

A Phase Space Theory for Roaming Reactions

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Introduction

The term "roaming" was first coined to describe an unusual mechanism in the photodissociation of H_2CO . A small fraction of the barrierless bond fission channel that produces $\text{H} + \text{HCO}$ becomes "frustrated"; although there is sufficient energy for dissociation, some of the energy is constrained in HCO internal degrees of freedom and not available in the reaction coordinate. In this case, the H atom escapes into the van der Waals region, where it undergoes large-amplitude "roaming" around the periphery of the HCO before abstracting the other H atom to yield molecular products; an alternative to the well known transition state (TS) route to molecular products. The roaming mechanism was confirmed by a combination of ion imaging experiments performed by Suits *et al.* and quasiclassical trajectory (QCT) calculations performed by Bowman *et al.* on a high-quality ab initio full dimensionality potential energy surface (PES). [2] Dynamical modeling, like QCT calculations, requires a significant effort to build a PES and then to run a statistically significant number of trajectories. If roaming is as ubiquitous as the rapidly emerging experimental and theoretical data seem to indicate, then a theoretical method is needed to predict the rate coefficient and branching for roaming, in a similar fashion to the way that transition-state theory (TST) and variational TST (VTST) are used for more conventional mechanisms.

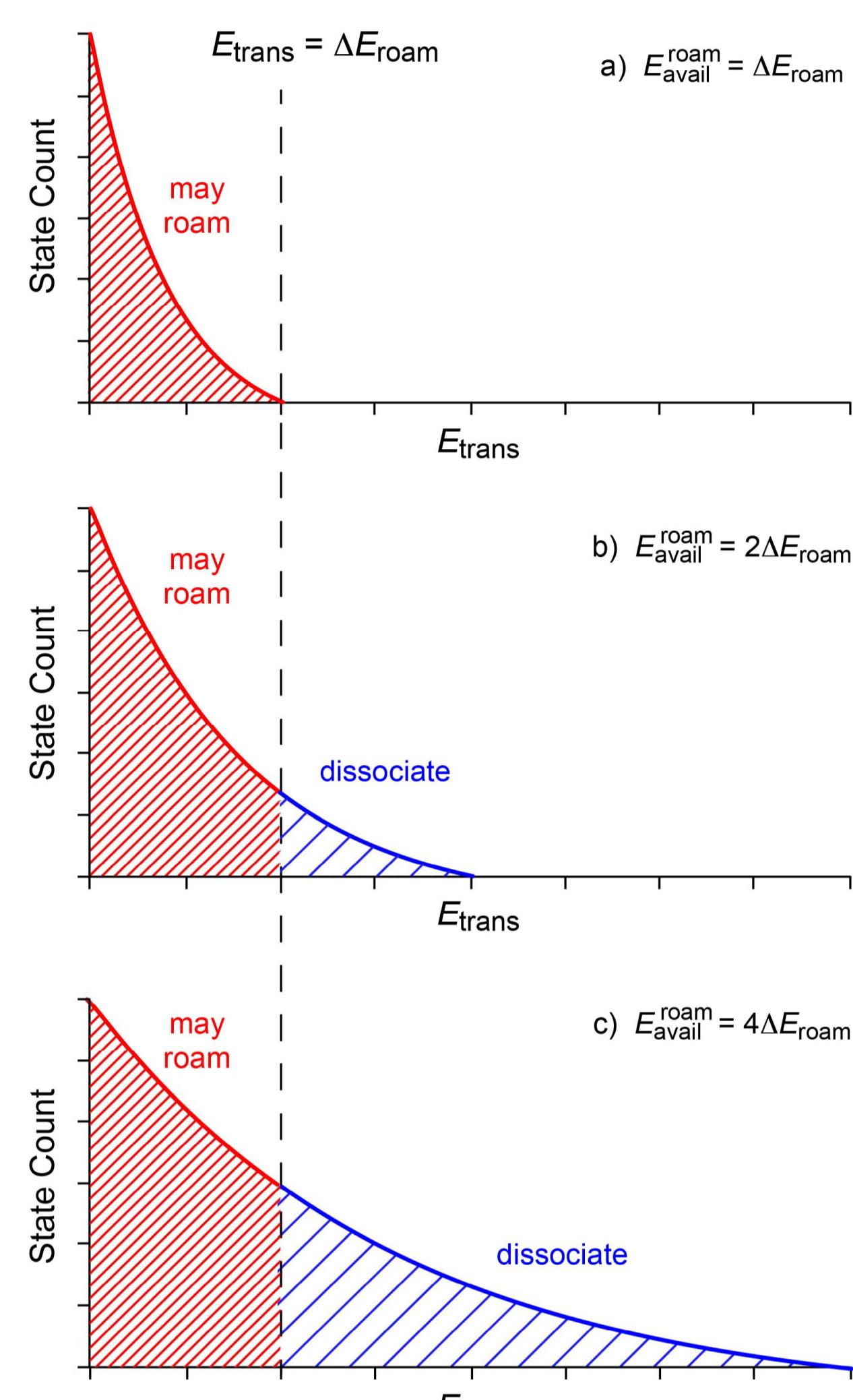


Fig 2. An illustration of how the total PST states are divided into dissociative and roaming states.

