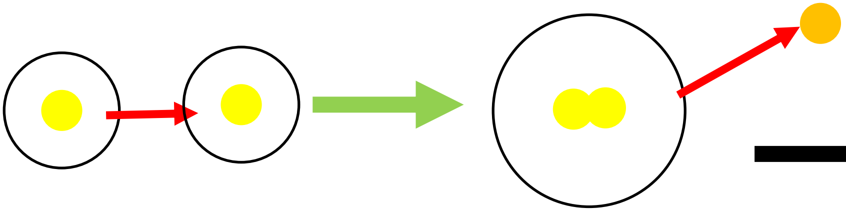
Effects of Including Excited States of N_2^+ in Dissociative Recombination Rate Coefficients of $N_2^+ + e^-$

Alex Plumadore

Mentor: Eve Papajak

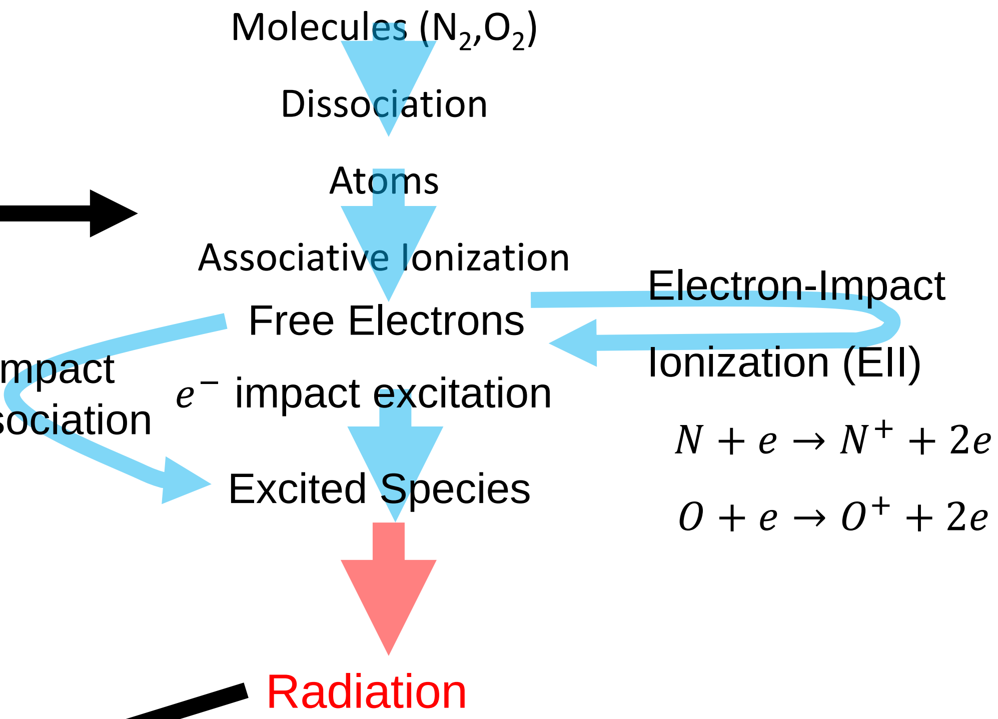
Division Presentation

Why is AI Important?



$$N + N \rightarrow N_2^+ + e$$

Associative Ionization (AI) is initiation process that creates starting electrons



Molecules (N_2,O_2)

Dissociation

Atoms

Associative Ionization

Free Electrons

Electron-Impact Ionization (EII)

