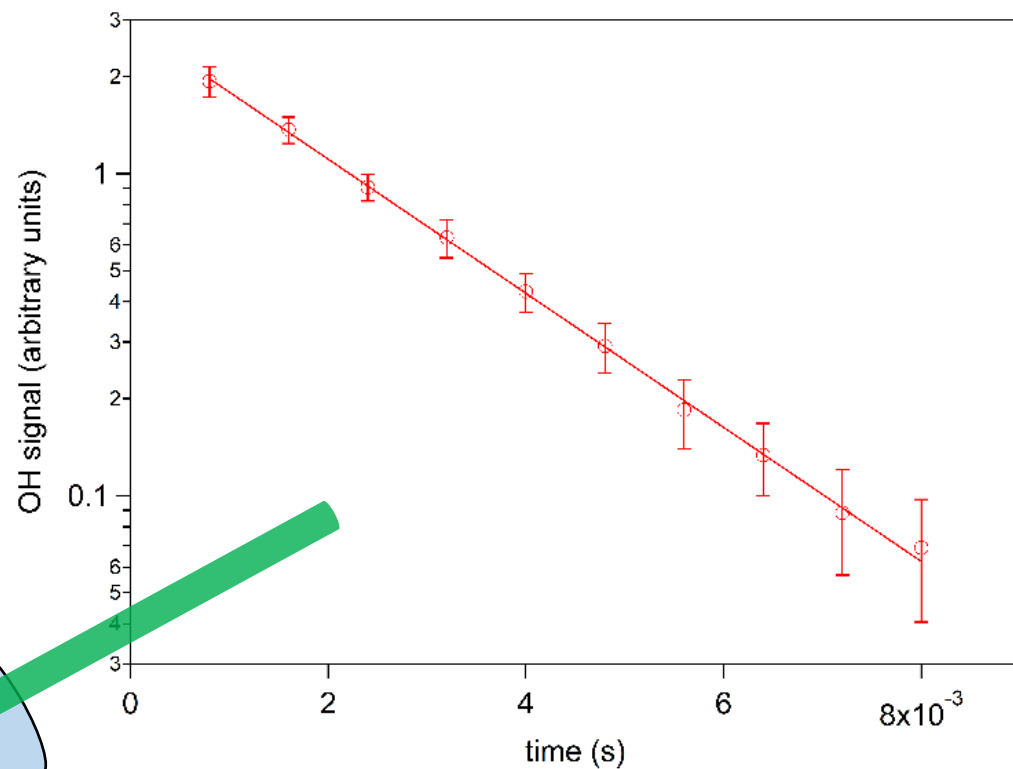
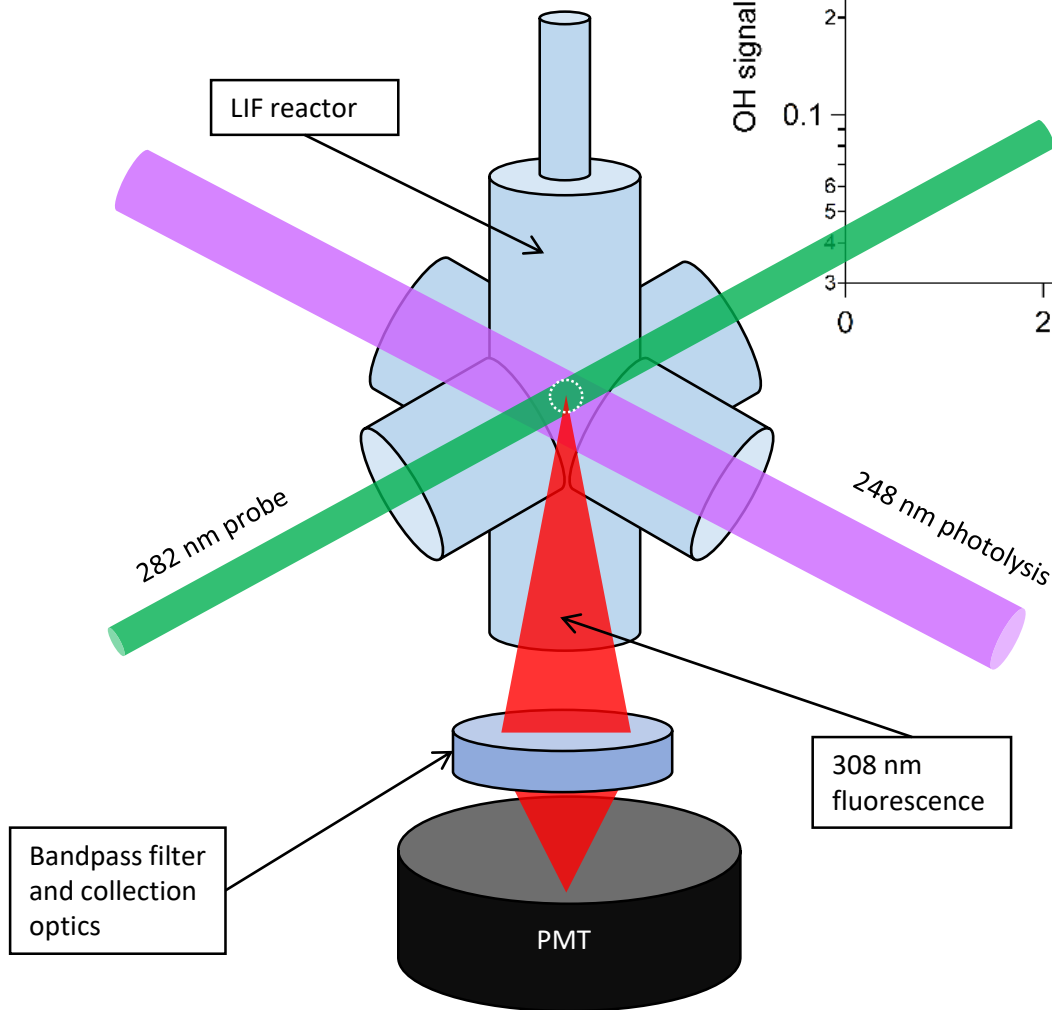


# Laser Induced Fluorescence

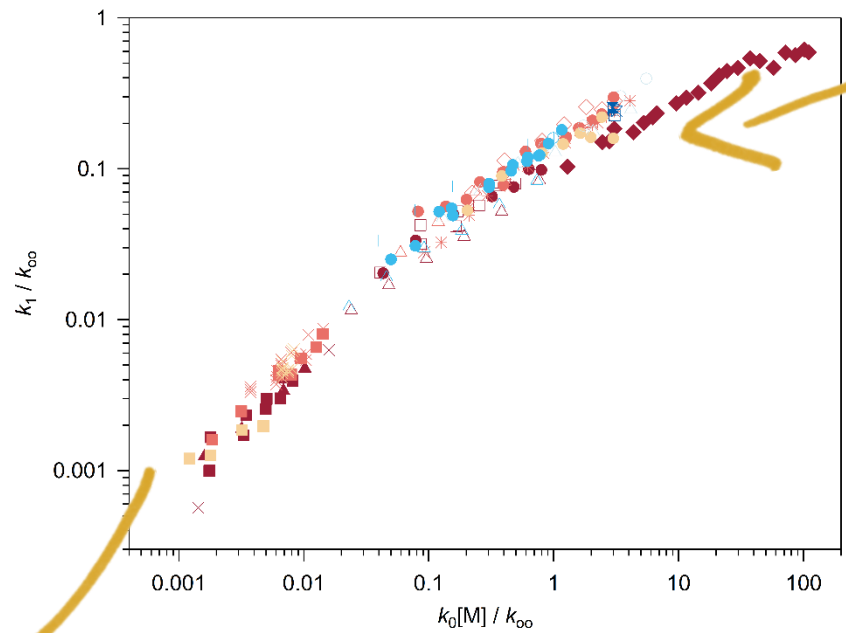
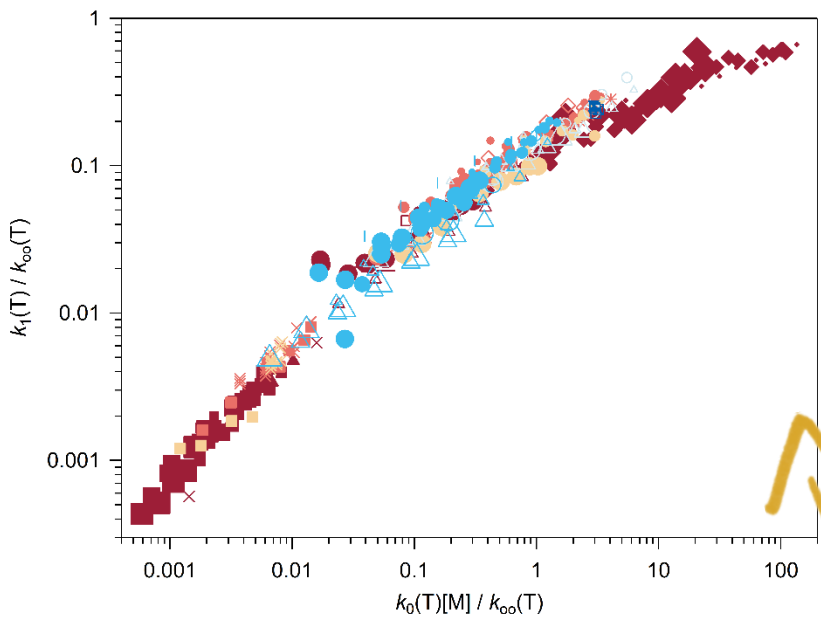
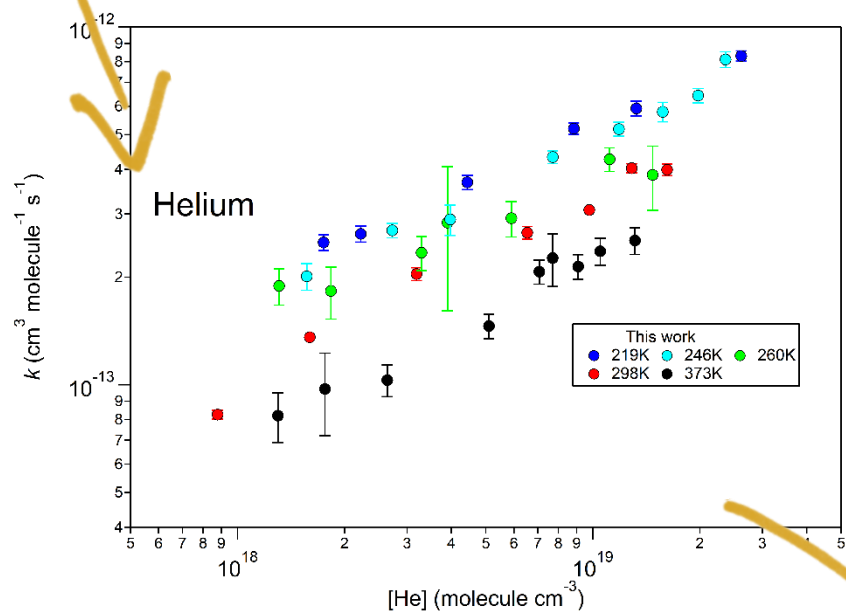
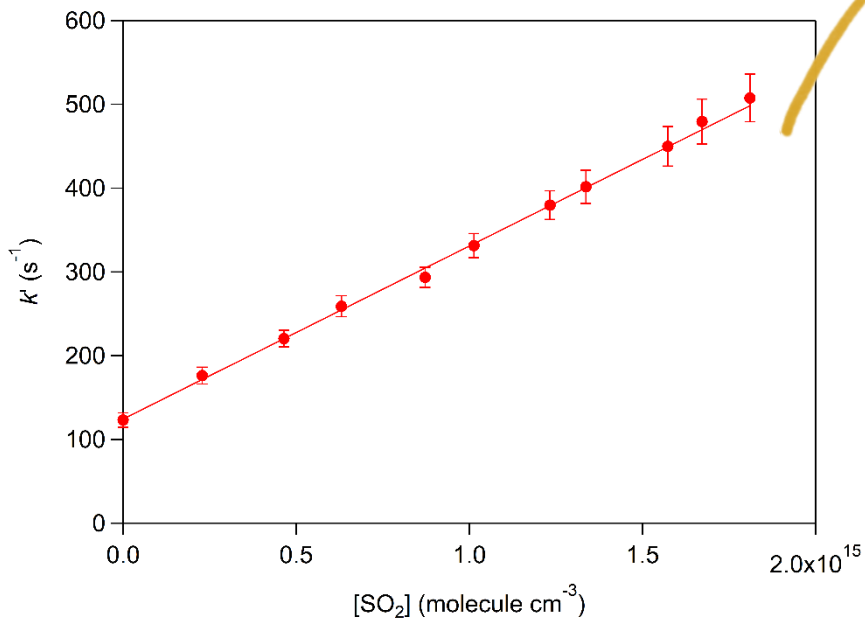


