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Hydrogen Abstraction from *n*-, *i*-Propanol and *n*-Butanol: A Systematic Theoretical Approach

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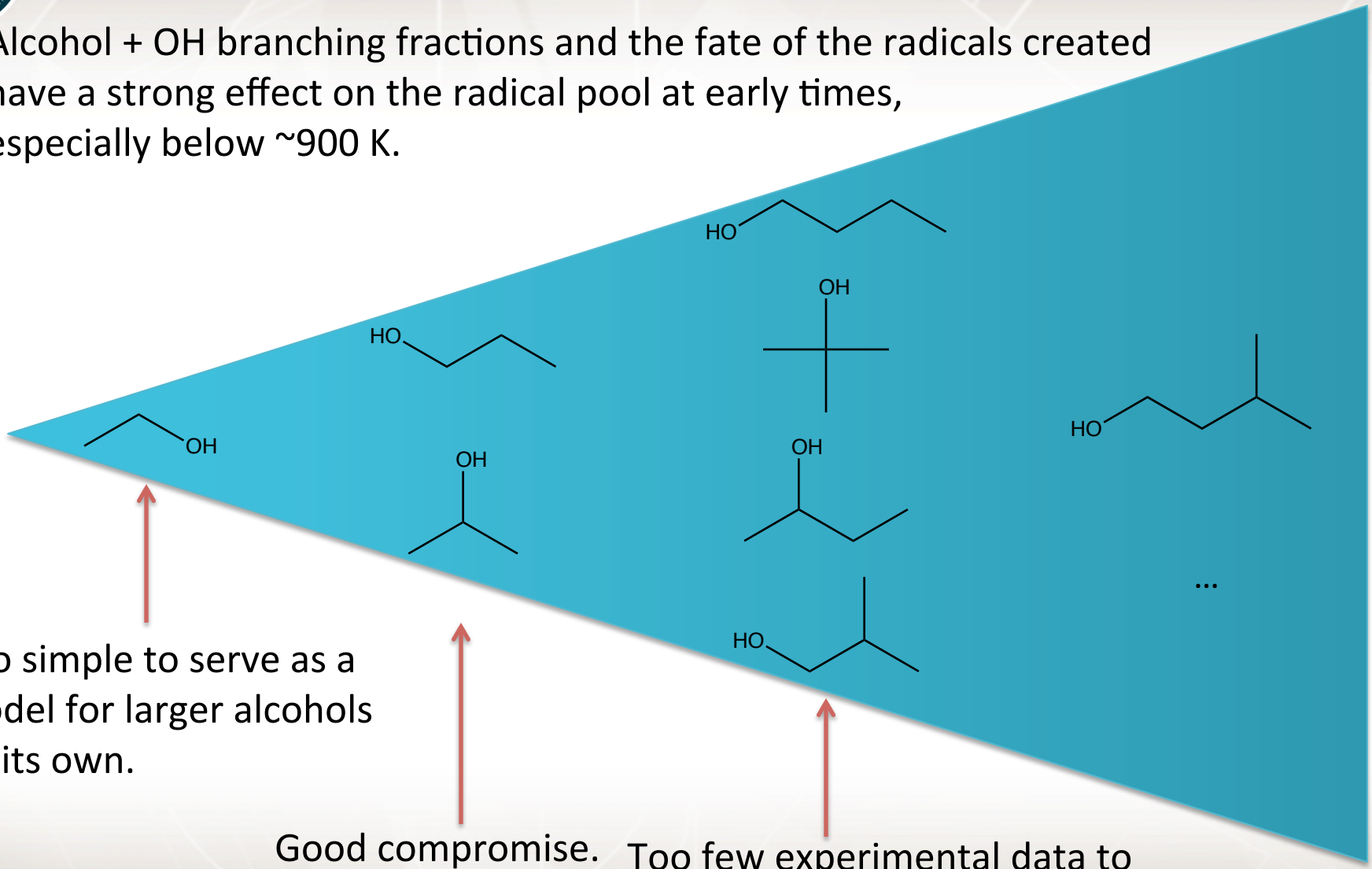
US Combustion Meeting

Ethanol, butanol and beyond

Alcohol + OH branching fractions and the fate of the radicals created have a strong effect on the radical pool at early times, especially below ~900 K.



Too simple to serve as a model for larger alcohols on its own.

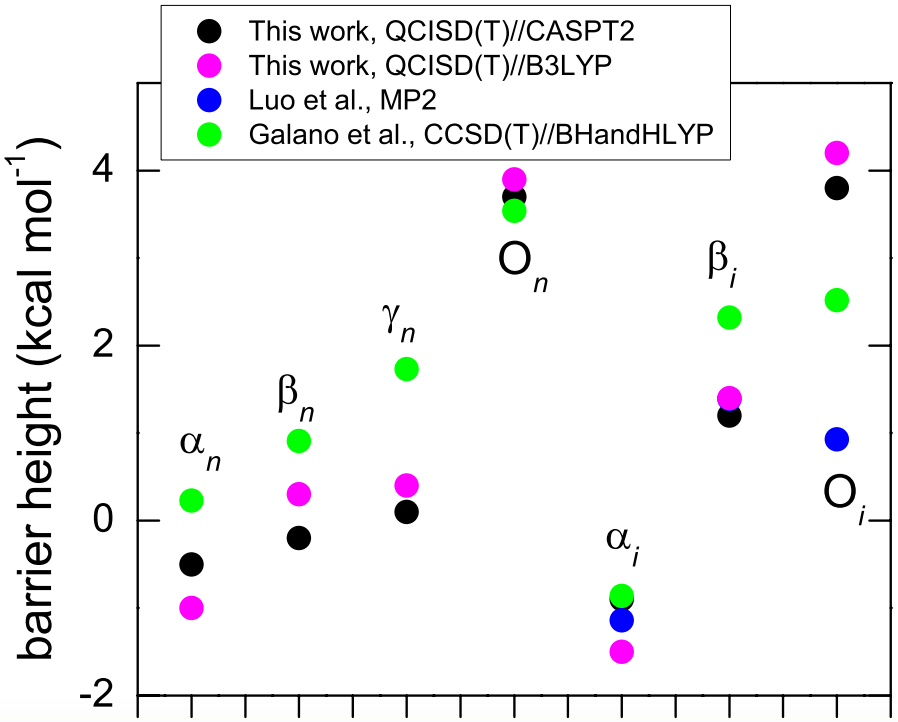
Good compromise.