$$N + e \rightarrow N^+ + 2e$$

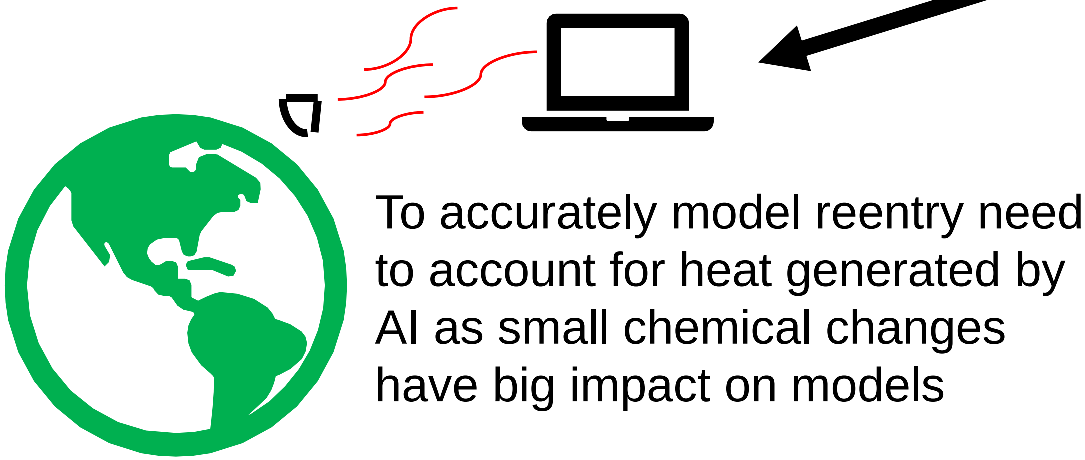
$$O + e \rightarrow O^+ + 2e$$

e^- impact dissociation

e^- impact excitation

Excited Species

Radiation



To accurately model reentry need to account for heat generated by AI as small chemical changes have big impact on models

Associative ionization (AI) →

$$N + O \rightarrow NO^+ + e$$

$$O + O \rightarrow O_2^+ + e$$

$$N + N \rightarrow N_2^+ + e$$

← Dissociative recombination (DR)

Methods of Code

We are interested in the rate of AI, but it is very computationally intensive to calculate directly. Thus, we study DR and work backward to get rate information of AI.

This project focuses on the accuracy of DR calculations.

- This starts by solving the Time-Dependent Schrödinger equation to get the wavefunction evolution over time

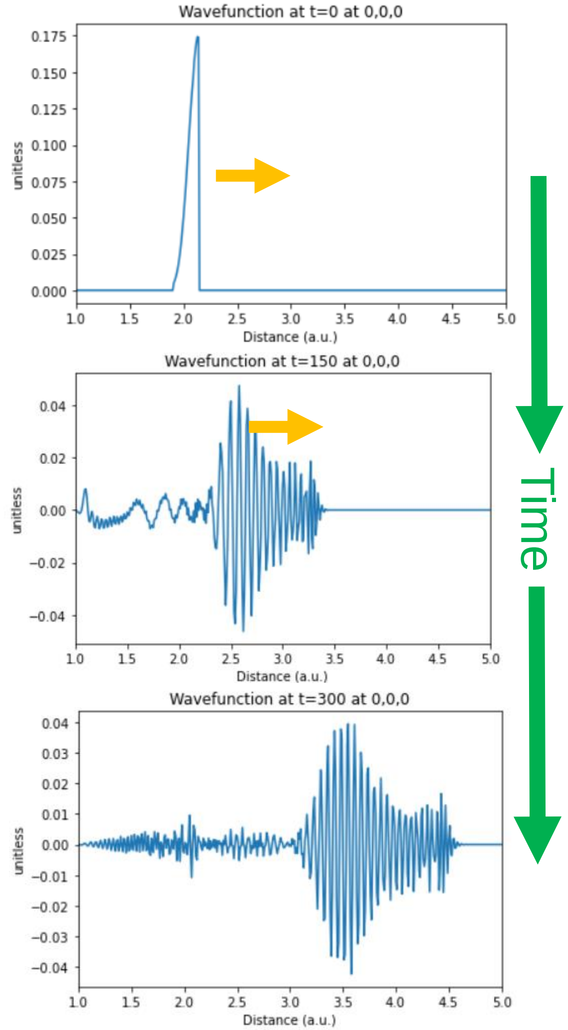
$$i\frac{\partial}{\partial t}\Psi(\vec{r},t) = H(\vec{r},t)\Psi(\vec{r},t)$$