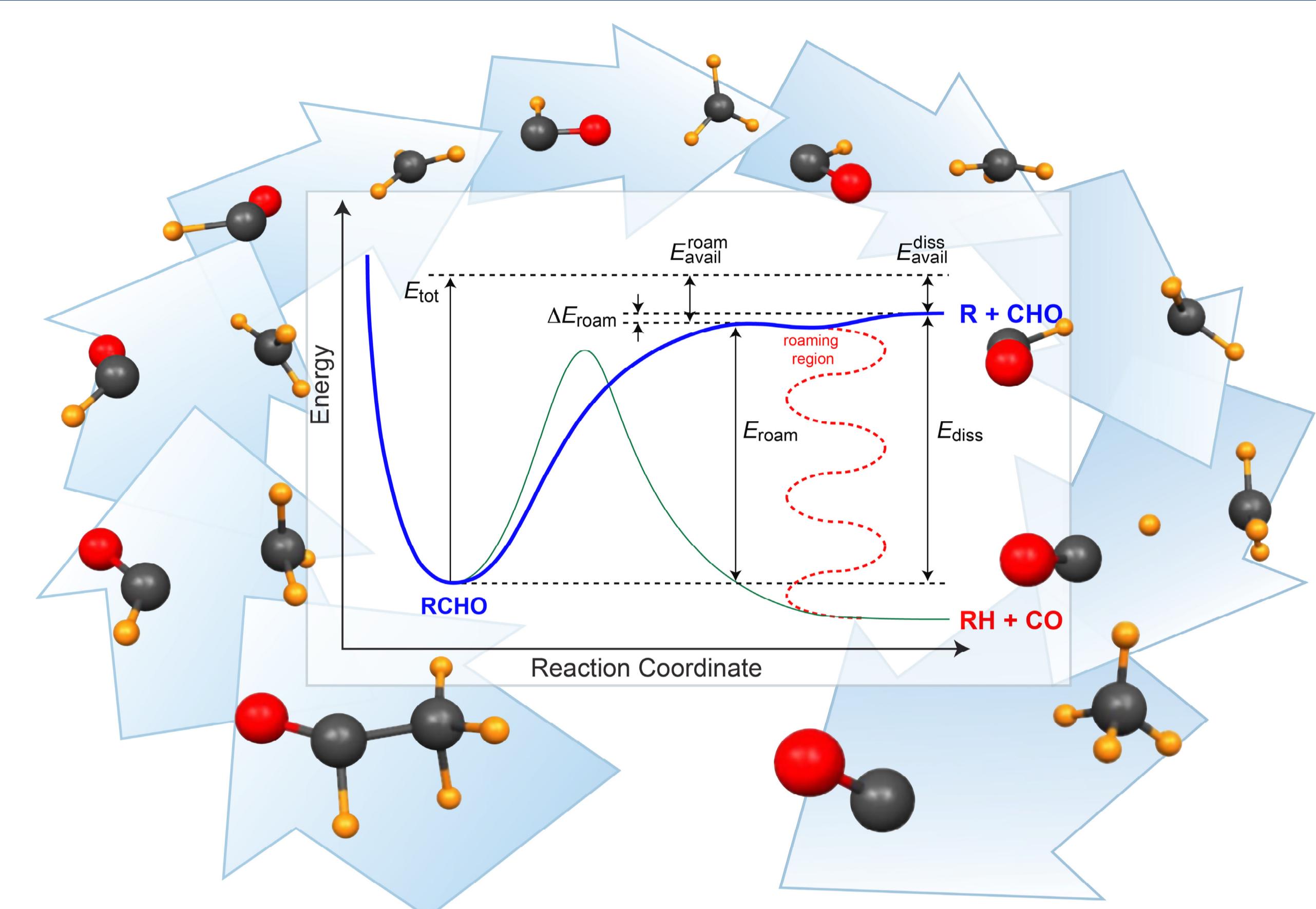


Fig 1. Frames from a roaming trajectory for acetaldehyde. Inset, a schematic of the photodissociation of an aldehyde, RCHO .

Phase Space Theory (PST) of Roaming

In the PST-roaming theory, we consider explicitly roaming to be a branching from the barrierless bond dissociation channel. Roaming is illustrated by the red dotted line in Fig 1. Our theory assumes that the roaming and conventional TS pathways to molecular products are dynamically independent. We assume the barrierless dissociation and roaming pathways are dynamically linked. The roaming threshold, E_{roam} , lies slightly below E_{diss} by an amount that we call ΔE_{roam} . When the nascent fragments enter the roaming region, the system ceases to be ergodic.

This divides phase space into two regions, which are illustrated in Fig 2. For a fixed total energy, E_{tot} , there will be (i) fragments with a sufficient kinetic energy, E_{trans} , to escape into simple bond dissociation products and (ii) fragments in which the internal energy reservoir is too large, that is, there is too little E_{trans} for the simple products to form. In our theory, these fragments may form roaming products. We use PST to determine the number of states that result in bond dissociation or roaming products. Our application of PST simply moves the threshold from E_{diss} to E_{roam} . The sum of states in (ii), ω_{roam} , is scaled by P_{roam} , the probability roaming states form products rather than reforming reactants. P_{roam} , is the only adjustable parameter in our model.

Results

H_2CO

The best-characterized roaming system is H_2CO . Experimentally, the roaming threshold has been observed between 30123 and 30241 cm^{-1} , that is, $87 < \Delta E_{roam} < 205\text{ cm}^{-1}$. [3] We choose the midpoint, $\Delta E_{roam} = 146\text{ cm}^{-1}$, and set $P_{roam} = 1$, Fig 3.