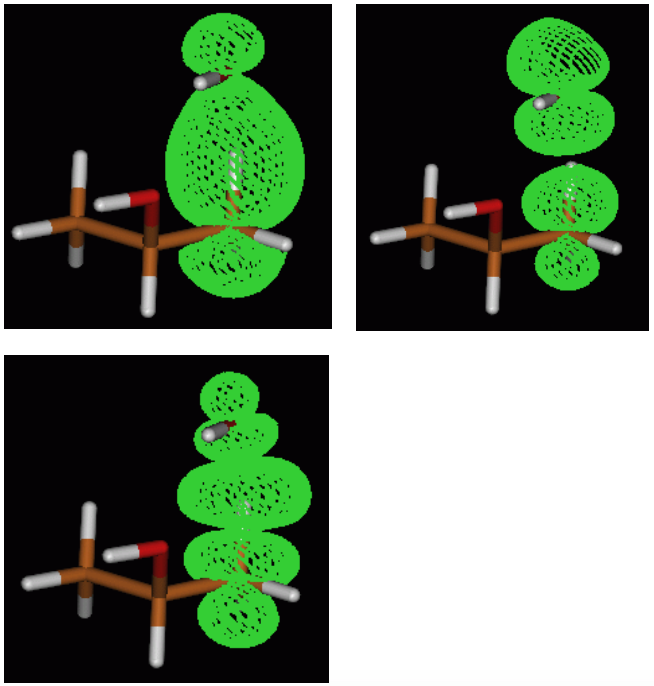
Too few experimental data to test theory rigorously.

n- and *i*-propanol + OH PES at the QCISD(T)/cc-pV∞Z//CASPT2/aug-cc-pVDZ level

Extrapolation: $E^{\infty}_{\mathrm{Q+M}} = E_{\mathrm{QCISD(T)/cc\text{-}pVTZ}} + E^{\infty}_{\mathrm{MP2/cc\text{-}pV(T/Q)Z}} - E_{\mathrm{MP2/cc\text{-}pVTZ}}$

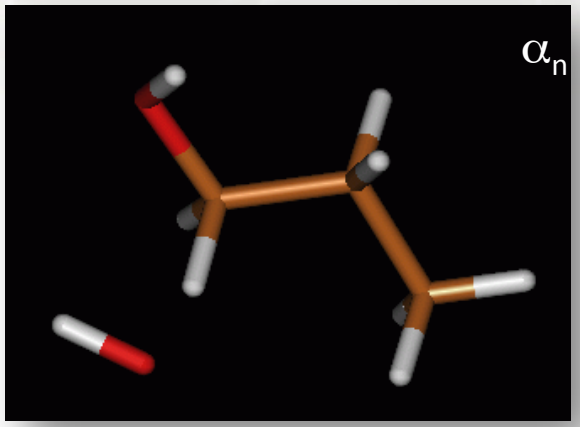
Differences are < ~1 kcal mol^{-1}, but because the barrier heights are close to zero, the rate coefficients are very sensitive to them.

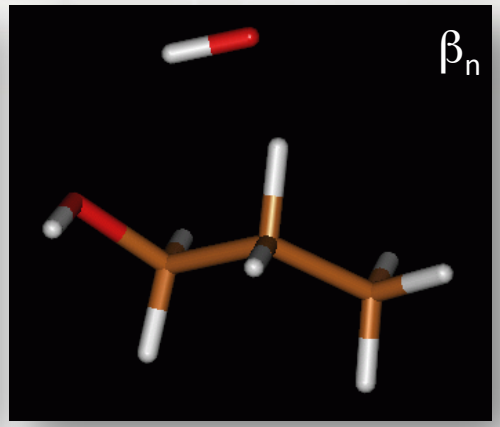


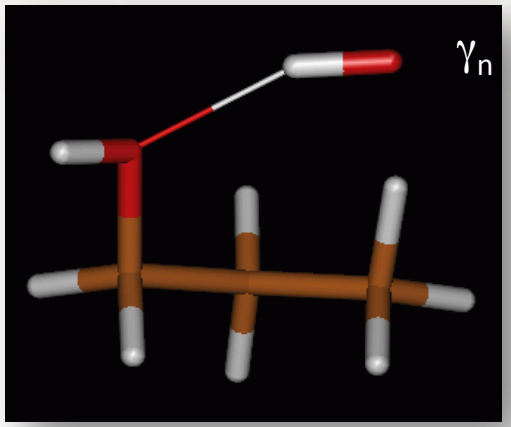


It is not possible to achieve sub-kcal mol^{-1} precision for a system of this size. Some of the differences are due to differences in structures.

