RELATION OF DISSOCIATION RATES TO THE CENTRIFUGAL BARRIER

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Objective and Overview

Hypersonic reentry flight experiences extreme temperatures leading to a state of chemical non-equilibrium in the flow. To analyze the state-to-state (StS) kinetics for these flows, we propose to fit the kinetics data using sparse regression techniques. The advantages of obtaining an expression for the state-to-state dissociation rates in terms of the position of the centrifugal barrier are two fold: it provides an insight into the relation of dissociation via various levels to the centrifugal barrier and can be used to arrive at a physics-informed grouping strategy to reduce the dimension of the kinetics system. This would further aid in modeling the reactions that take place in the flow in a computationally efficient way.

O_3 Chemical System

To assess the effect of the centrifugal barrier on dissociation, a set of StS rovibrational rates for the O_3 system are obtained via Quasi-classical trajectory (QCT) calculations carried out using CoarseAir, developed by Dr. Bruno Lopez and Simone Venturi [1]. The potential energy surfaces (PESs) used for QCT have been developed by Varga et al. [3]. The effective diatomic potential is found by accounting for the rotational contribution in addition to the rotation-less pairwise interaction term, V_{Diat}, of the PES:

$$V_{Diat,J}(r, J) = V_{Diat}(r) + \frac{J(J+1)h^2}{2\mu r^2} \quad (1)$$

where J is the rotational quantum number, h is the reduced Planck's constant, and μ is the molecular reduced mass. Figures 1 and 2 show the diatomic potential as a function of the distance between atoms r and rotational quantum number J. In Figure 1, the rovibrational levels (marked as dots) are colored based on their vibrational quantum number v, whereas in Figure 2, the levels are colored based on their dissociation rate coefficients.
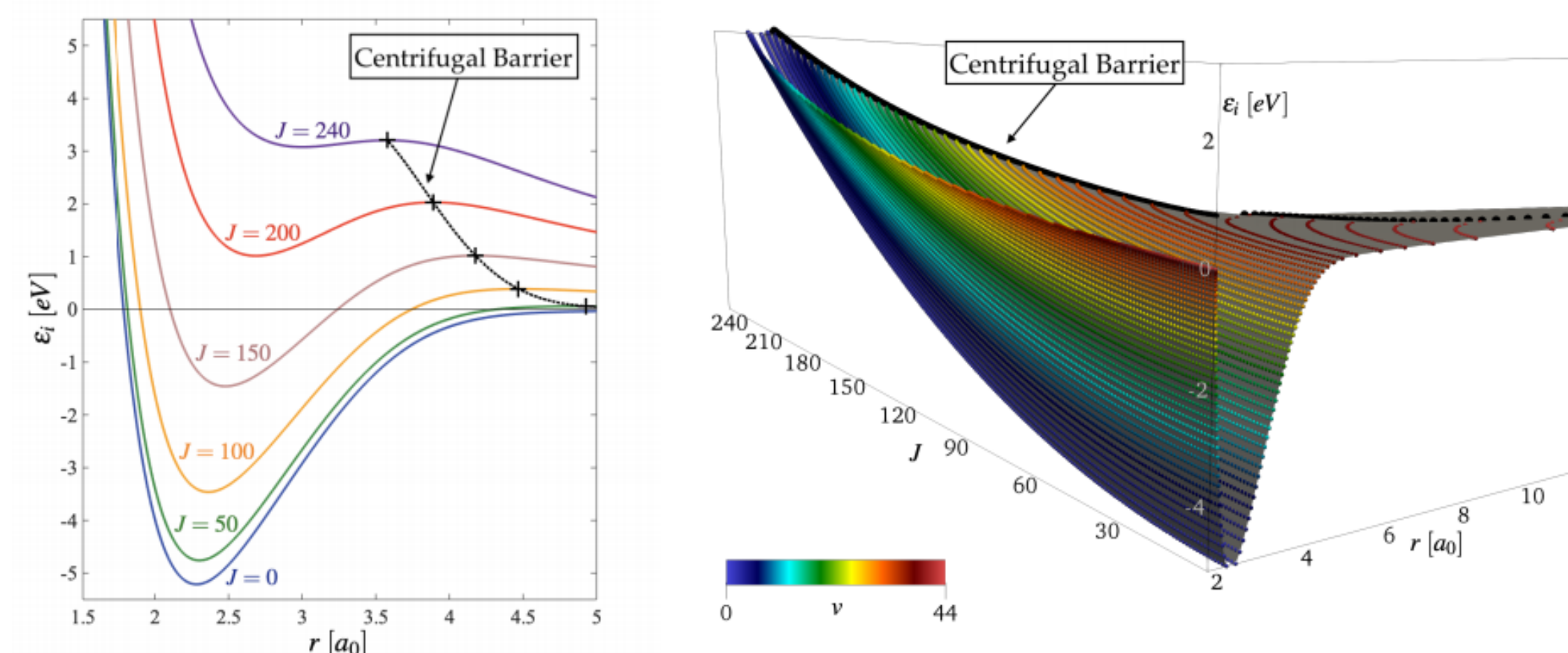