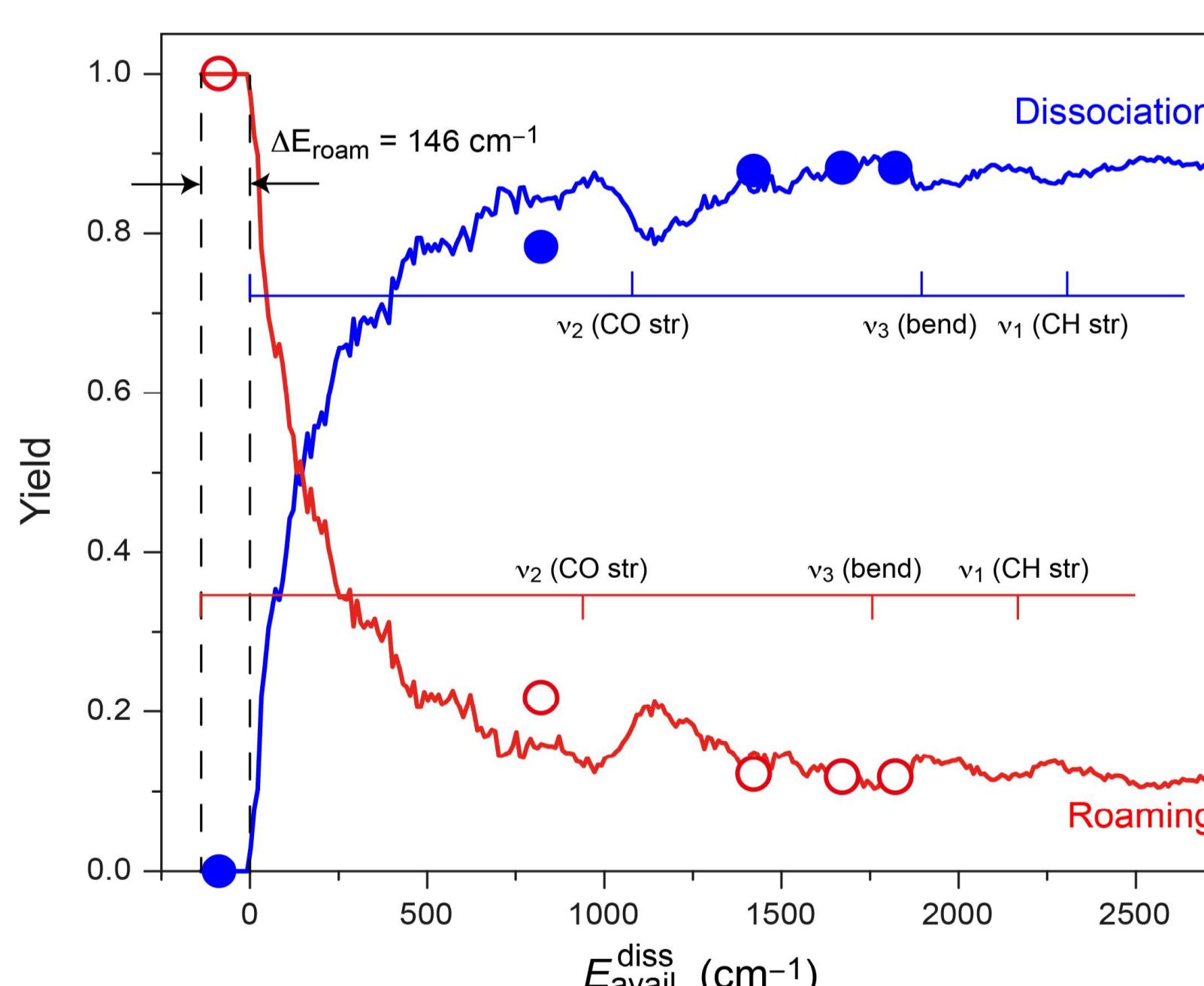


Fig 3. Predictions from our PST-roaming model for roaming (red) and radical (blue) branching fractions for H_2CO compared to experiment (red circles and blue dots). [3, 4]

NO_3

All of the NO_3 experiments are carried out from parent molecules with a range of internal energies. For NO_3 , experimental thresholds provide $\Delta E_{roam} = 258 \pm 20\text{ cm}^{-1}$. [5] The best fit to low temperature ($T_{\text{vib}} = 300\text{ K}$ and $T_{\text{rot}} \approx 0\text{ K}$) experimental branching fractions is obtained for $P_{roam} = 0.0075$, Fig 4.

This is consistent with the known geometric constraints to formation of $\text{NO} + \text{O}_2$. Using this value and the experimental rotational and vibrational temperatures, we can accurately model the quantum yield, ϕ , data for room temperature NO_3 photolysis, Fig 5, and a low temperature NO yield spectrum, Fig 6. To simulate this yield spectrum, we evaluated ϕ_{roam} for the reported experimental conditions ($T_{\text{vib}} = 0\text{ K}$ and $T_{\text{rot}} = 25\text{ K}$) and multiplied this by the reported NO_3 absorption strength at 230 K .