The structure of the lowest-energy saddle points show strong interaction between ·OH and (R)OH.

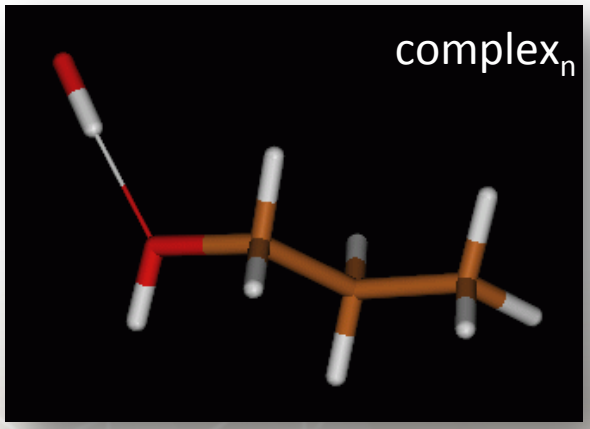






The interaction is most pronounced for the γ structure, where the OH—O bond is ~1.9 Å and the OHO angle is ~160°. This is a H-bond.

These saddle points are preceded by a weakly bound complex of OH an propanol, formed in a process with no saddle point.



Details of the kinetics calculations

RRHO approximation

Hindering potentials

Relaxed 1D scans at the B3LYP/6-311++G(d,p) and MP2/6-31G levels

5th order Fourier fits