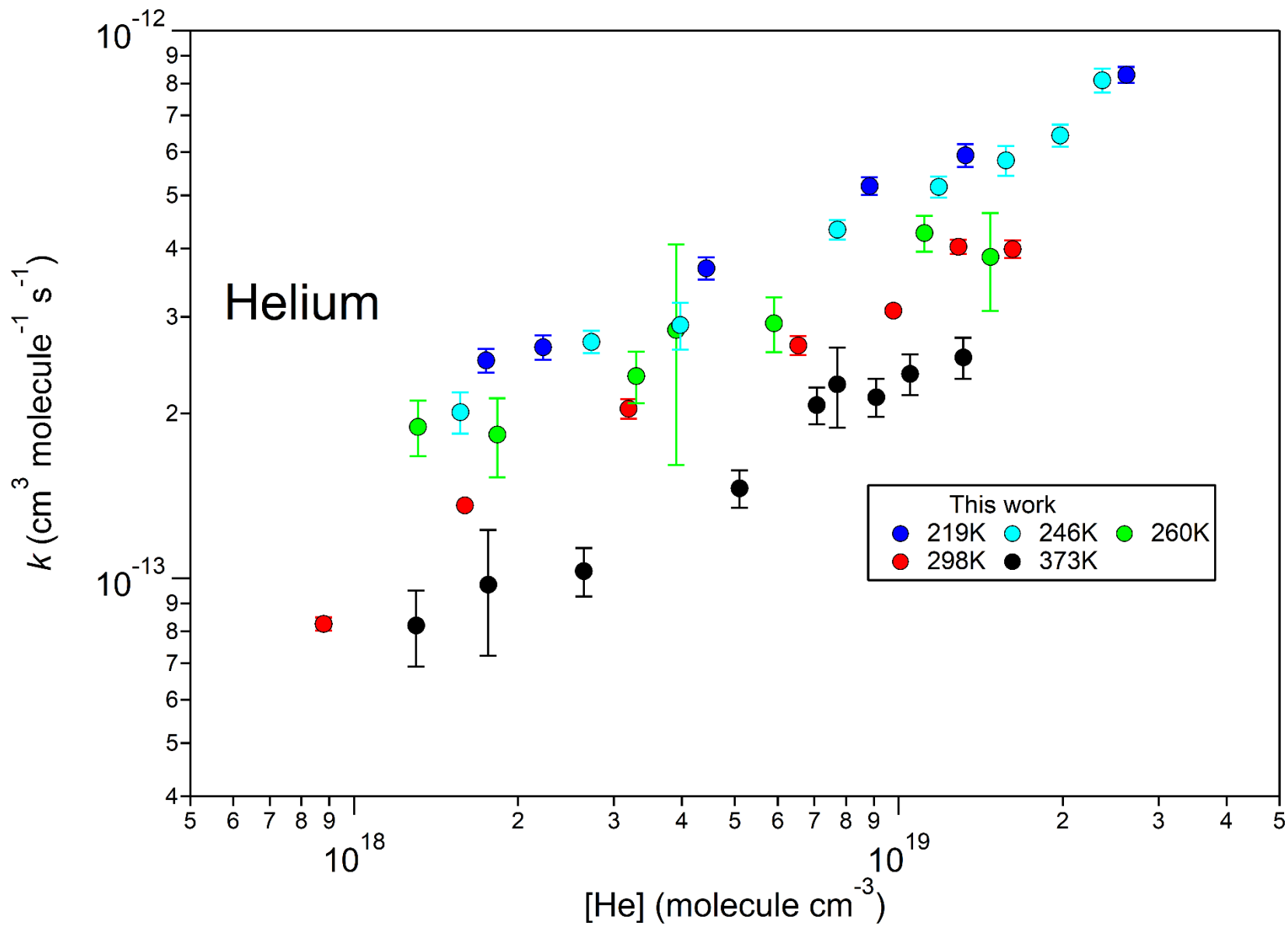
- Temperature range: 220–373 K
- Pressure range: 30–600 Torr
- Bath gases: He, Ar, N<sub>2</sub>, O<sub>2</sub>
- OH precursors: H<sub>2</sub>O<sub>2</sub>, HNO<sub>3</sub>
- On-line measurement of [SO<sub>2</sub>]
- Supporting RR measurements (N<sub>2</sub>, Ar, O<sub>2</sub>, Air)