Hamiltonian

$$\mathrm{H} = \left(-\frac{1}{2\mu}\frac{\partial^2}{\partial R^2} + E_{res}(R) - i\frac{\Gamma(R)}{2}\right)$$

Gamma

$$\Gamma(R) = 2\pi|V_E(R)|^2$$



Probability density moving from left (low interatomic distances) to right (large distances) represents N_2^+ molecule dissociating in time

Methods of Code 2

- To start the Time-Dependent Schrödinger equation calculation we use the initial wave function below

$$\Psi(R,t=0) = V_E(R)\chi_{v_i}(R)$$

- Then once the Time-Dependent Schrödinger equation is solved we calculate cross sections

$$\sigma(E) = \frac{2\pi^3}{E}|T(E)|^2 \longleftarrow T(E) = \lim_{t\to\infty}\left[-i\int_0^\infty \sqrt{\frac{\mu}{2\pi k}}\,\mathrm{e}^{i\mathrm{kR}}\Psi(R)\,\mathrm{d}R\right]$$

Plane Wave
(represents dissociating N+N atoms
with varying amounts of kinetic energy)

Wavefunction
(as calculated
at every point in
time)

- Then we take the cross sections to calculate DR State Specific Rate Coefficients

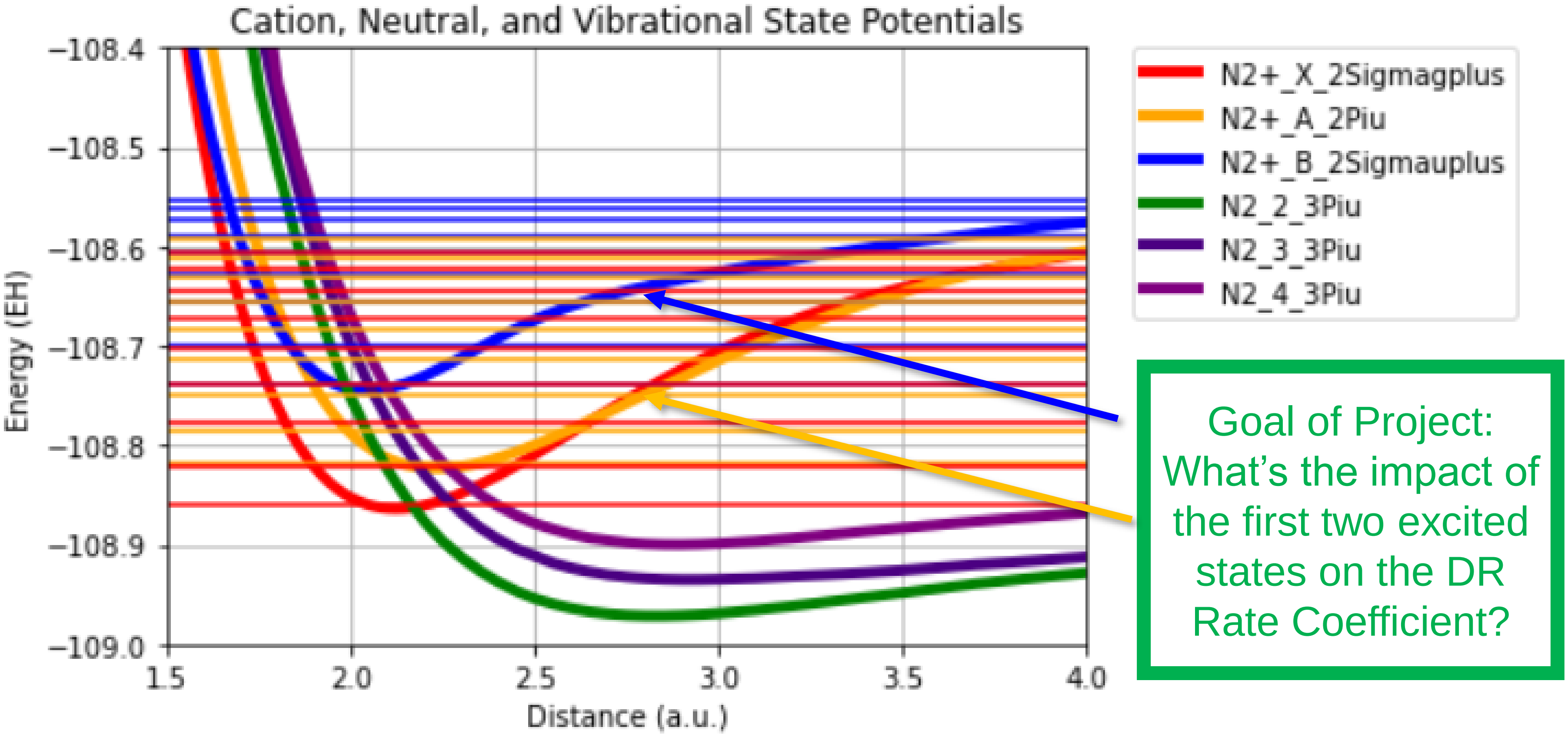
$$k(i,T) = \left(\frac{1}{\pi\mu}\right)^{1/2}\left(\frac{2}{\kappa T}\right)^{3/2}\int_0^\infty \sigma_{AB,R}(E)\,E\;\;e^{-\frac{E}{\kappa T}}dE$$