Fig. 1: Diatomic potential with levels colored based on their vibrational quantum number v
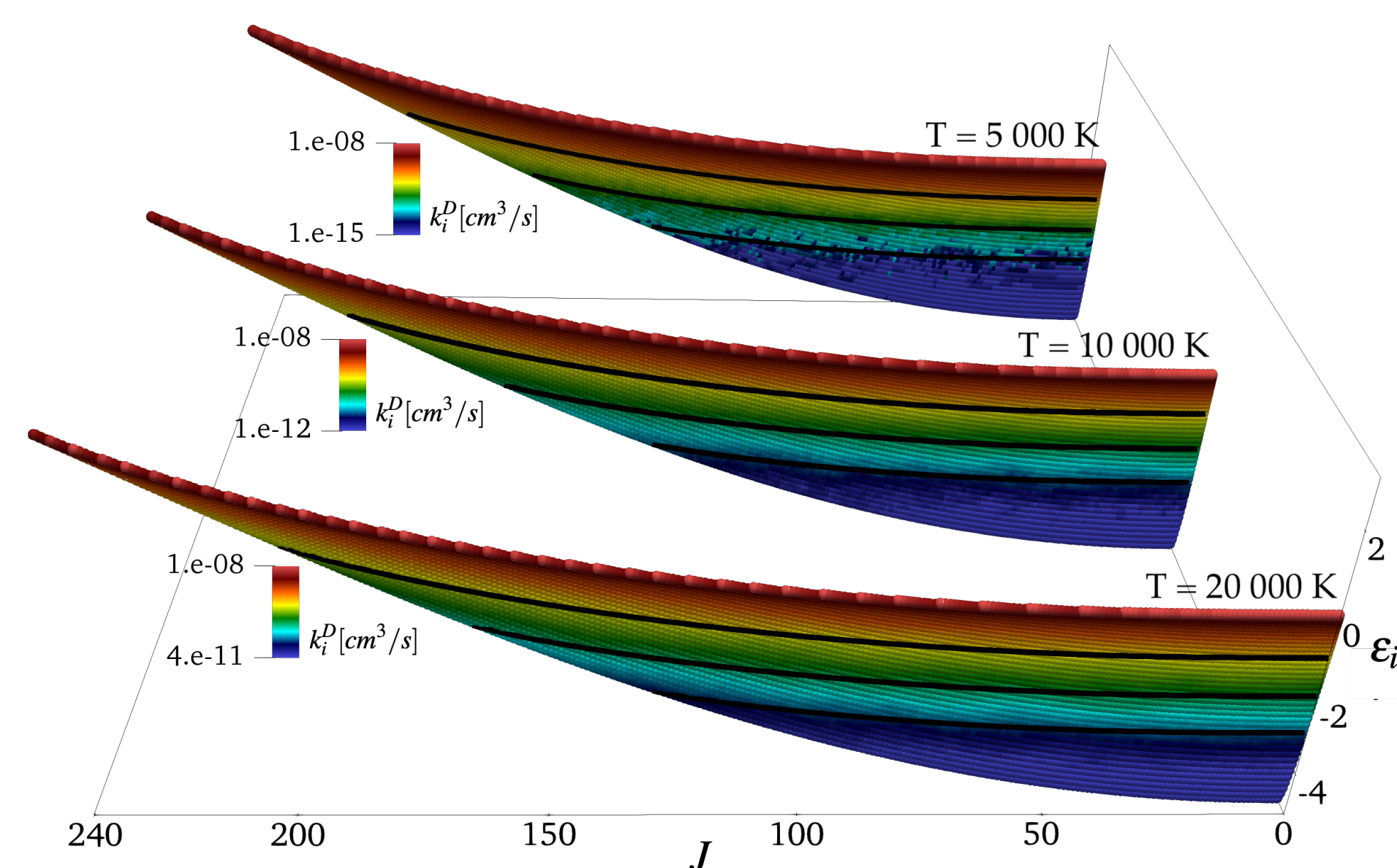