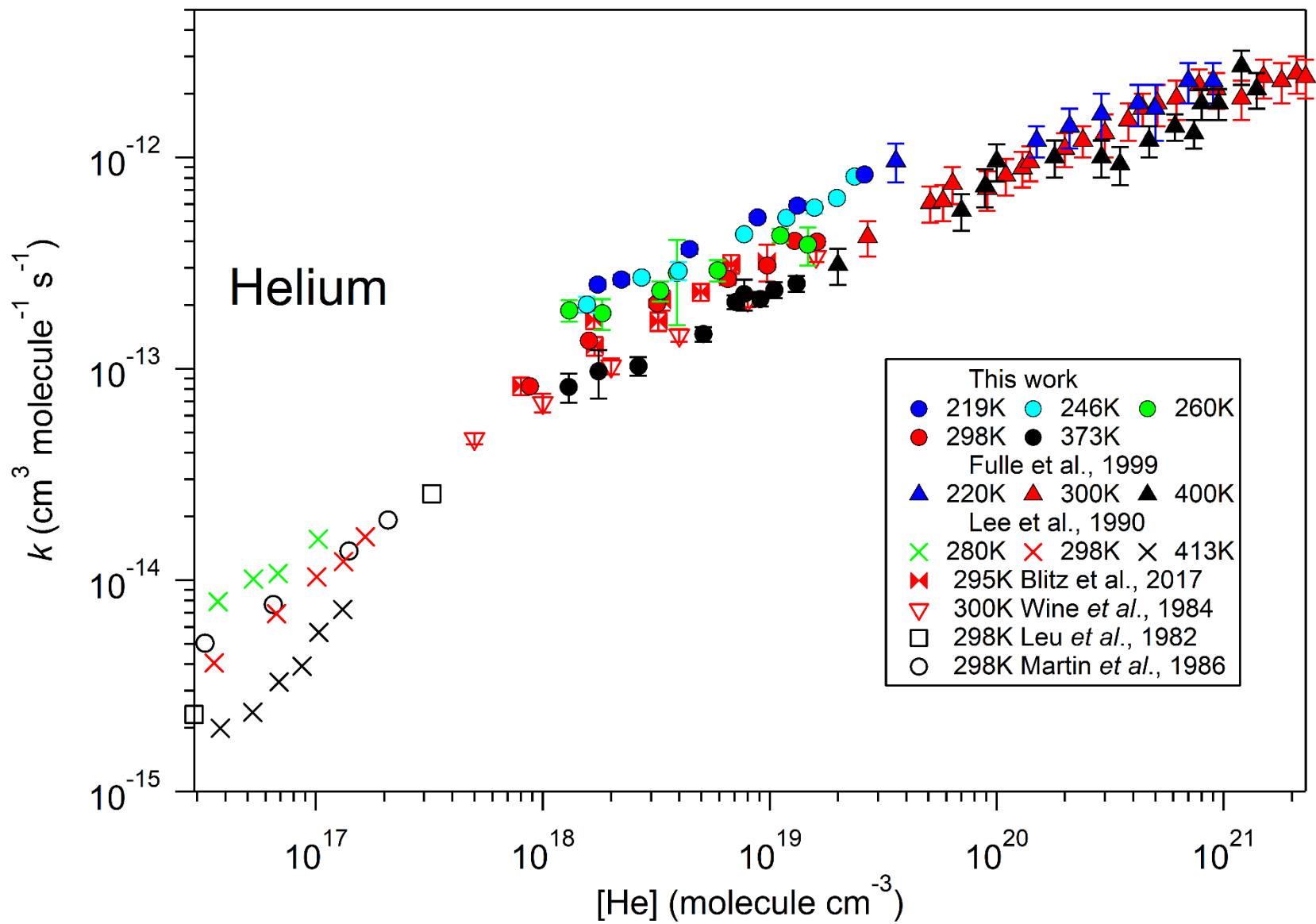
# Laser Induced Fluorescence

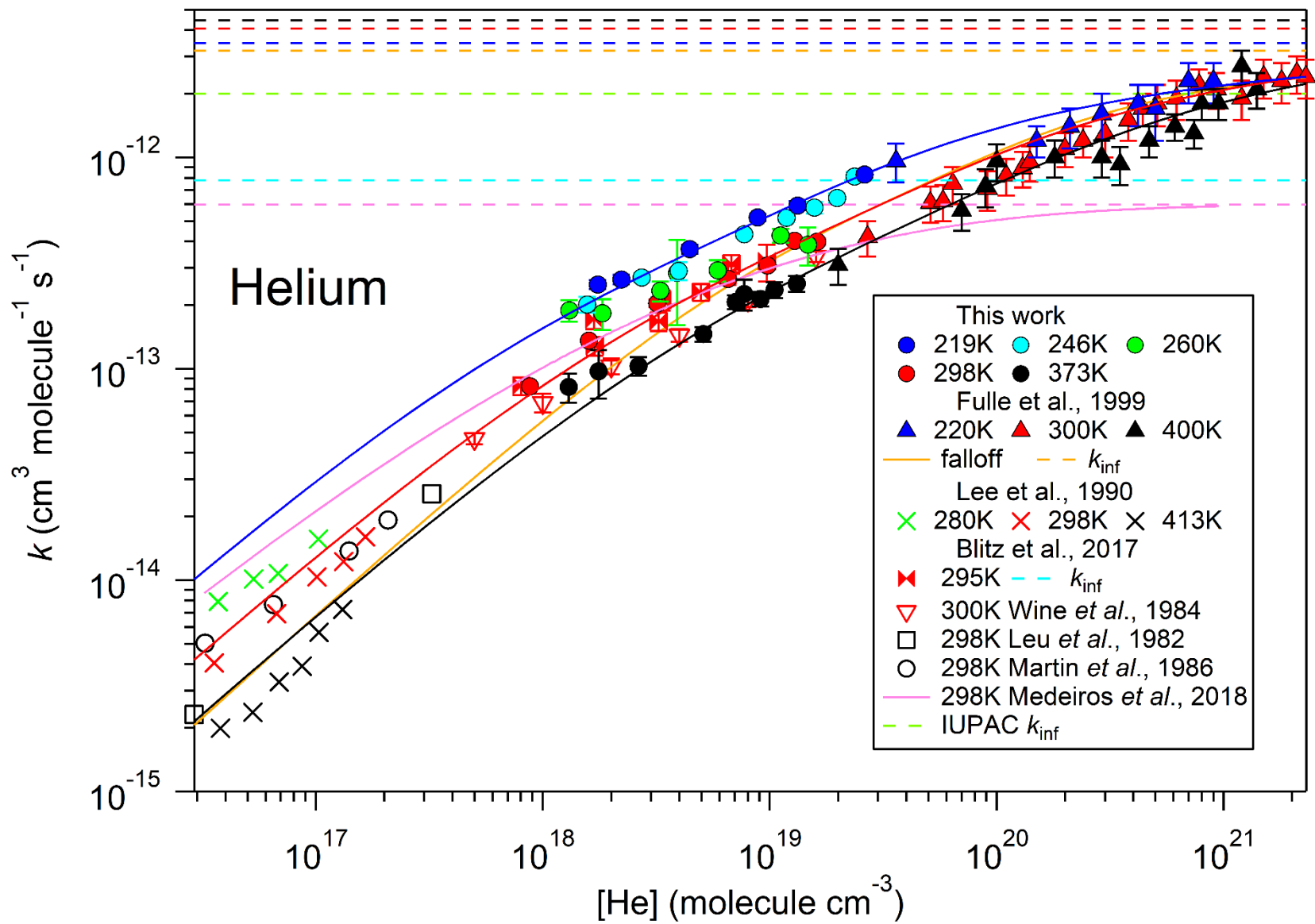


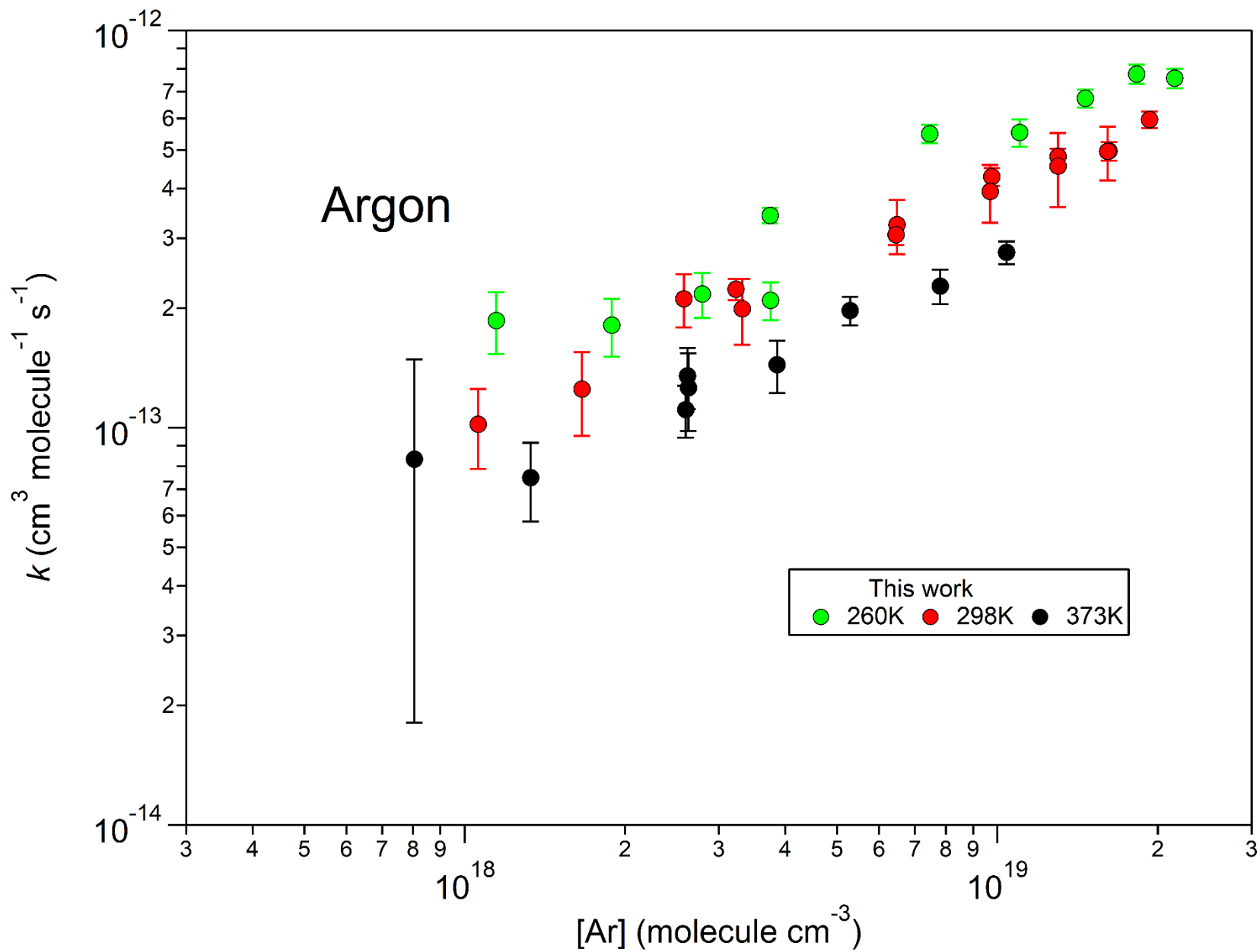


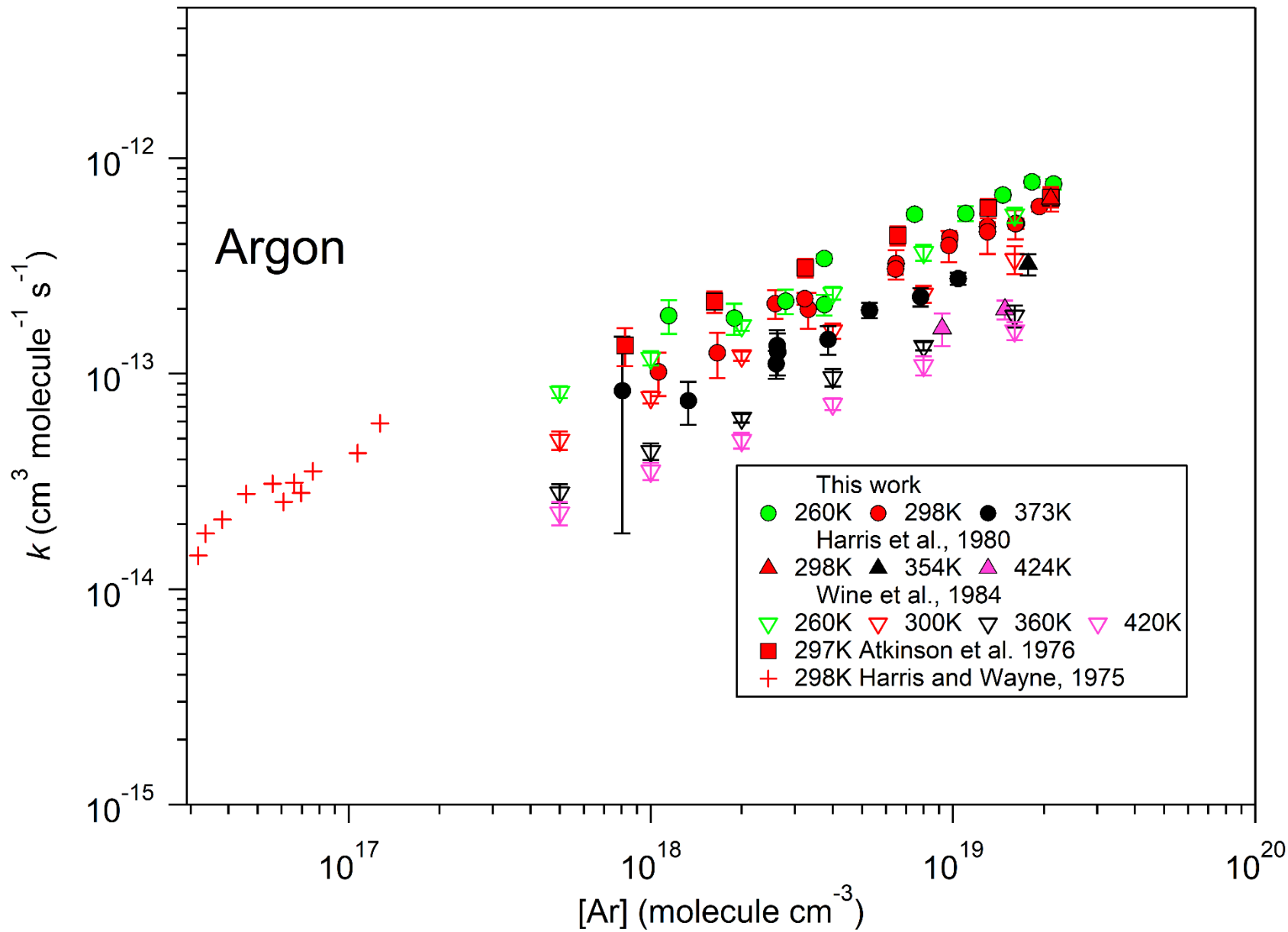




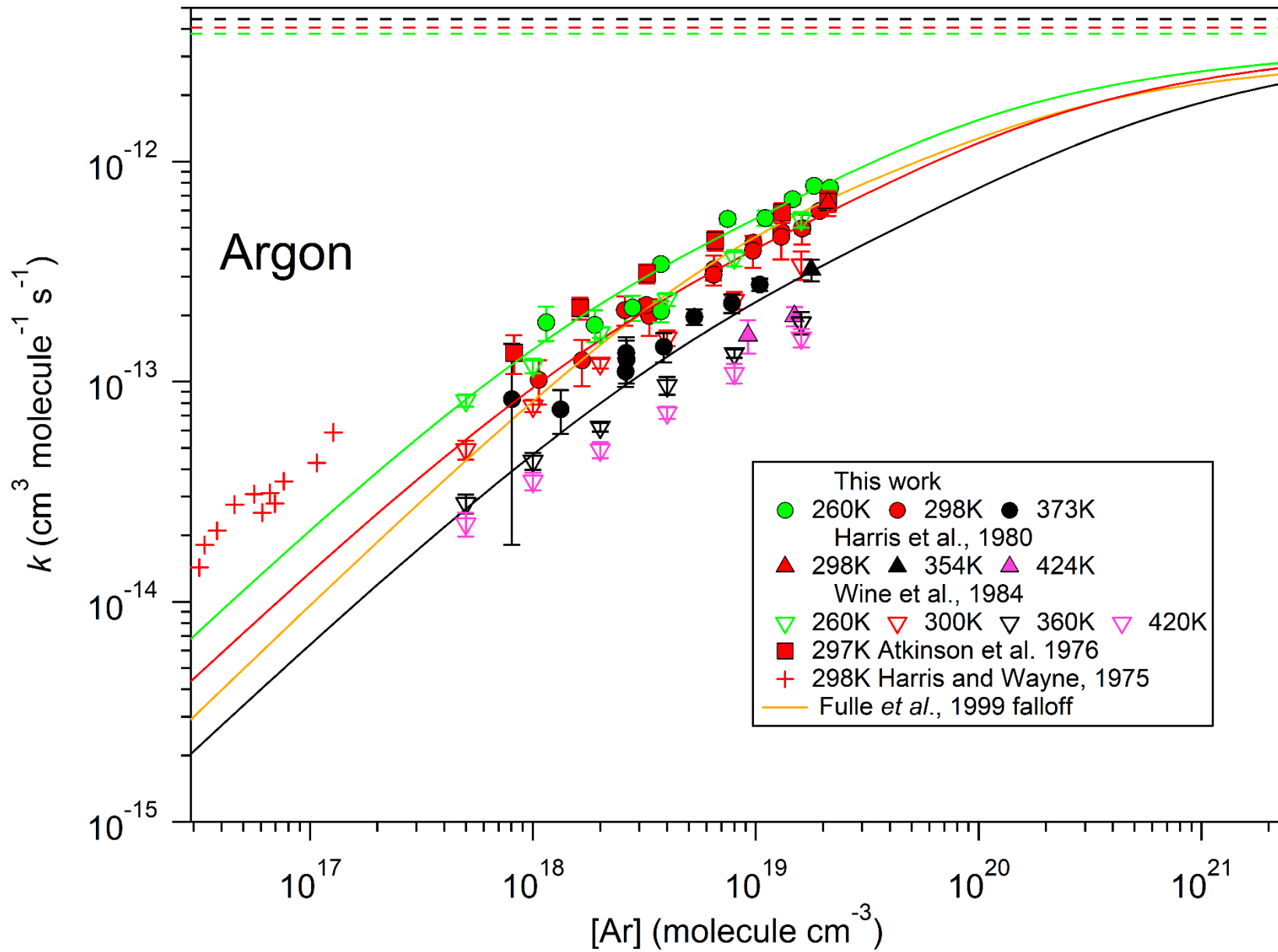