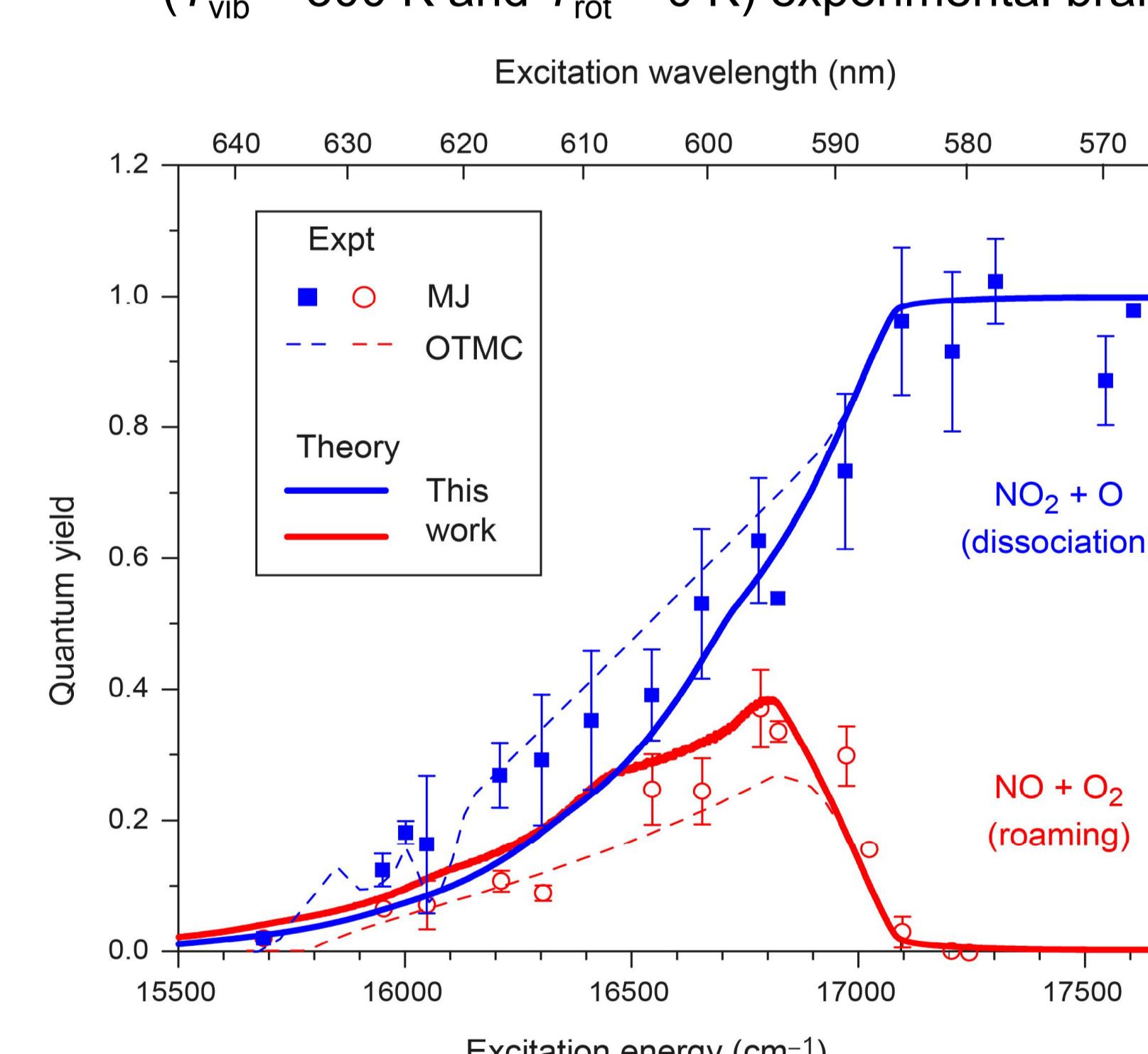


Fig 5. Quantum yields for room-temperature NO_3 photolysis. Predictions from our PST-roaming model for roaming compared to experiment. [7, 8]

CH_3CHO

Although roaming has been long-established in CH_3CHO , branching ratios have only been published for roaming versus TS production of $\text{CH}_4 + \text{CO}$. In the absence of directly comparable experimental data, the reduced dimensionality trajectories (RDTs) results by Harding *et al.* (HGK) provide a theoretical benchmark with which we compare the PST-roaming theory, Fig 7. We use $\Delta E_{roam} = 385\text{ cm}^{-1}$ (1.1 kcal/mol), as used by HGK, obtaining $P_{roam} = 0.21$. [10]