Fig. 2: Diatomic potential with levels colored based on their dissociation rate coefficients
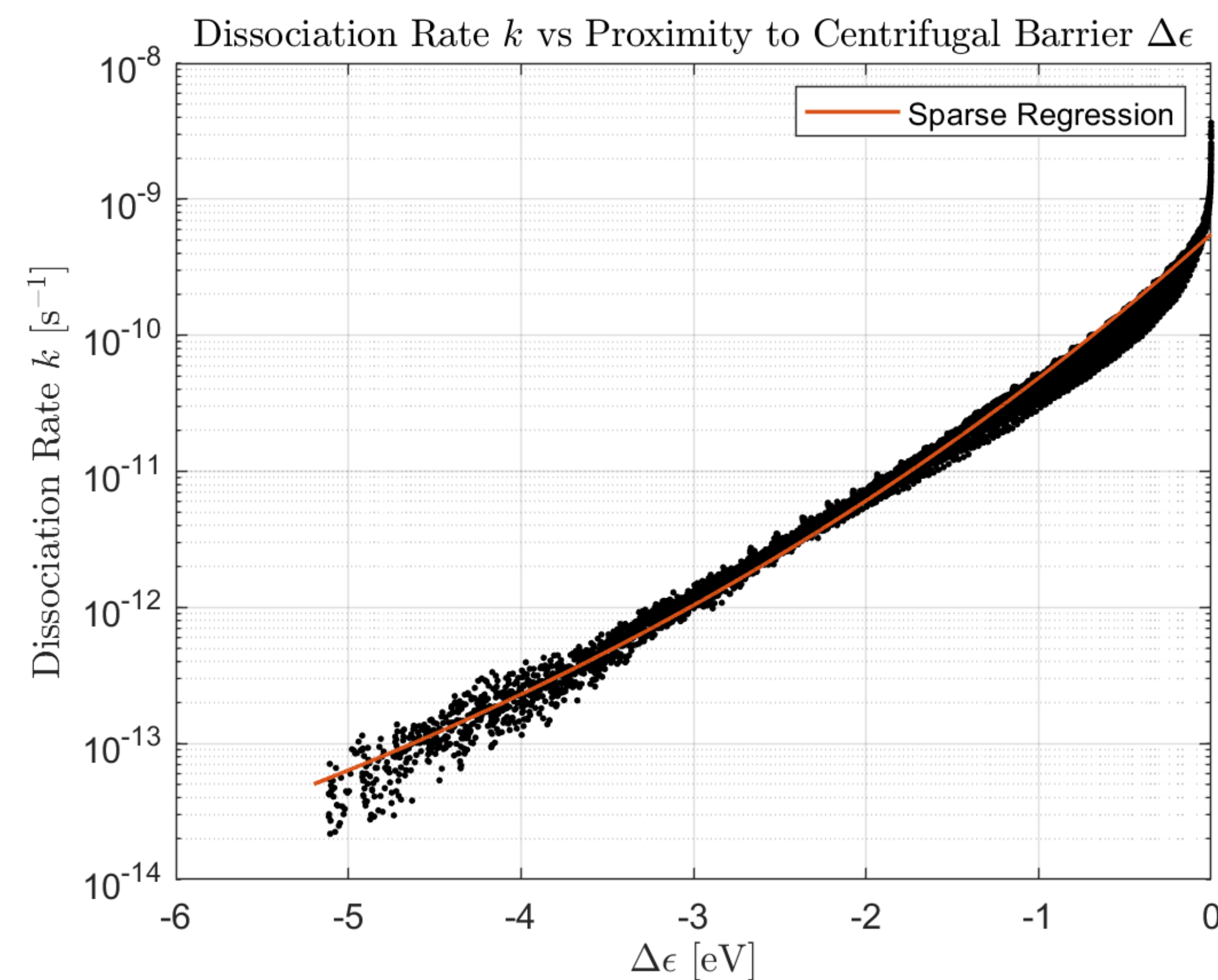
Results