Cross Section

Boltzmann Distribution

Methods of Code 3

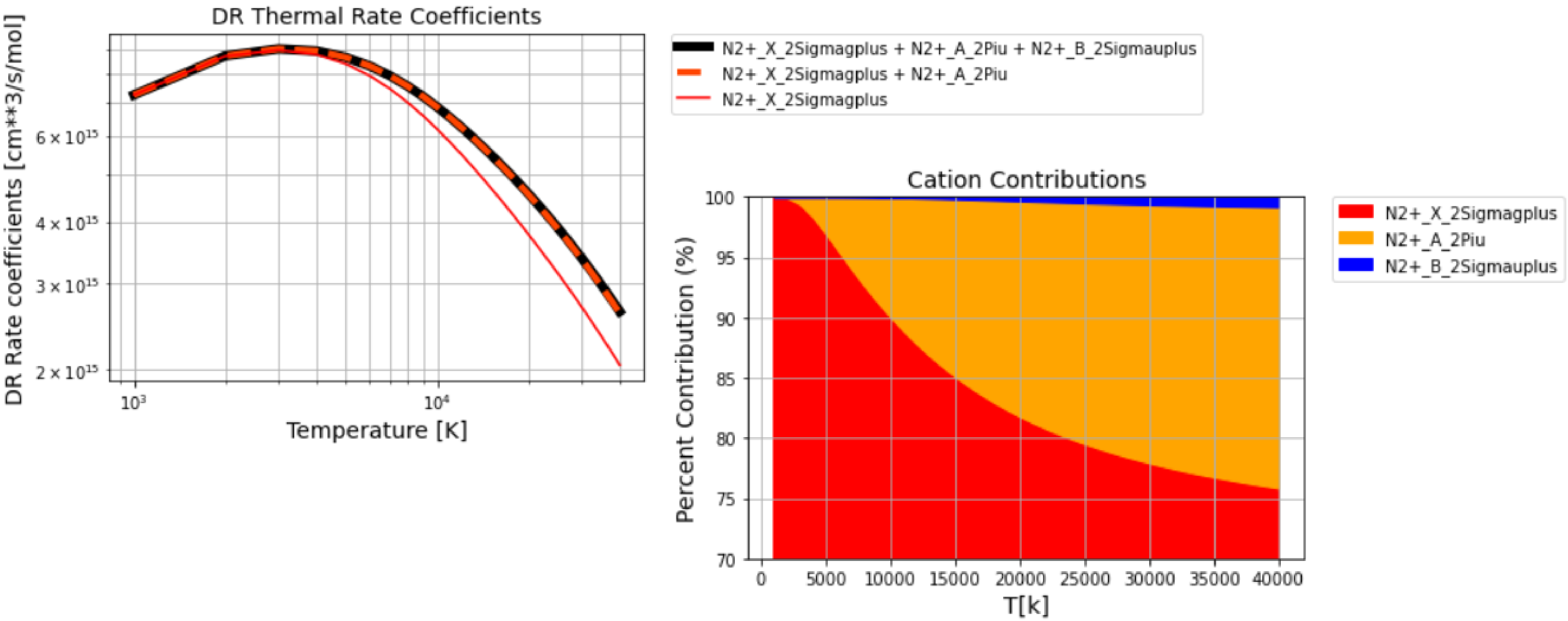
- Use a custom Python program to run through the calculation
- The DR rate coefficient can be used to calculate AI information based on molecular reversibility
- Inputs are potentials
- Numerous excited cations can be included to make an increasingly more complete calculation