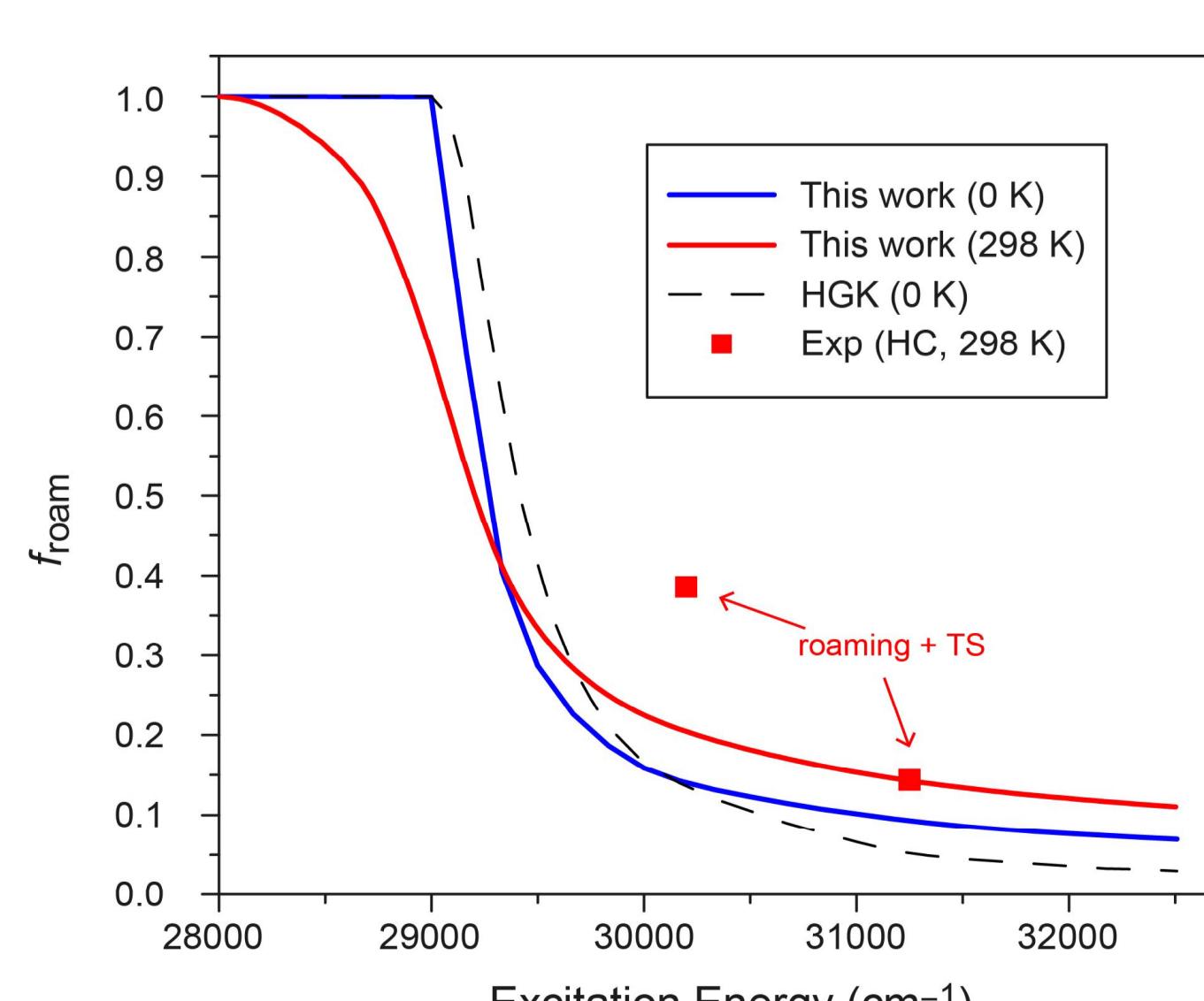


Fig 7. Predicted branching fractions for roaming in CH_3CHO and an experimental comparison. [10, 11]

Conclusions

The PST-roaming theory was applied to the roaming reactions in H_2CO , CH_3CHO , and NO_3 . The theory quantitatively reproduced the branching between bond dissociation and roaming products for all reaction energies that have been experimentally measured for H_2CO and NO_3 . It also gave reasonable agreement with the energy dependence of roaming in CH_3CHO , as calculated using RDTs. The PST-roaming theory was developed as a way to calculate branching ratios without the need for extensive calculations of the PES. When combined with conventional kinetic theories, such as TST or VTST the PST-roaming theory will provide rate coefficients for roaming as a function of energy or temperature.