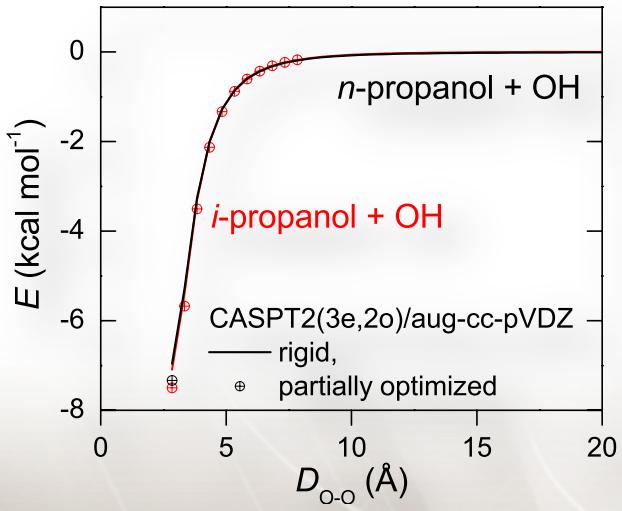
Pitzer-Gwinn approach

Outer transition state

VRC-TST

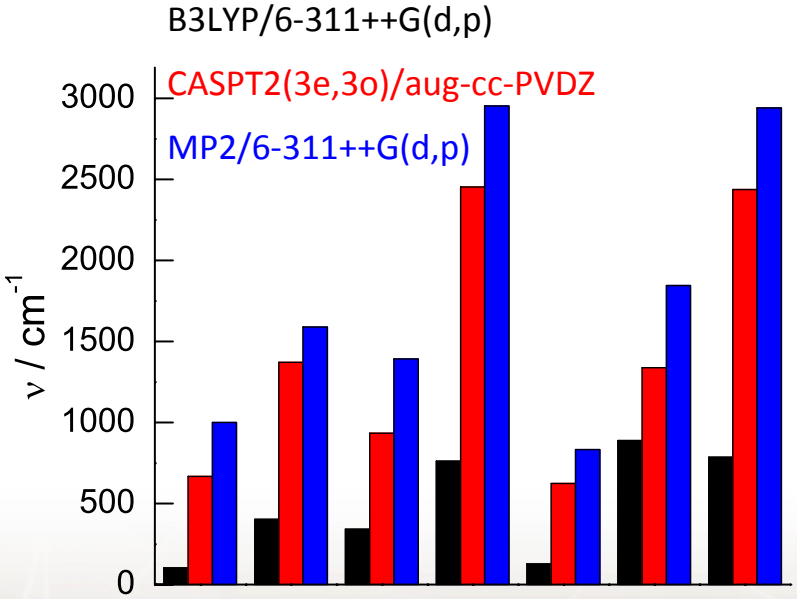
CASPT2(2e,3o)/aug-cc-pVDZ

rigid fragments

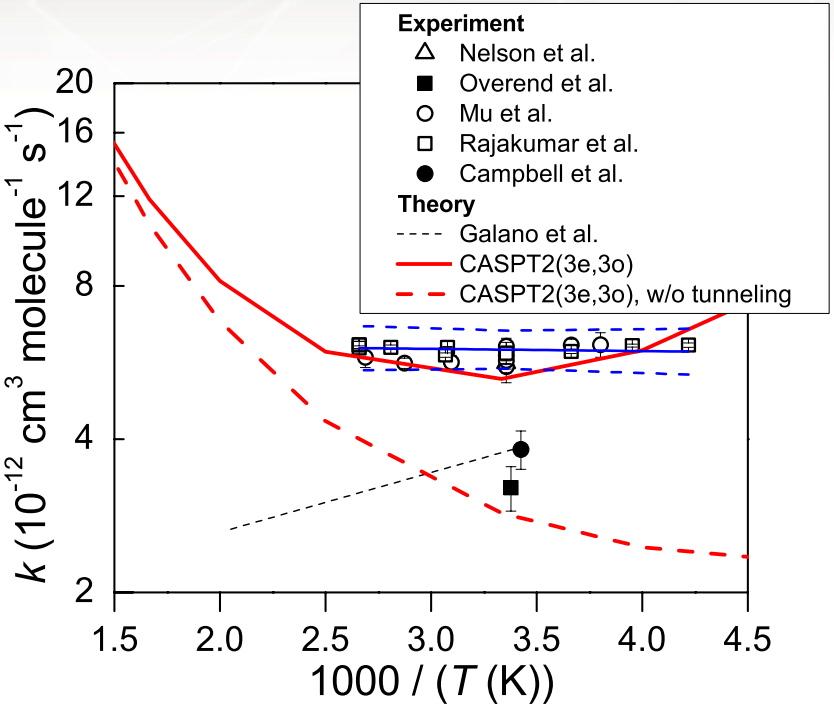


Tunneling

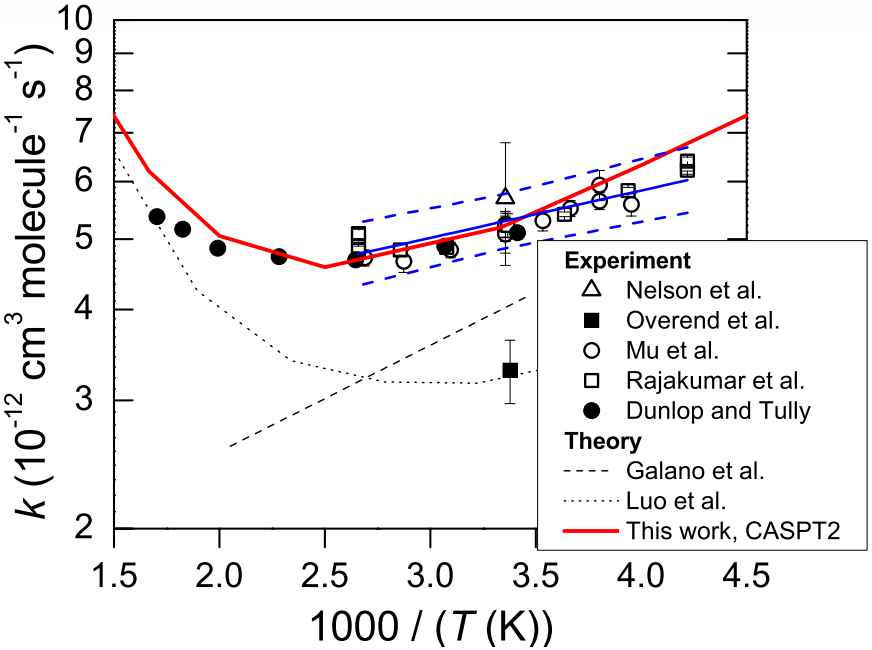
Asymmetric Eckart barriers



The total *k*'s for *n*- and *i*-propanol agree with the experiments within the uncertainties.



***n*-propanol + OH**



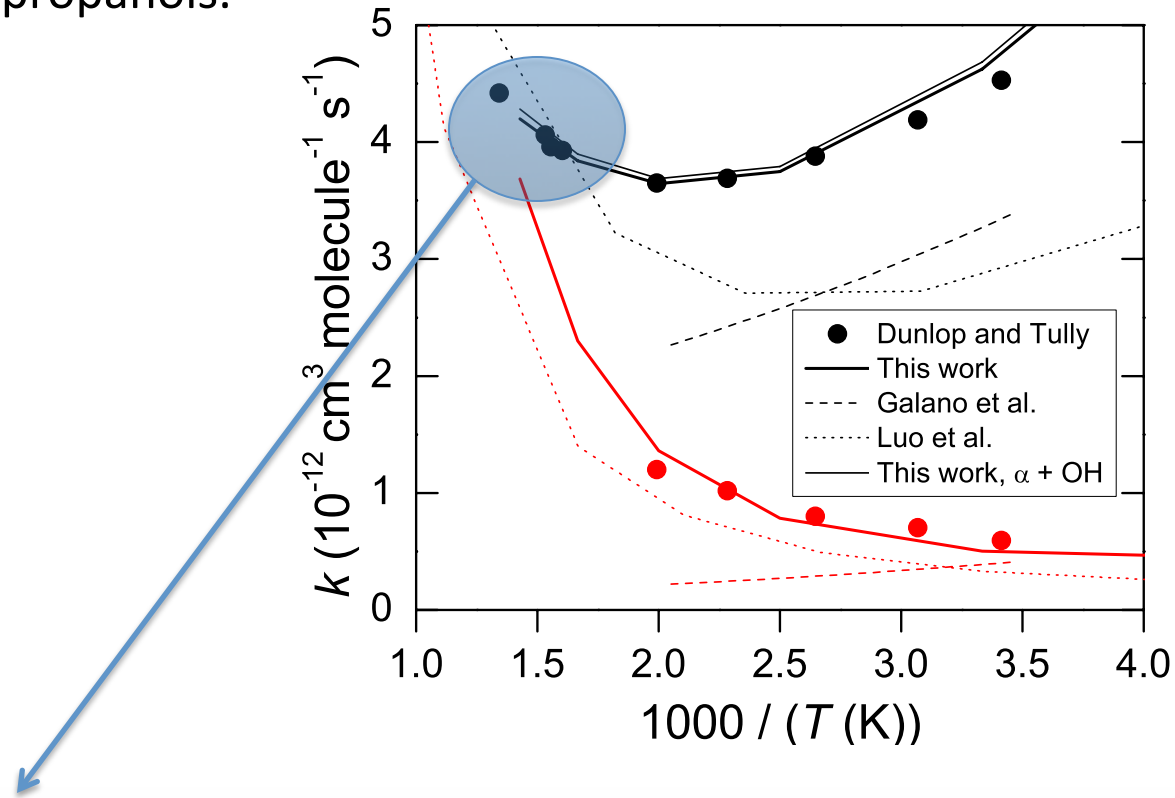
***i*-propanol + OH**

The effect of the outer transition state is < 10% at the lowest temperature.