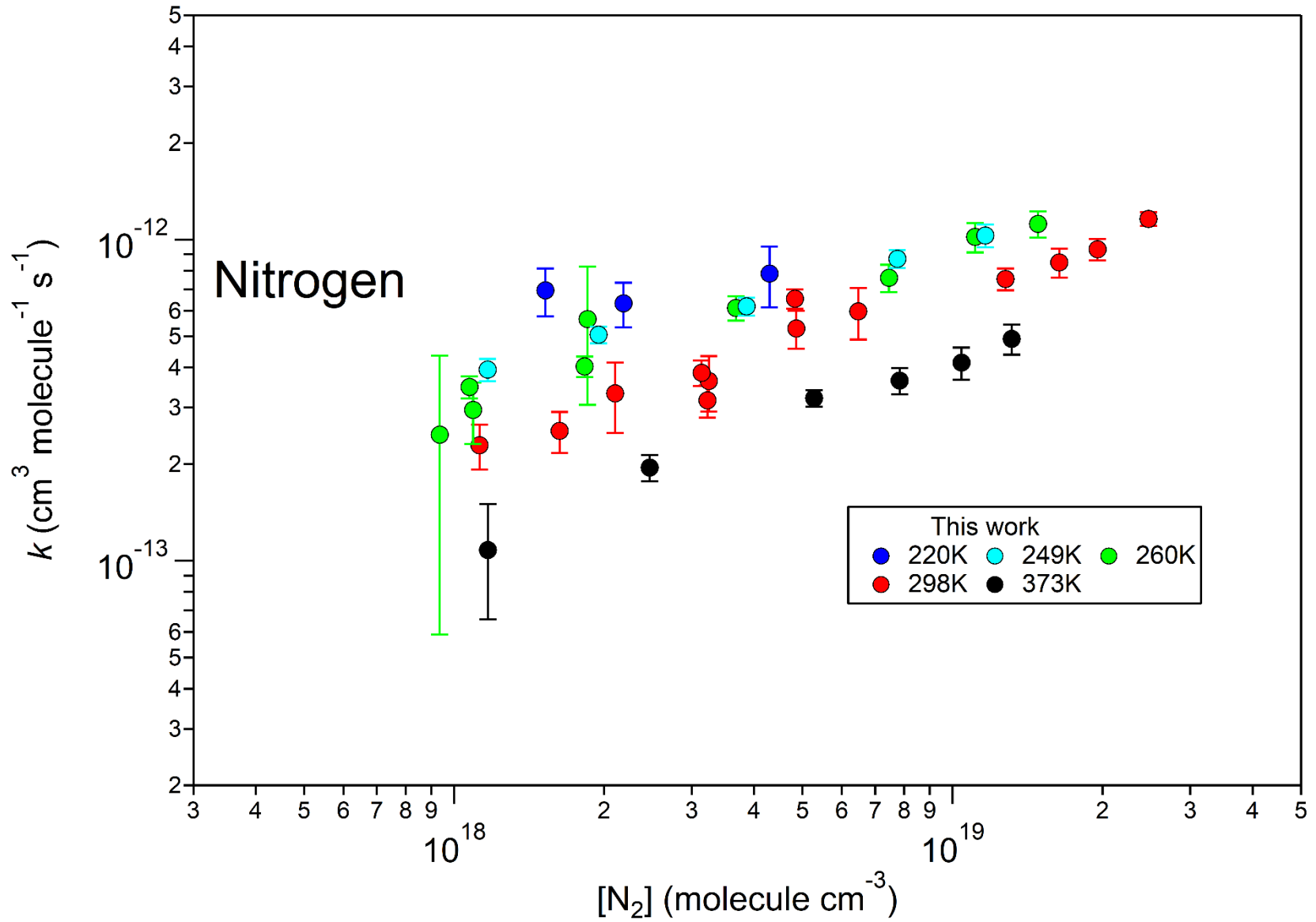


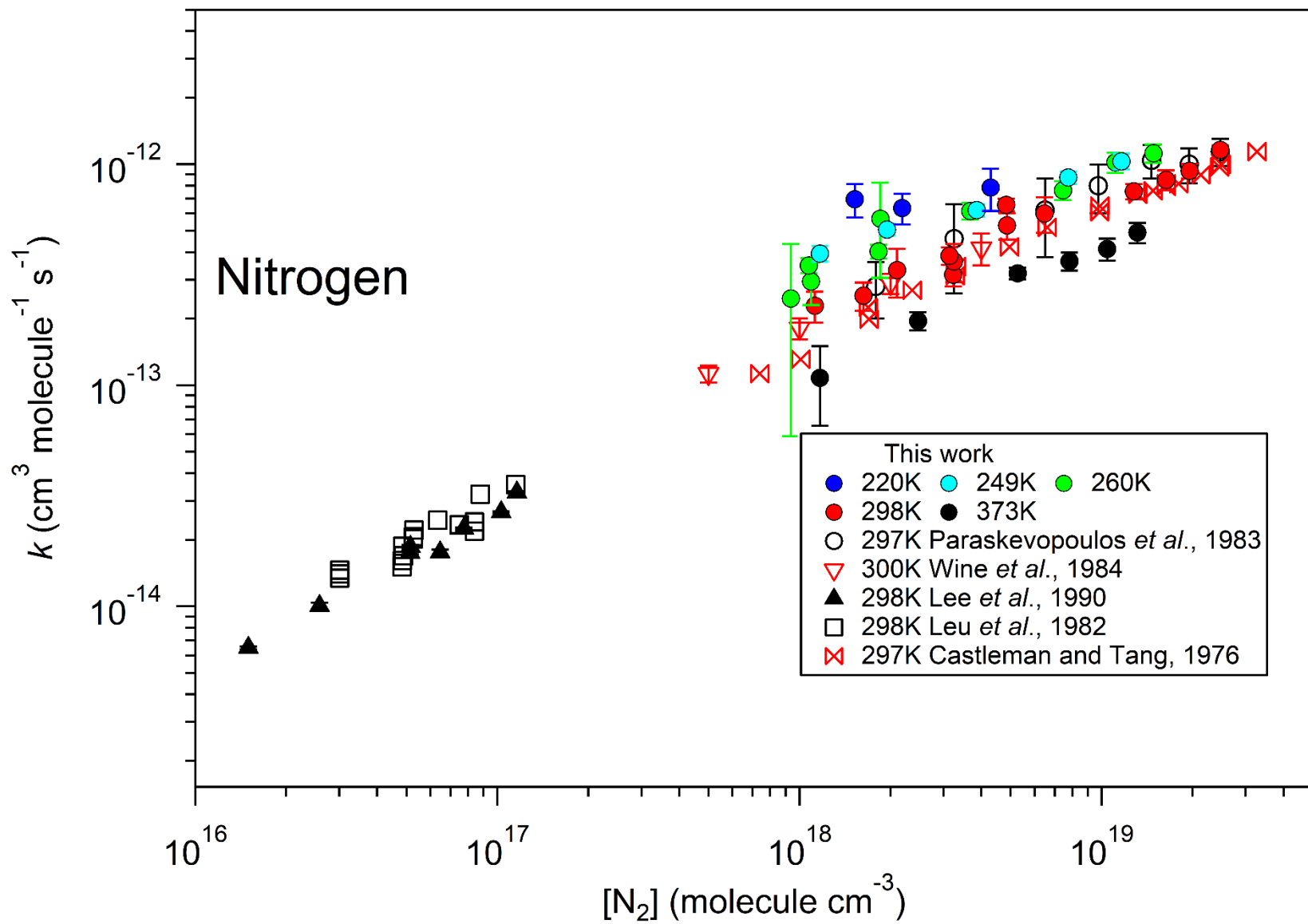


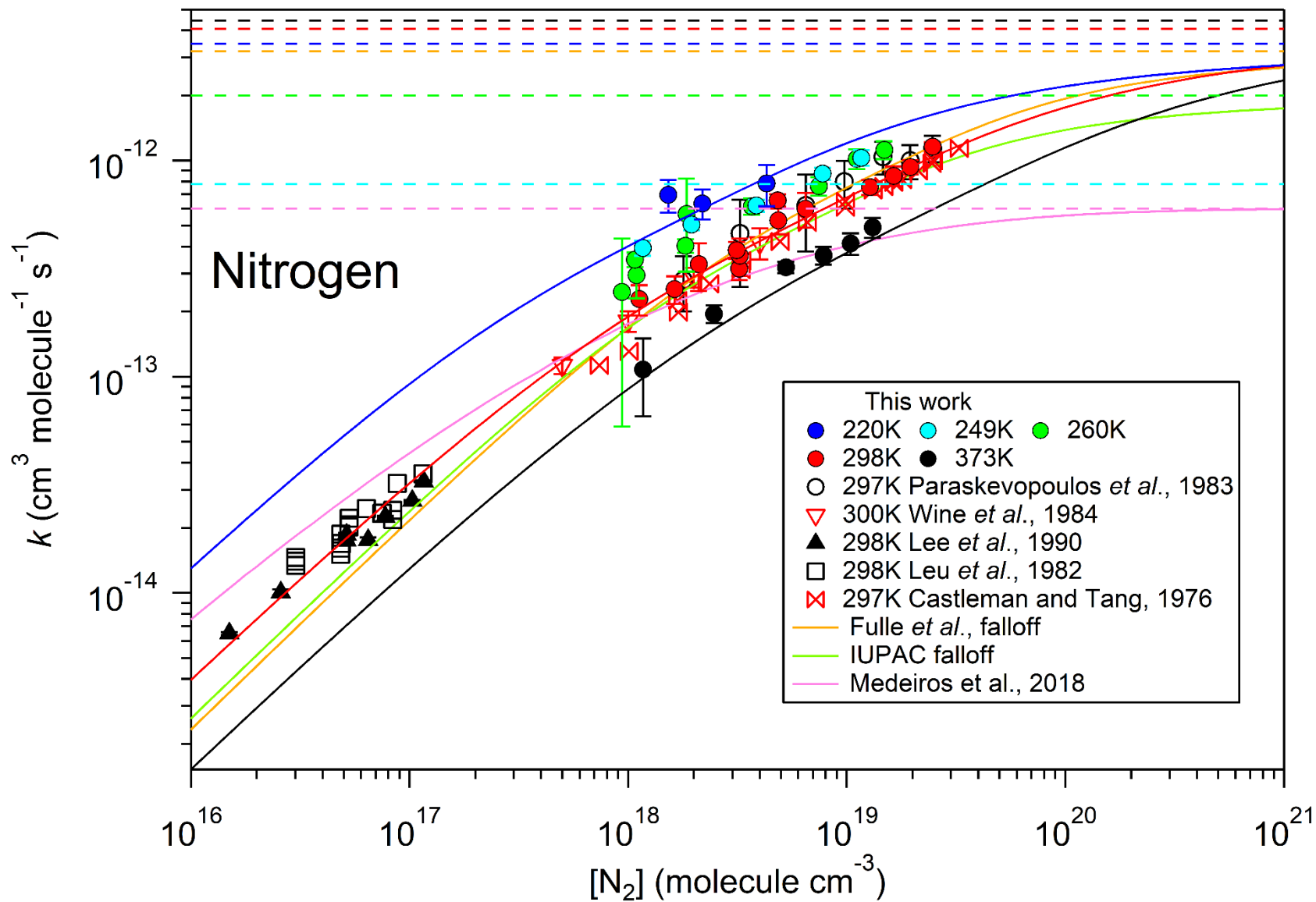


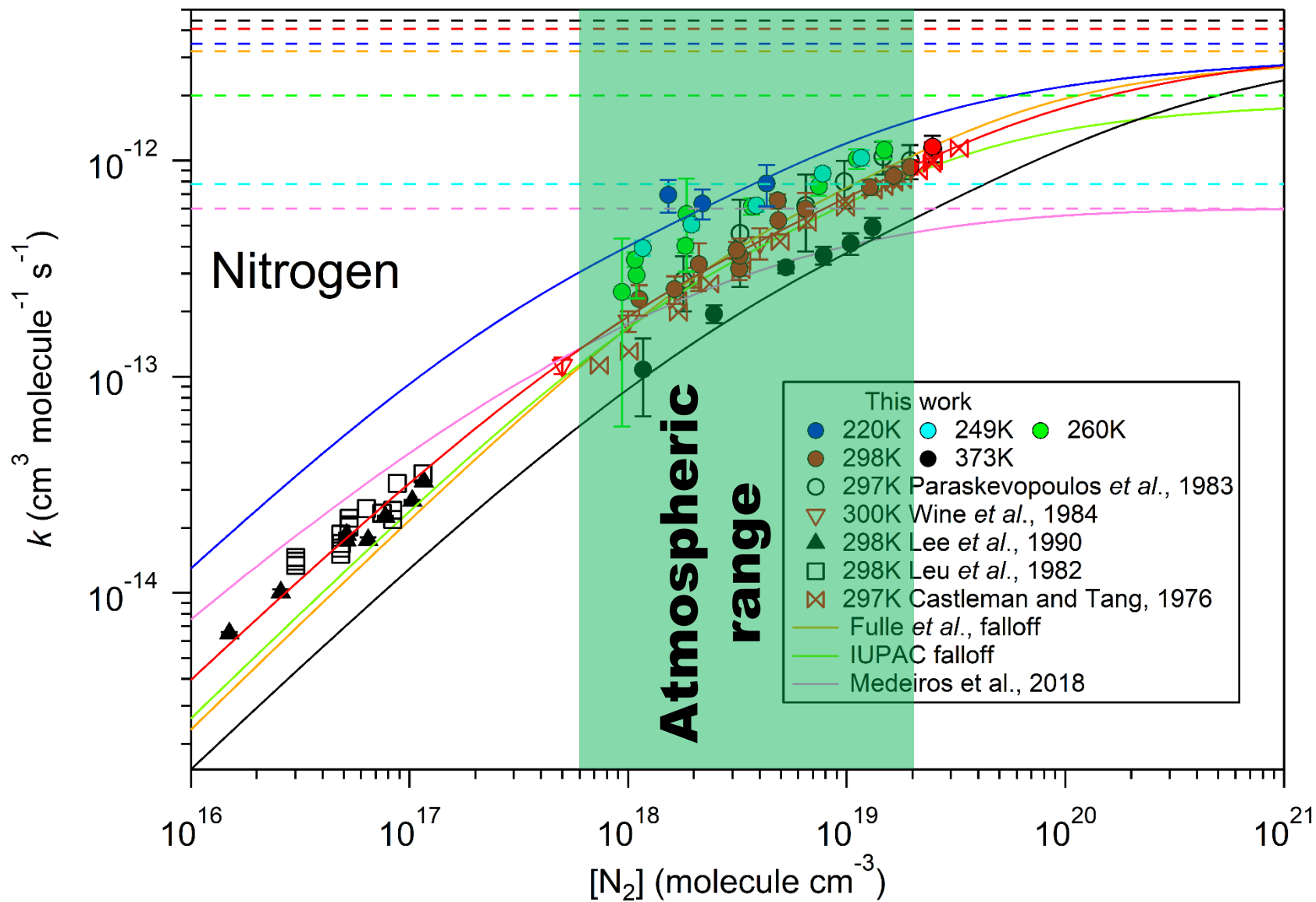


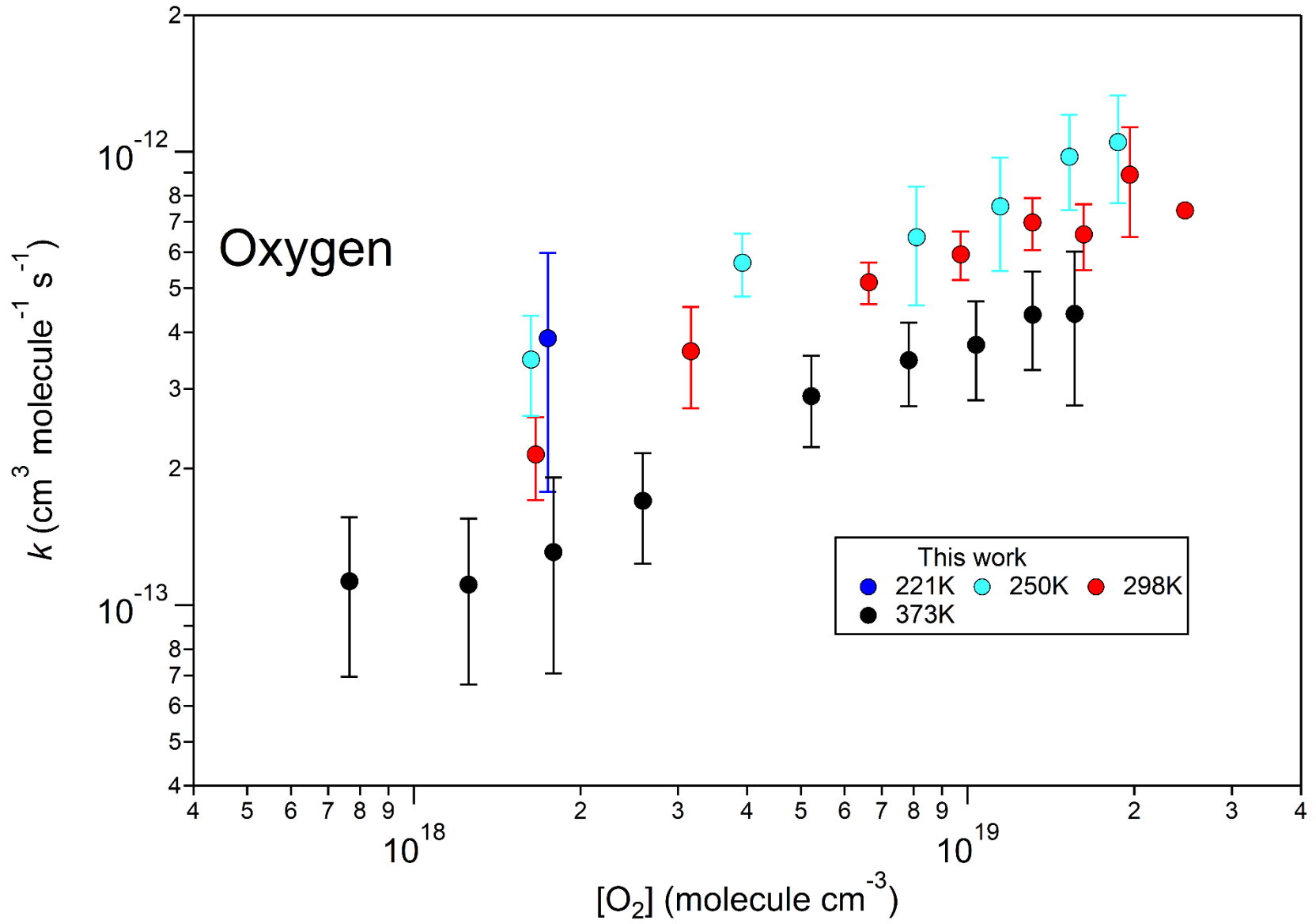