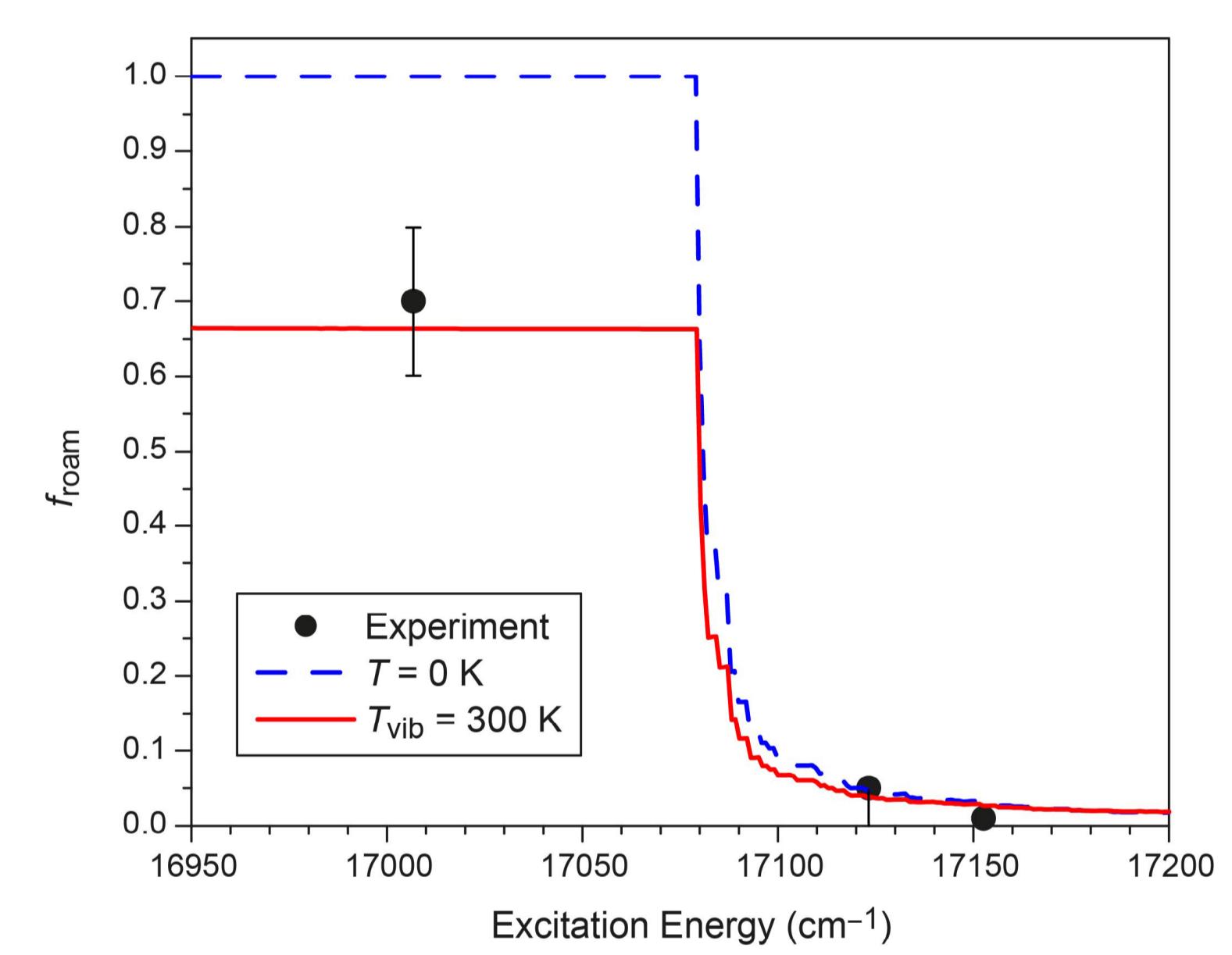


Fig 4. Low temp branching fractions for NO_3 and predictions from our PST-roaming model. [6]