Tunneling increases the rate coefficient by >2x at the lowest temperature.

Branching fractions can be tested in the case of *i*-propanol.

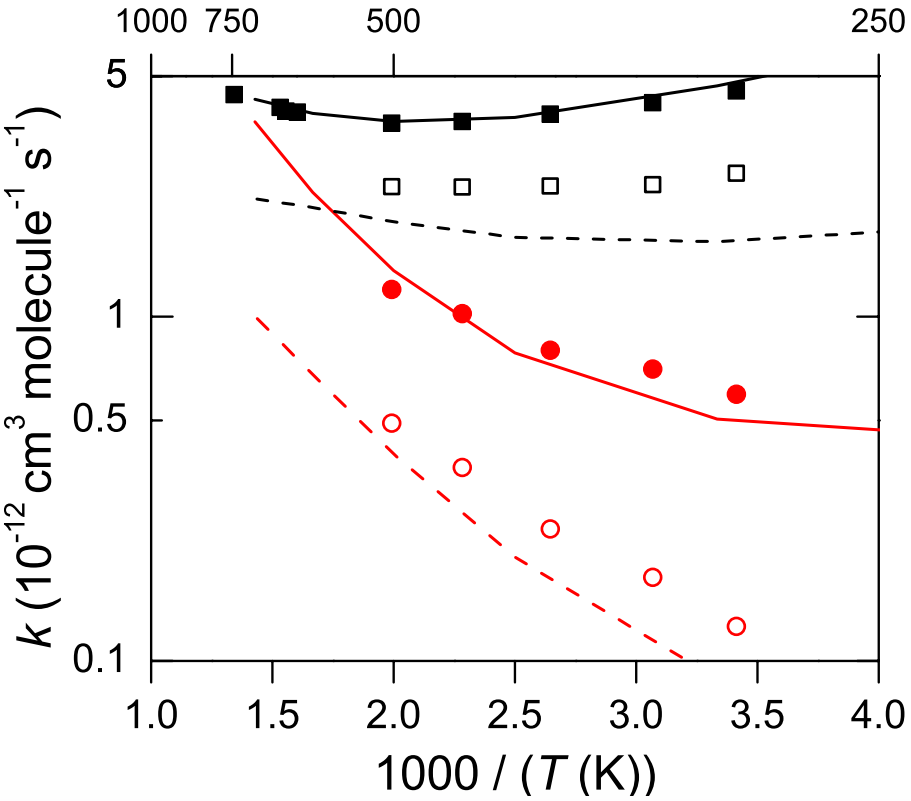
Branching was measured by Dunlop and Tully using selectively deuterated *i*-propanols.



Above ~650 K the β-hydroxypropyl radicals dissociate instantaneously, i.e. the overall rate coefficient is only the α+O in this case.

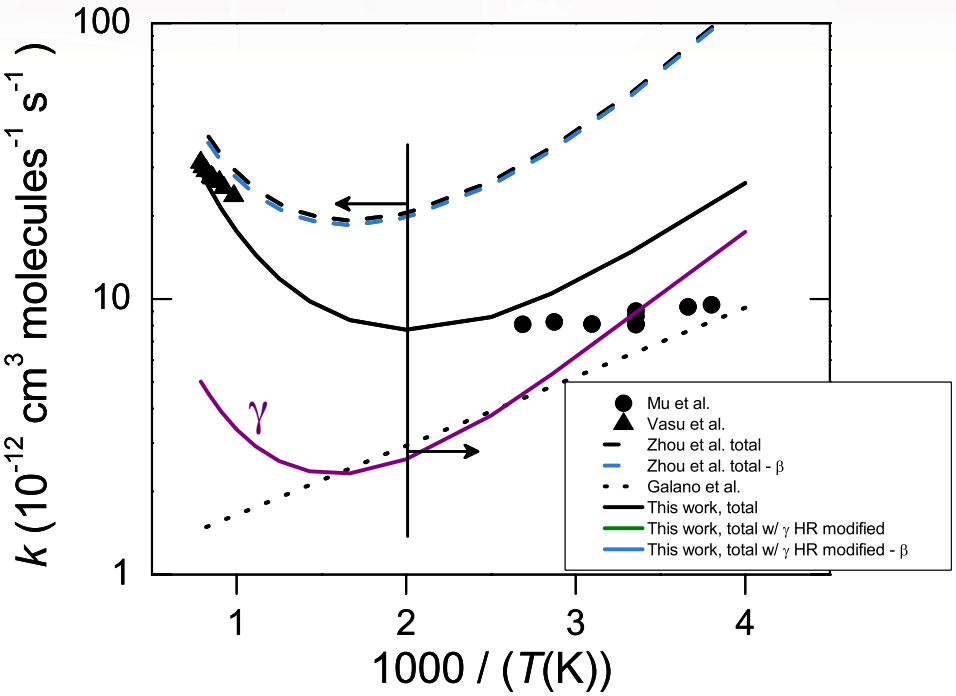
The comparison of the calculated and measured KIE's show how well tunneling is accounted for.