Cation, Neutral, and Vibrational State Potentials

Goal of Project: What's the impact of the first two excited states on the DR Rate Coefficient?

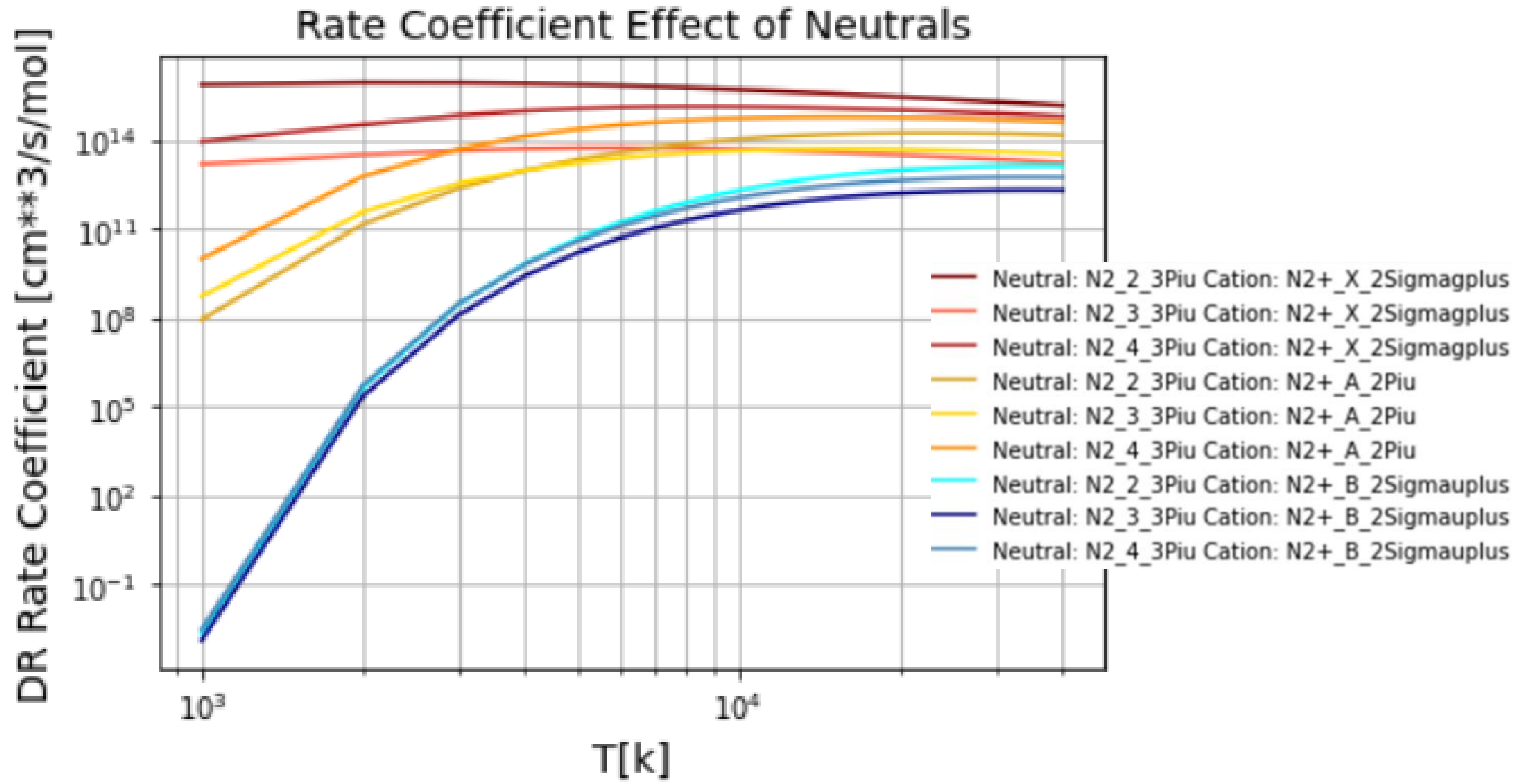
DR Rate Coefficient (k)