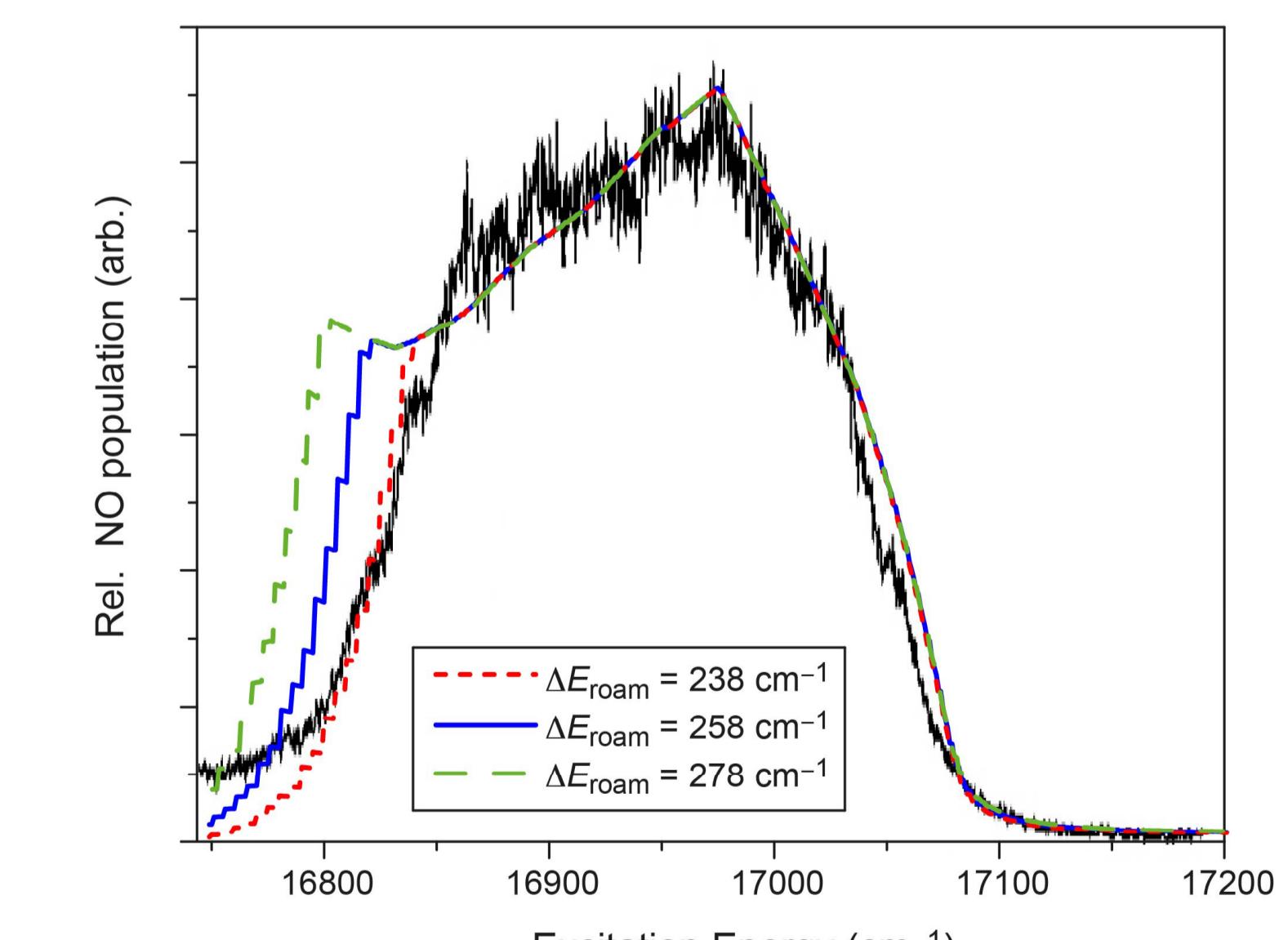


Fig 6. Low temp NO yield spectrum and predictions from our PST-roaming model varying ΔE_{roam} . [9]