Channel-dependent (primary) KIE in the case of *i*-propanol:



This and the previous results indicate that the current methodology is likely to give reliable results for higher alcohols.

n-butanol: Results and comparison to experimental data



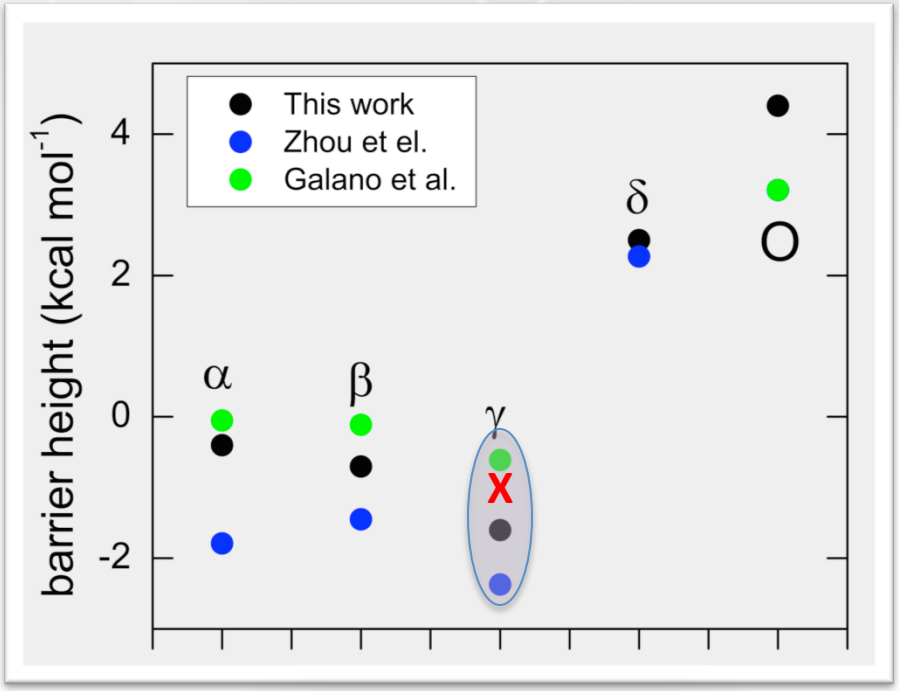
The total rate coefficient is greatly overpredicted at low temperature (2x and 7x @300 K).

Why?

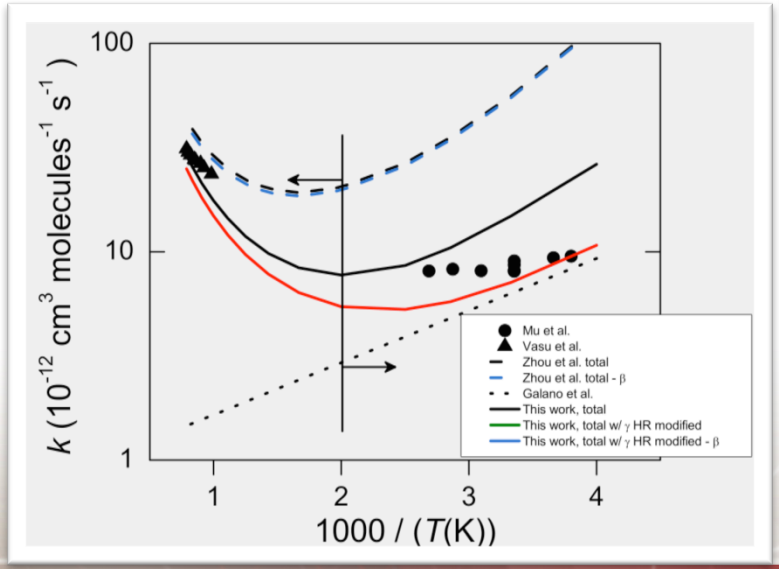
The γ channel is the fastest channel at low *T*.
Secondary γ H-abstraction was not part of the test set for propanols!!

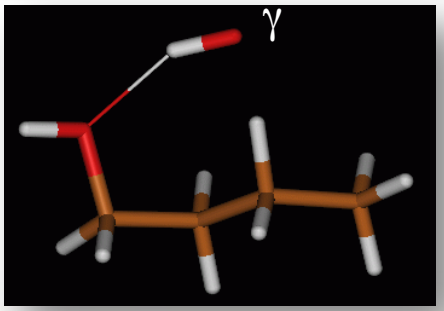
PES and structures for *n*-butanol

n-butanol	
α, primary	*n*-propanol
β, secondary	*n*-propanol
γ, secondary	NO
δ, primary	NO
O, primary	*n*-propanol