Fig. 3: Sparse regression fitting of kinetics data with dissociation rate k against proximity to centrifugal barrier $\Delta\epsilon$ with fitting function having no dependence on the vibrational quantum number v
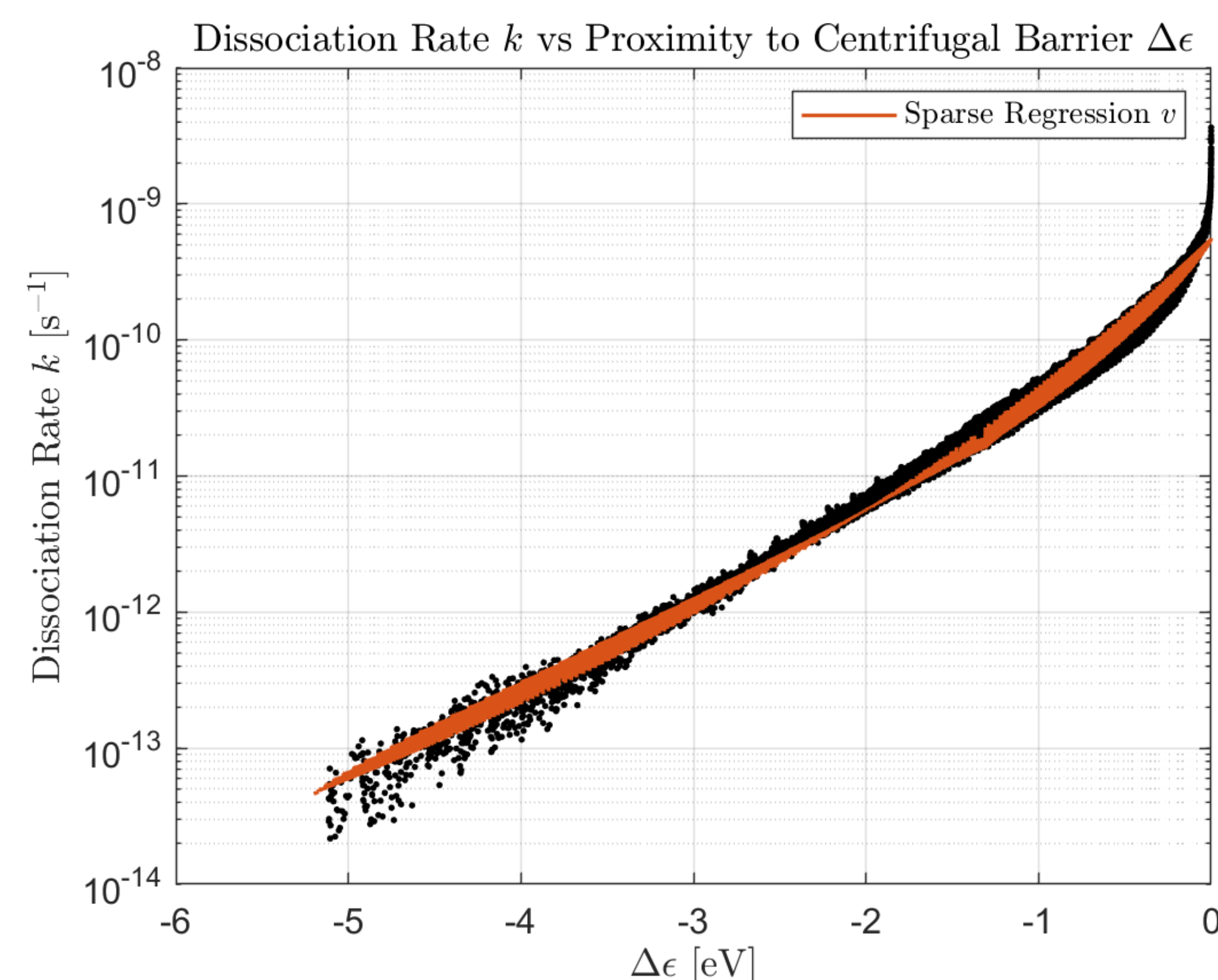