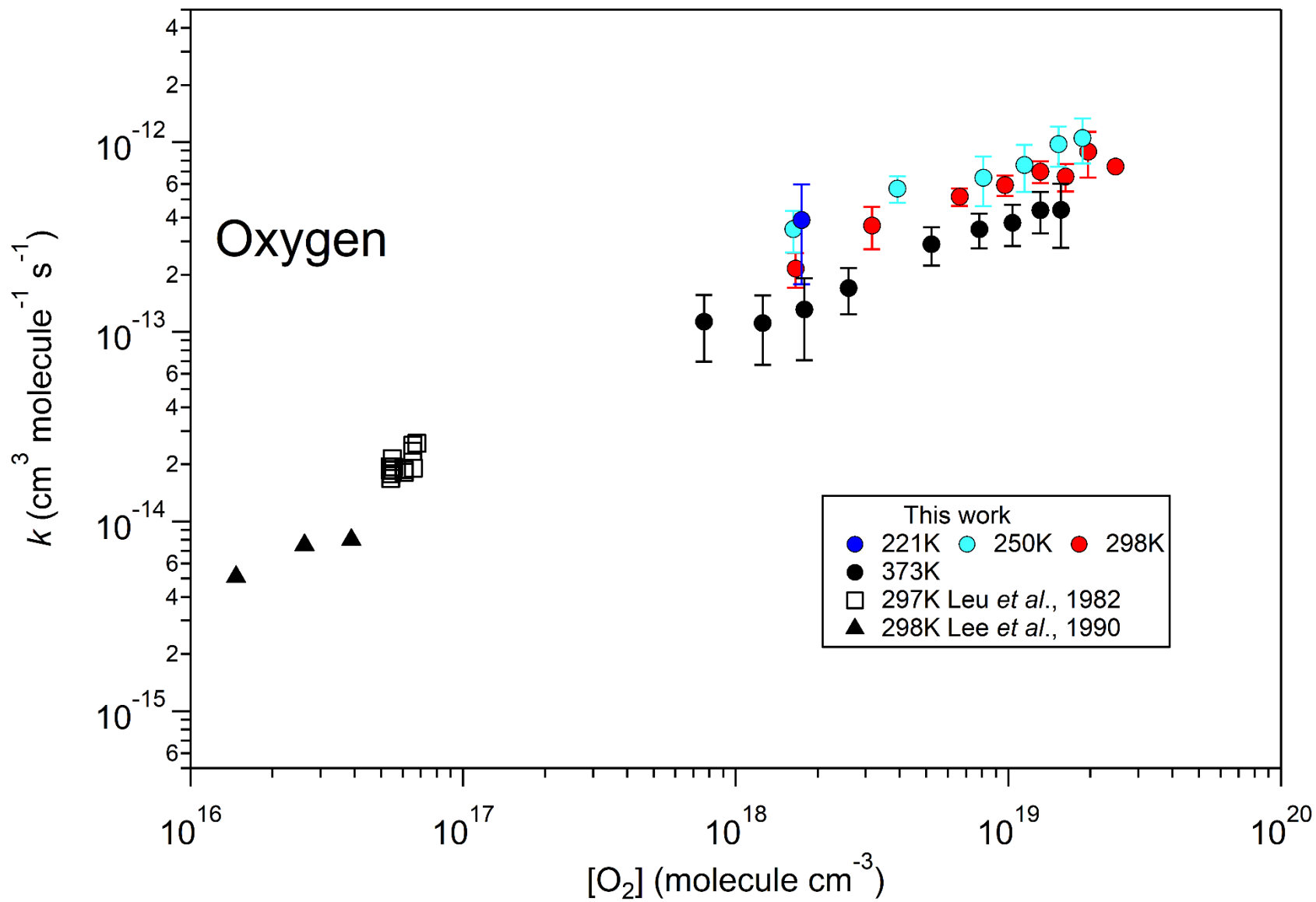


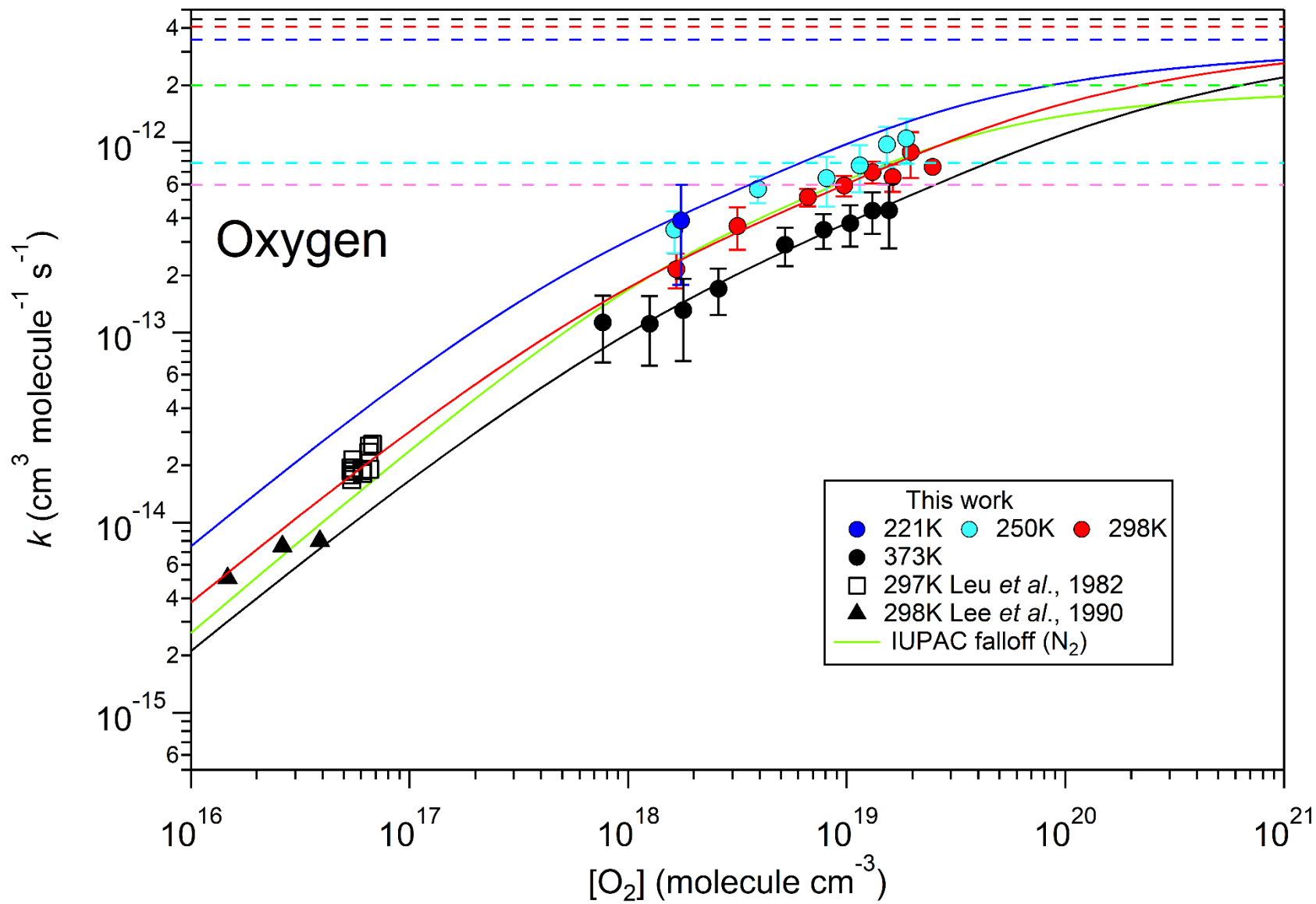


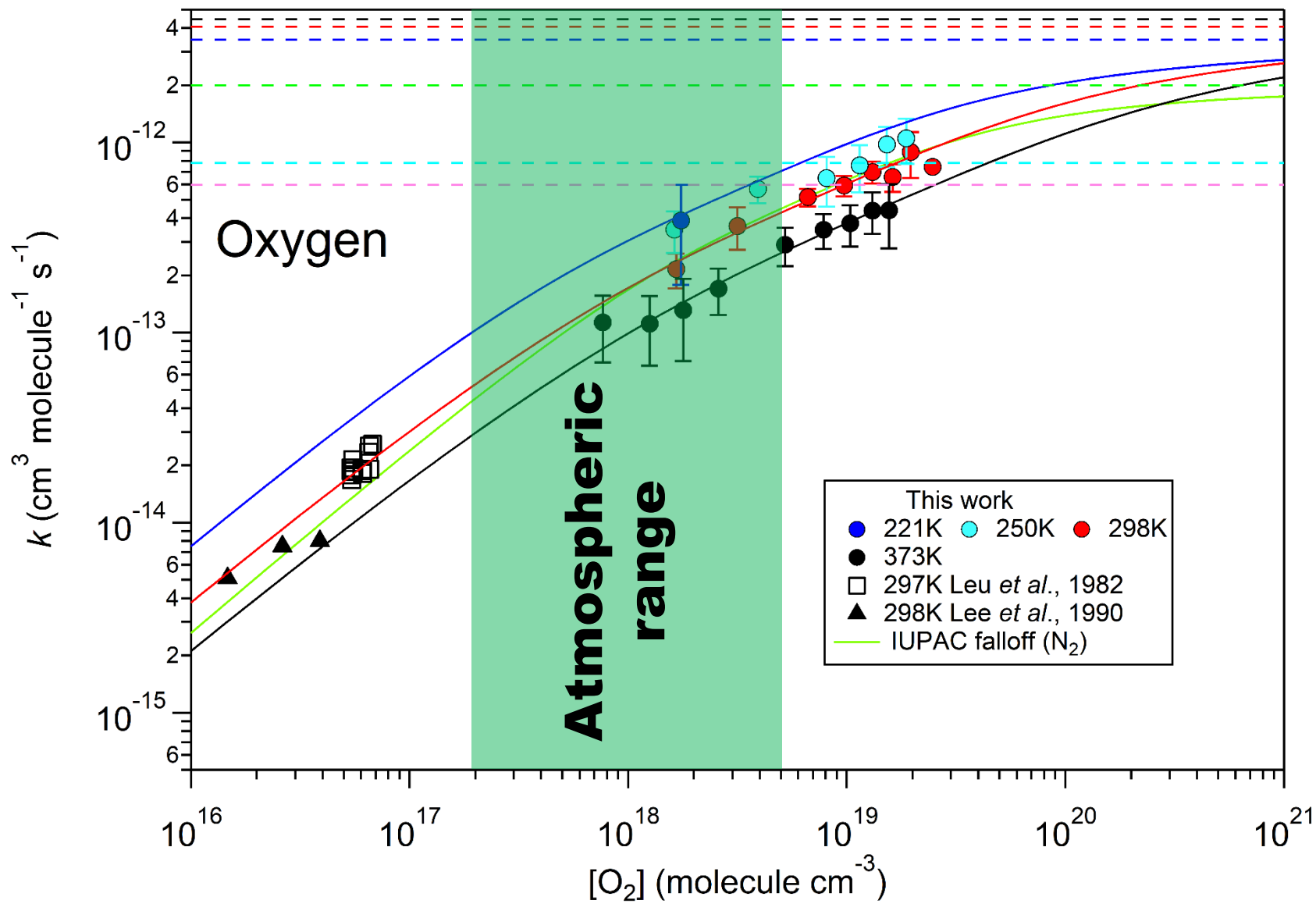




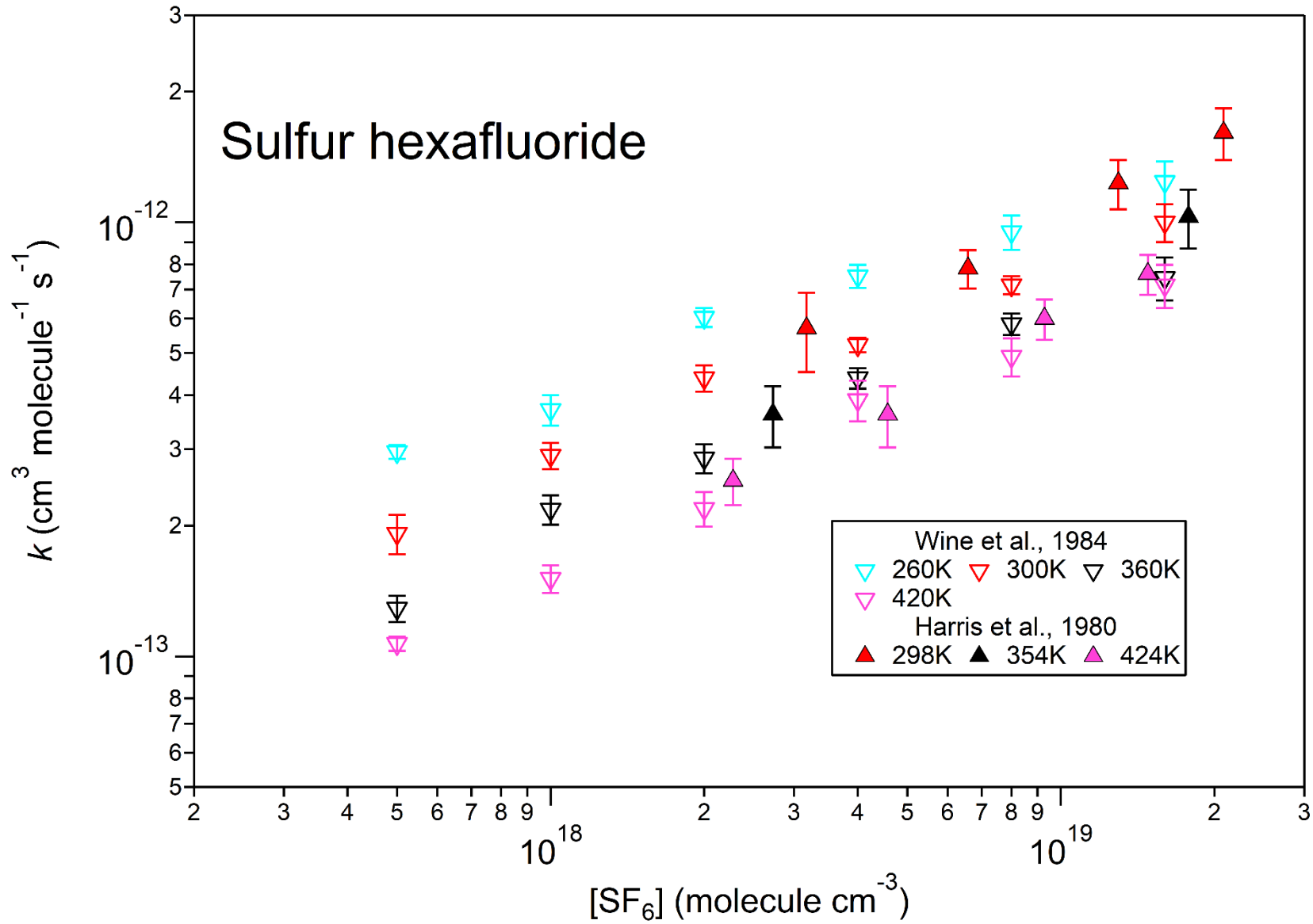


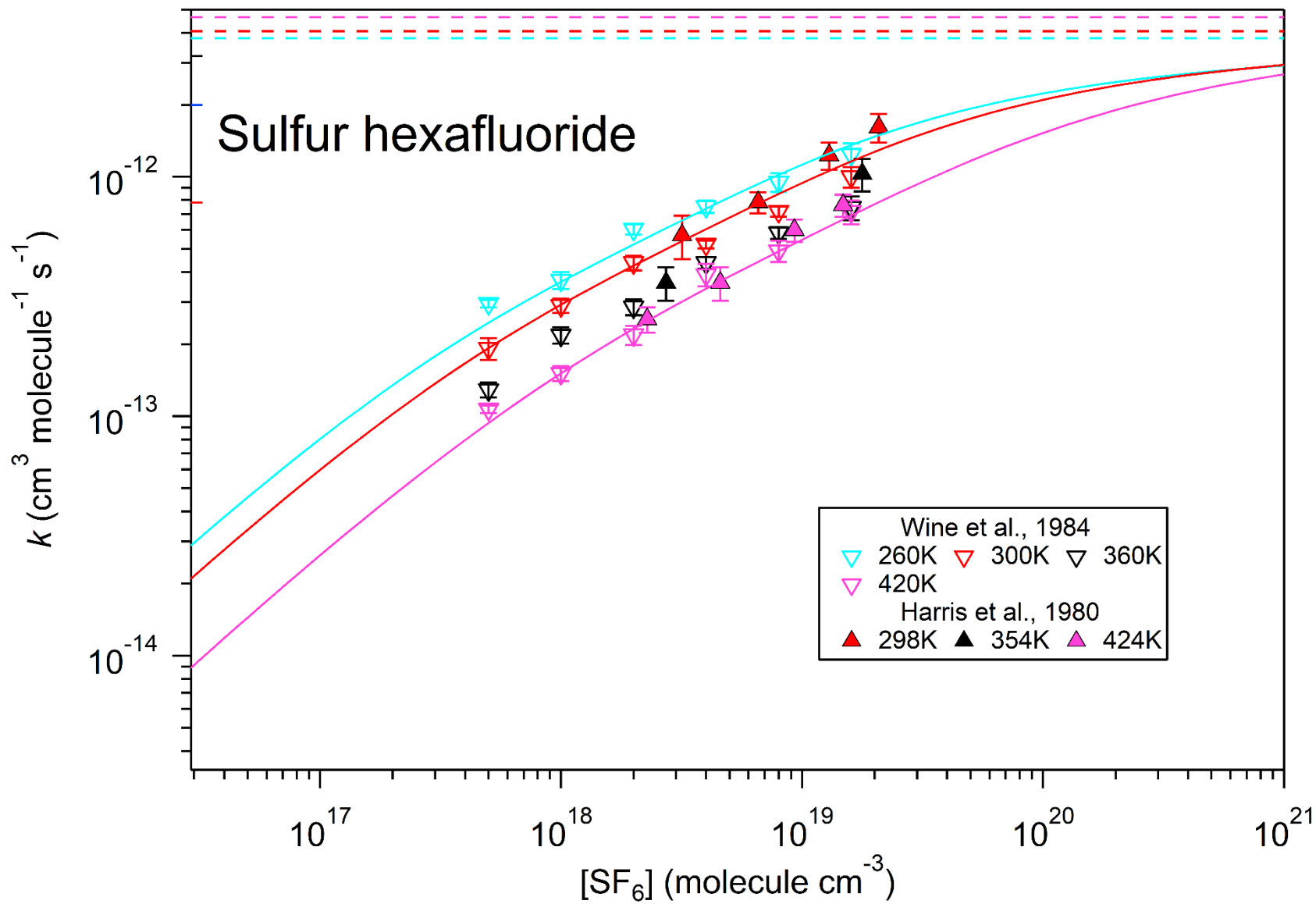