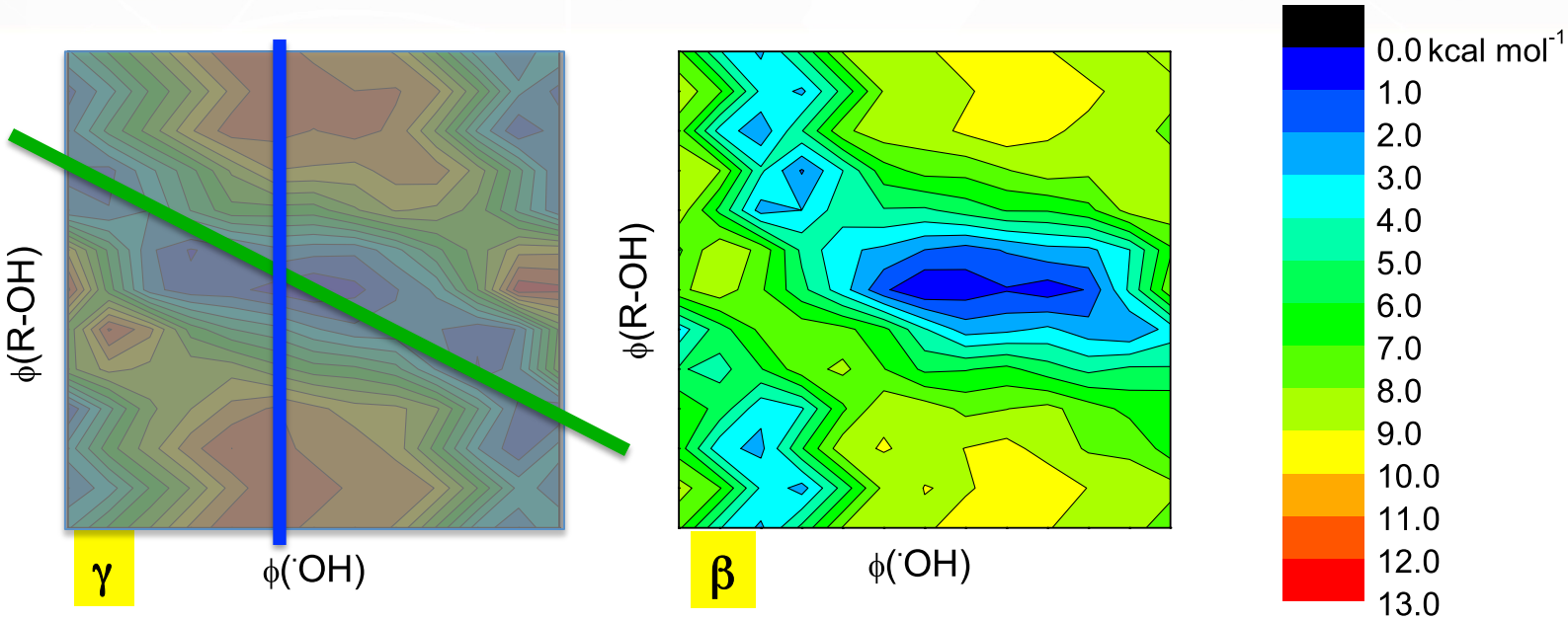
"Quick fix":
change the barrier height for γ
+0.5 kcal mol^{-1}





Barrier height is very important at low *T*, but it is not the only key parameter.

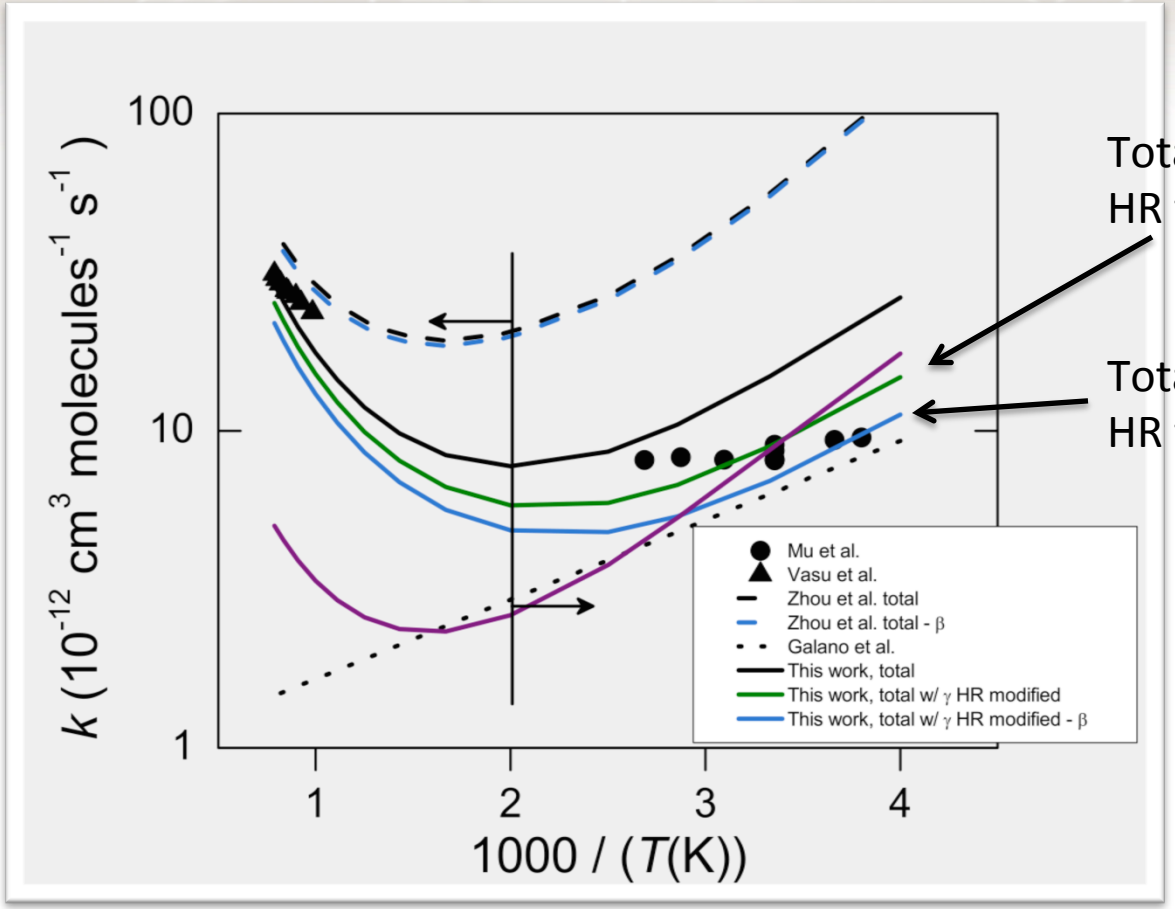
The hindered rotors are strongly coupled for the γ and to a smaller extent for the β channels.