Fig. 4: Sparse regression fitting of kinetics data with dissociation rate k against proximity to centrifugal barrier $\Delta\epsilon$ with fitting function accounting for the vibrational quantum number v

In the above fits, the spread is accounted for by including the vibrational quantum number in the fitting function. The fitted function is shown below:

$$k(v) = \exp(-0.0125v(\Delta\epsilon + 2))\exp(0.0117\exp(0.1671\Delta\epsilon + 7.2332) - 37.5) \quad (2)$$

The results in Figures 3 and 4 show that the dissociation rates primarily depend on the energy-distance from the centrifugal barrier and thereby are strongly governed by rotation. This is an important result since the state-of-the-art vibrational-specific models in hypersonics neglect the effect of rotation completely. Figure 5 also shows that high-v states have close proximity to the centrifugal barrier and are governed primarily by dissociation as determined by Venturi et al. [1].

Fitting Tools

Dissociation rates are dependent on effective diatomic potential and can be fitted based on the distance from the centrifugal barrier using the following:

$$k(v, J) = C_1 \exp\frac{-(\Delta\epsilon_{cent} - C_2)}{\bar{k}T} + C_3 \quad (3)$$

where $\bar{k}$ is the Boltzmann constant. The motivation for this form is taken from transition state theory [2] as well as the visualization in Figure 2. MATLAB's Curve Fitting Toolbox (cftool) enabled solving for these coefficients based on initial estimates and the additions of other constants to fit the function to the kinetics data. Apart from their dependence on centrifugal barrier, from Figure 5, it is also inferred that the vibrational quantum number should be explicitly accounted for in the fit.
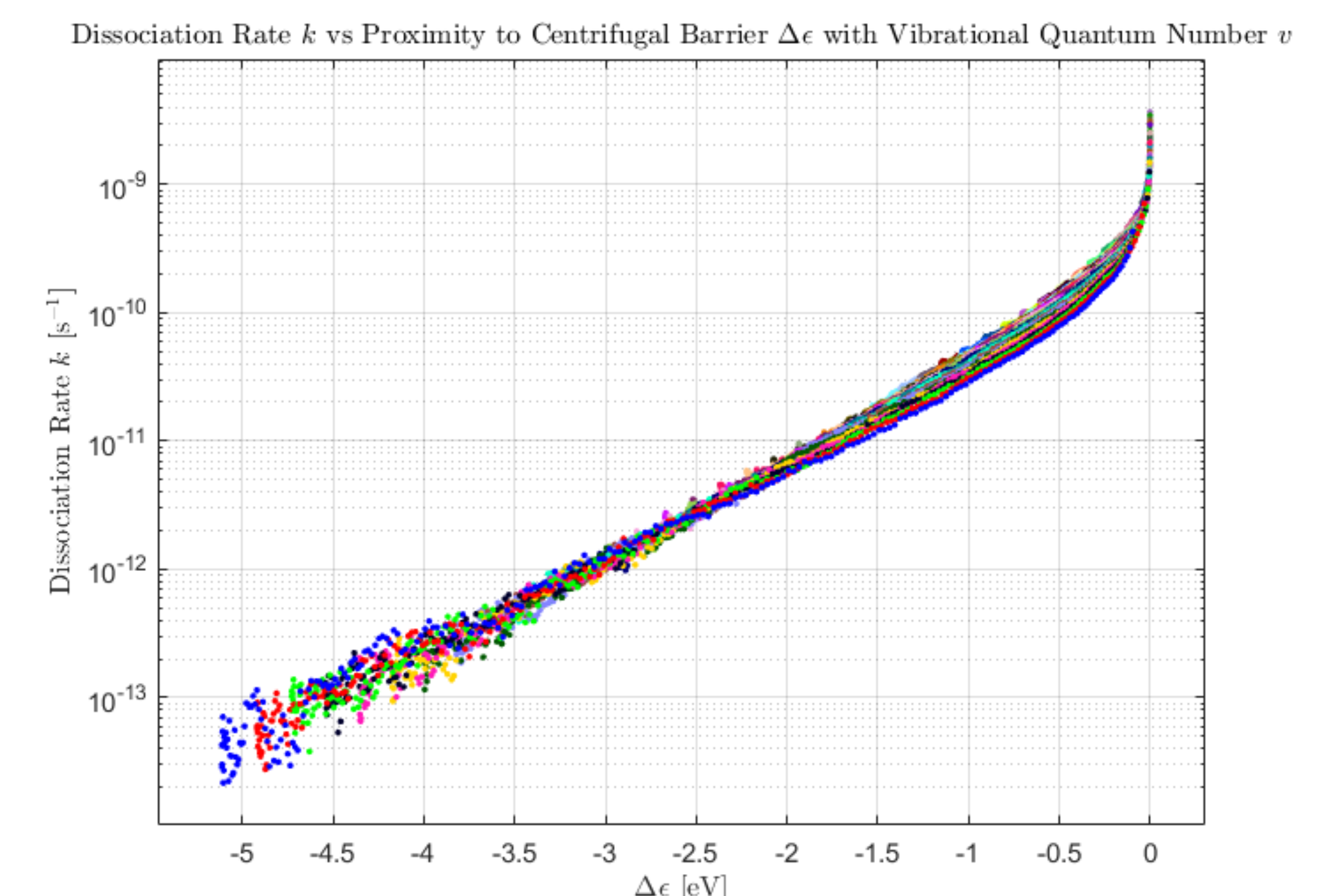

Fig. 5: Dissociation rate k against proximity to centrifugal barrier $\Delta\epsilon$ with distinguishable vibrational quantum numbers v

Conclusions

The dissociation rates are seen to depend very strongly on the distance of the rovibrational level from the centrifugal barrier. Using the fit proposed, we have been able to fit the StS rates with good accuracy. To account for the spread, we have included the vibrational quantum number in the fit. However, accurate capture of the spread needs to be investigated further and is part of the future direction for this work.

Acknowledgements

References

[1] S. Venturi, M. P. Sharma, and M. Panesi. "Role of Rotational Non-Equilibrium on O₂+O Dissociation Kinetics". In: (Apr. 2020).

[2] EV Waage and Benton S Rabinovitch. "Centrifugal effects in reaction rate theory". In: *Chemical Reviews* 70.3 (1970), pp. 377–387.

[3] Y. Paukku Z. Varga and D. G. Truhlar. "Potential energy surfaces for O+O₂ collisions". In: *J. Chem. Phys. 147, 154312/1-17* (2020).