- A $^2\Pi_u$ cation rises in importance up to greater than 20% contribution at 40,000K
- B $^2\Sigma_u^+$ cation rises in importance up to less than 1% contribution at 40,000K

- 1^{st} excited state important to include in k as has large impact
- 2^{nd} excited state and higher are less important for entry systems purposes

DR Rate Coefficient (k) Breakdown



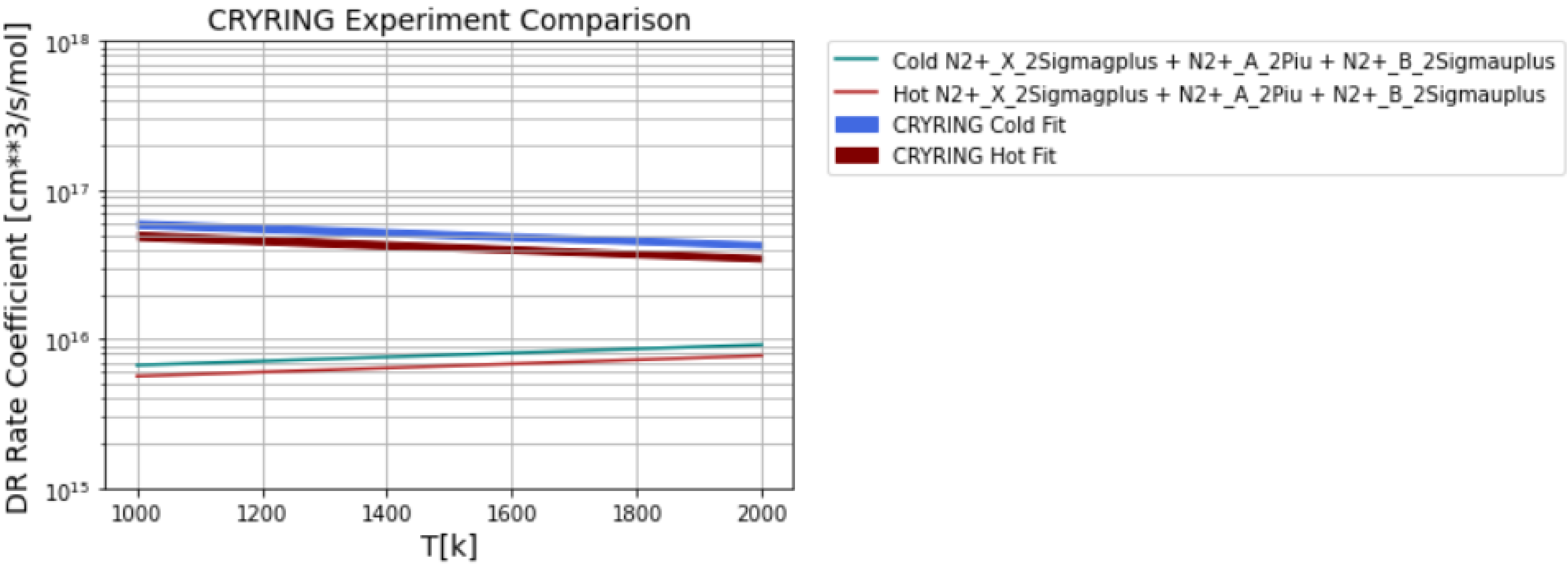
- All neutrals contribute to the calculation
- For cations, the first excited cation contributes significantly, and the second excited cation contributes slightly