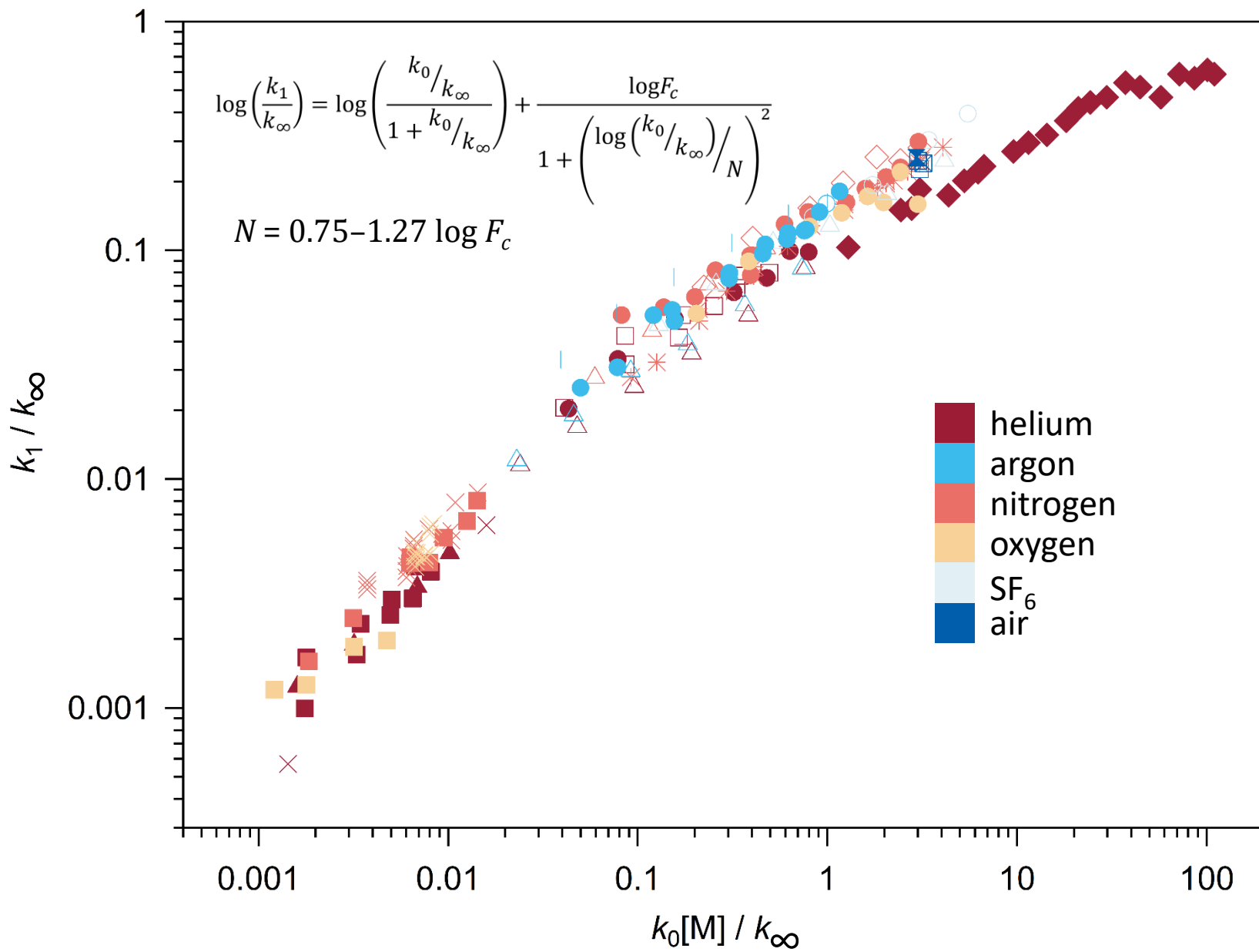




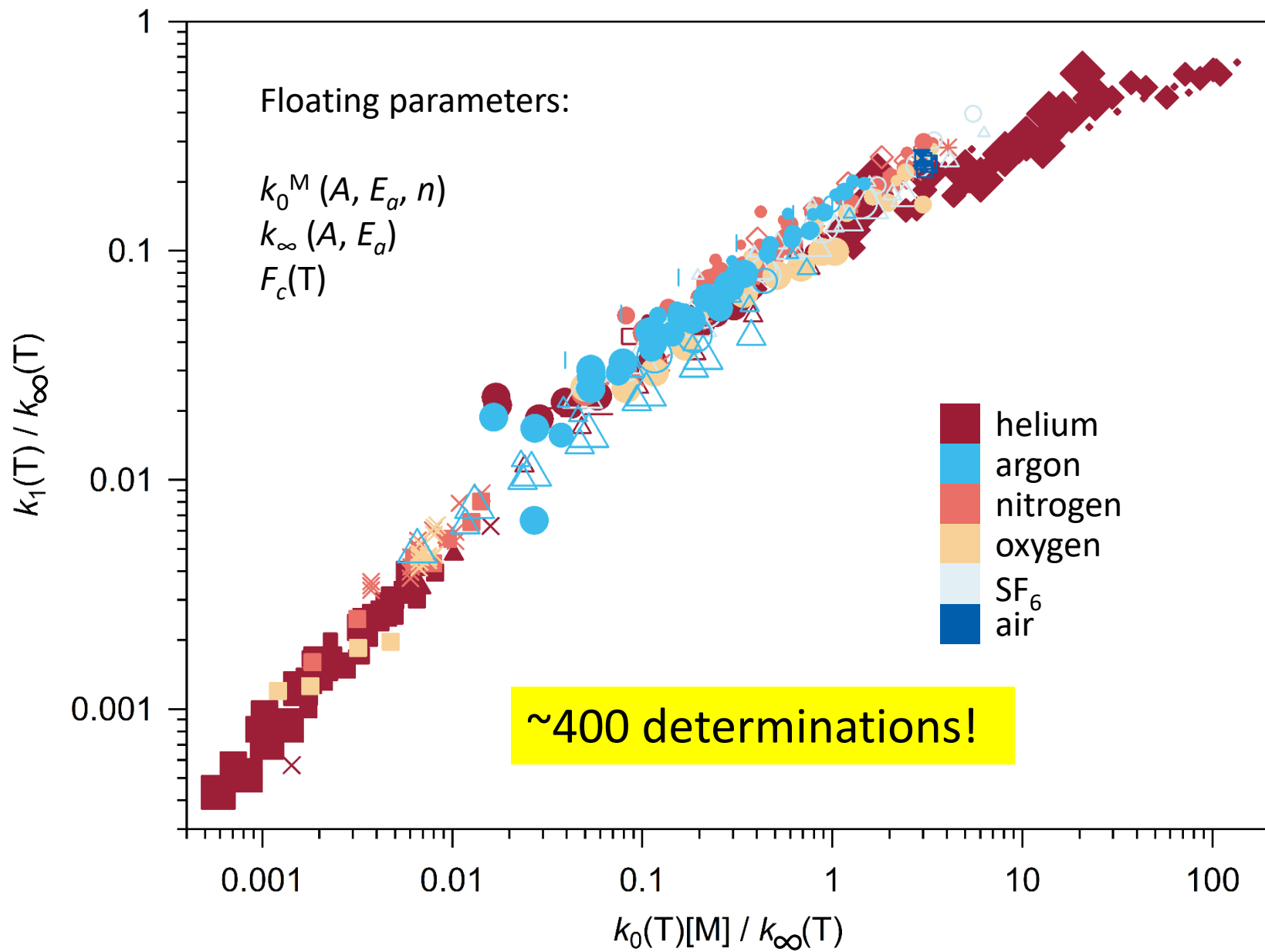
# Sulfur hexafluoride

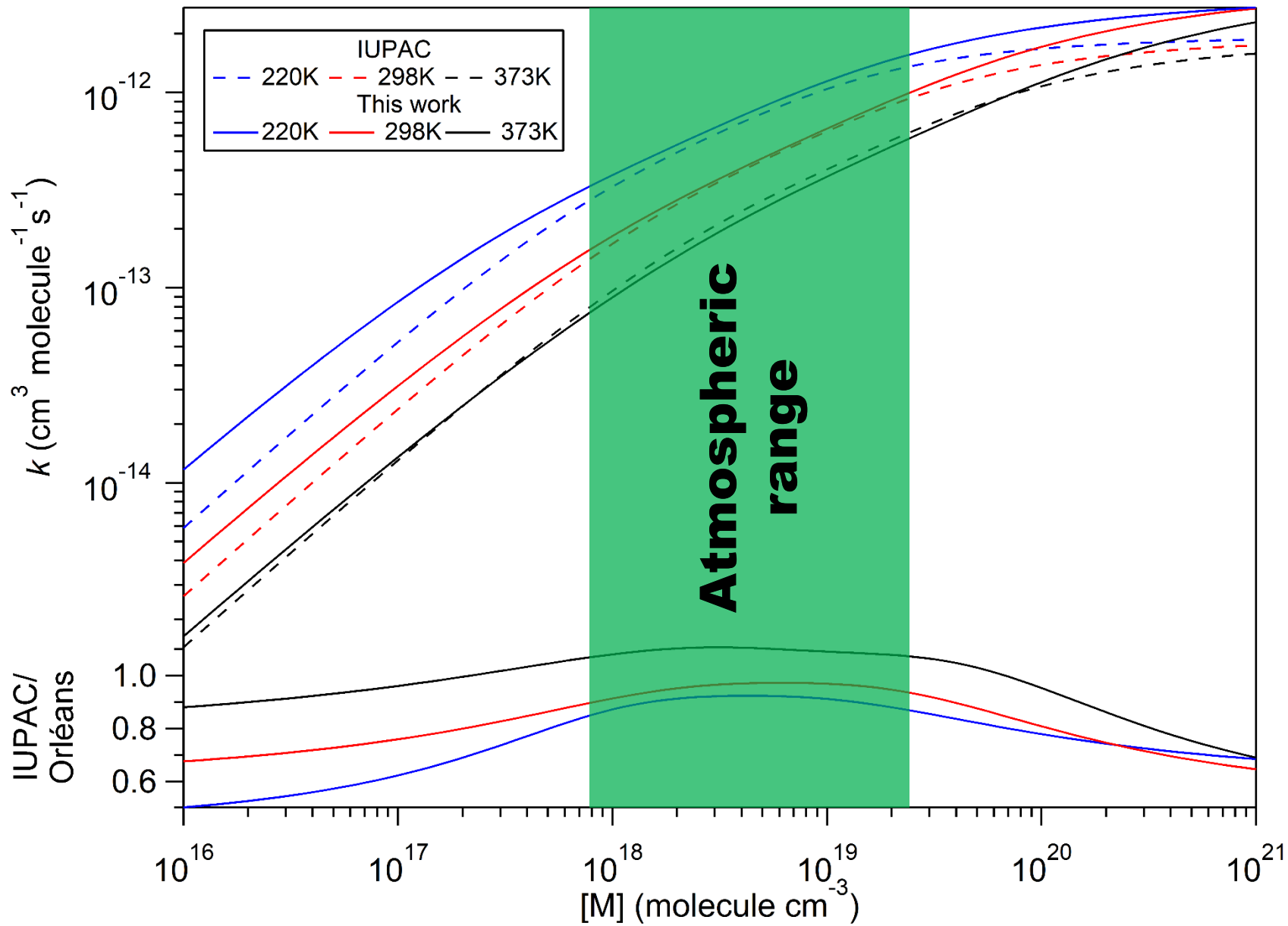












# Conclusions

- First T-dependence under atmospherically relevant conditions
- Much of new data (M = N<sub>2</sub> and O<sub>2</sub>) inconsistent with reduced high pressure limit suggested by Blitz and co-workers
- Preliminary parameterizations indicates a good general consistency with IUPAC
- This result was obtained from a much larger pool of data (some old, and some new)

# Acknowledgements

- A big thank you to my hosts here in Orléans
- Le Studium
- ICCK organizers
- My co-authors
- You, for your attention