Comparisons with Experiments

- DR experiments are carried out at different temperature ranges and for different excited states
- Thus we need to take different subsets of our data to make sure it matches the experimental conditions
- In the following slides, three different literature k situations are examined

Comparison to CRYRING Experiment

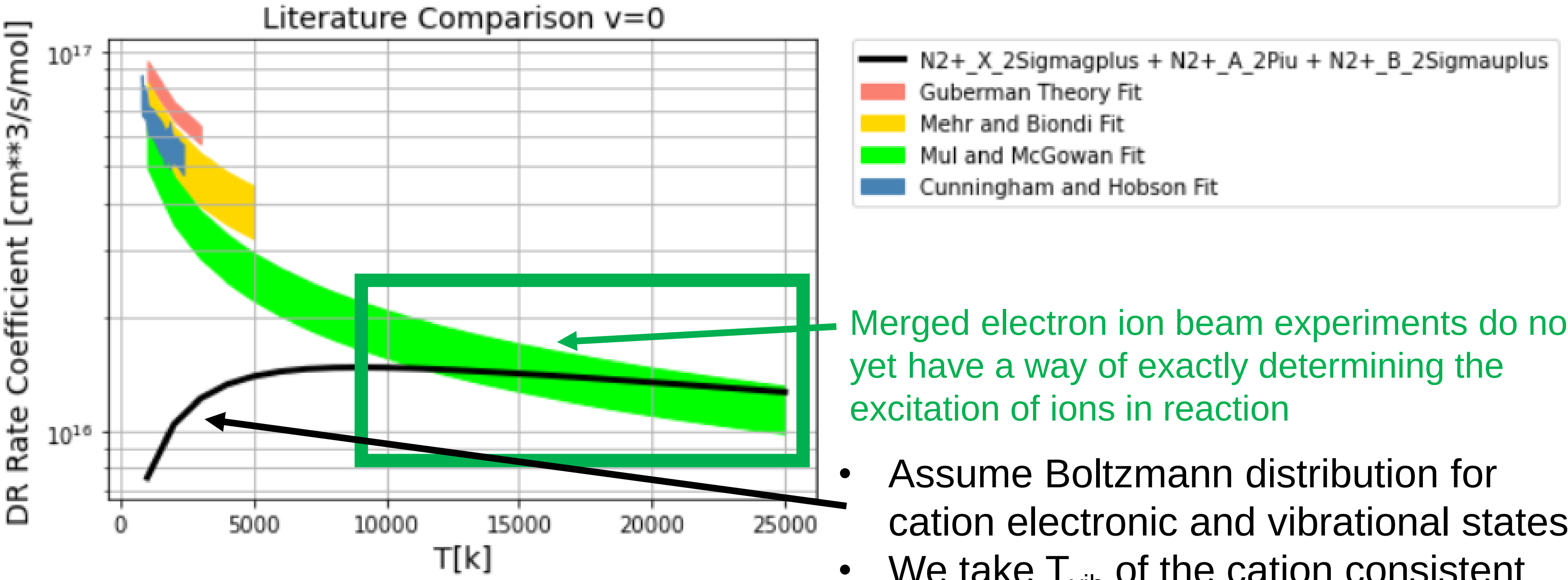
Comparison with CRYRING Experiment at low temperatures below 2,000K for v=0-3



- Temperatures are outside of entry conditions
- Our "cold" results are more reactive than our "hot" results which matches experimental trend

Comparison to Literature for v=0

Comparison with four literature results at various temperature ranges for v=0



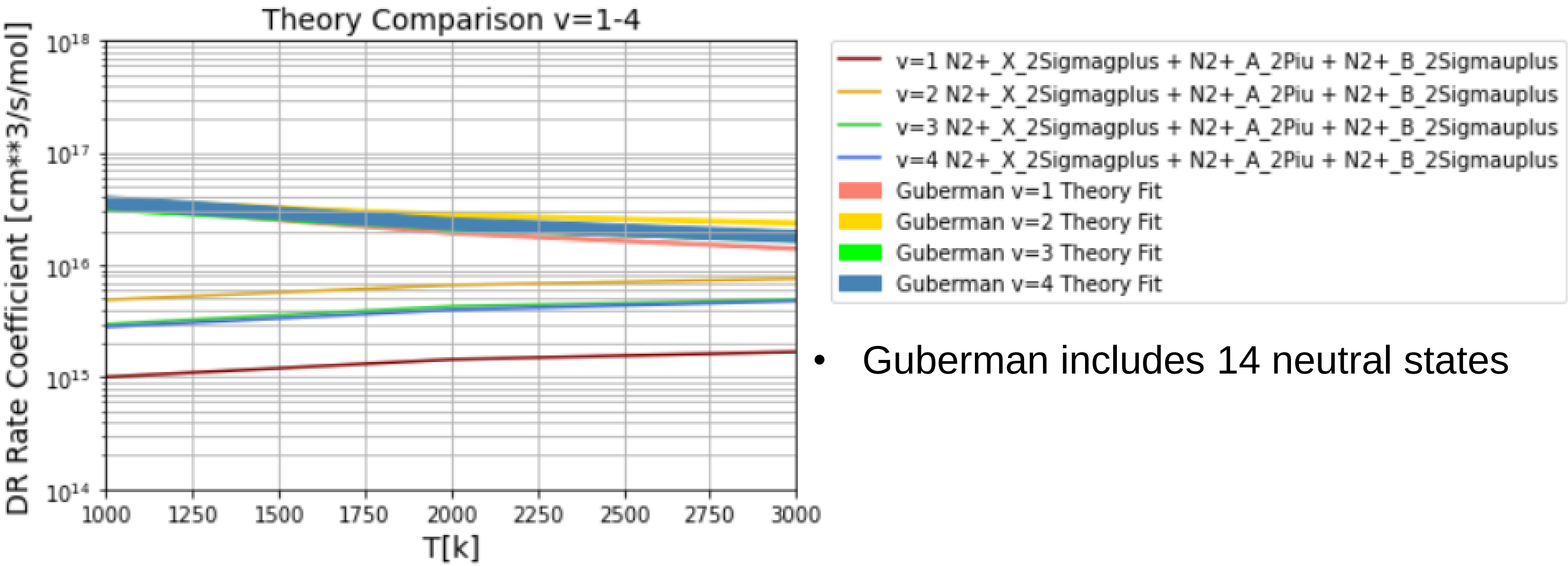
Merged electron ion beam experiments do not yet have a way of exactly determining the excitation of ions in reaction

- Assume Boltzmann distribution for cation electronic and vibrational states
- We take T_{vib} of the cation consistent with $T_{electron}$

- Outside entry Conditions, below 10,000K, results are within an order of magnitude compared to experiment
- Above 10,000K agreement is excellent

Comparison to Literature for v=1-4

Comparison with Guberman theory at low temperatures below 3,000K for v=1,2,3,4



- Guberman includes 14 neutral states

- Temperatures are outside of entry conditions
- We agree with Guberman that v=1 contribution is the lowest and v=2 is the highest

References

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[2] Huo, W. M., Panesi, M., Magin, T. E. (2012). *Ionization Phenomena behind Shock Waves.* In: Brun R. (eds) High Temperature Phenomena in Shock Waves. Shock Wave Science and Technology Reference Library, vol 7. Springer, Berlin, Heidelberg. https://doi.org/10.1007/978-3-642-25119-1_5

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Conclusions

- For k calculations need to include the A $^2\Pi_u$ cation
- For precise k calculations it is important to include B $^2\Sigma_u^+$
- Entry conditions cover the range of 10,000K to 40,000K and in this range the agreement of our rate coefficients with experiment is very good

Questions?