Using fully relaxed scans overestimate the looseness of these transition states. This effect is more pronounced for the γ channel.

Multidimensional integration of the density and sum of states would be desirable. Here, instead, the hindering potential is – somewhat arbitrarily – decomposed along two directions.

Results with modified HR treatment



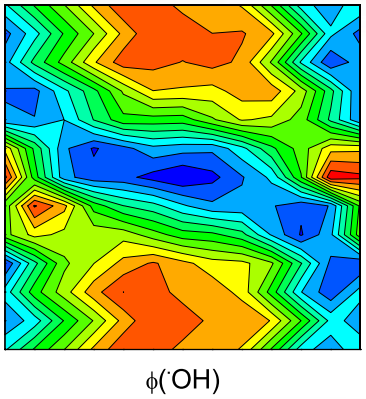
Total k w/ modified HR treatment

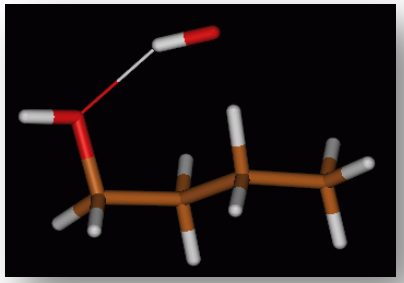
Total k – β w/ modified HR treatment

The effect of the coupling of HR's is comparable to the effect of the change in barrier height by 0.5 kcal mol^{-1}.

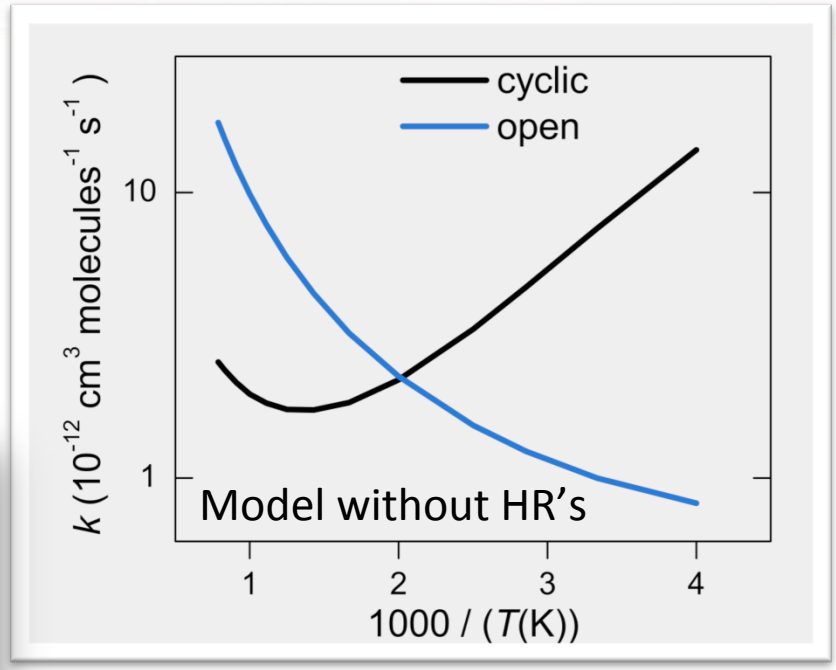
The largest model-experiment discrepancy is 30%.

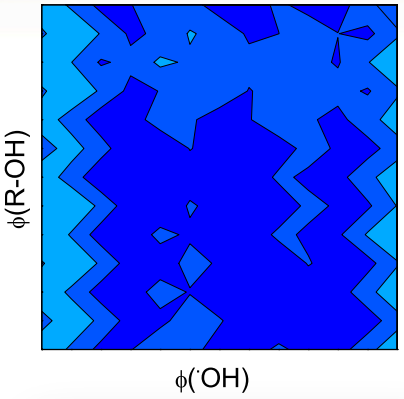
Cyclic vs. open structures: Can entropy win over energy?

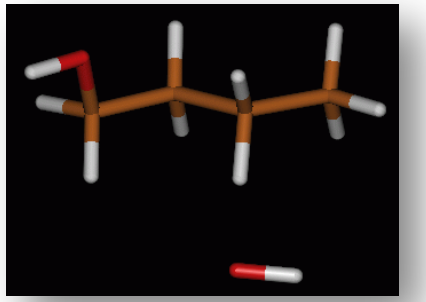




-1.6 kcal mol^{-1}



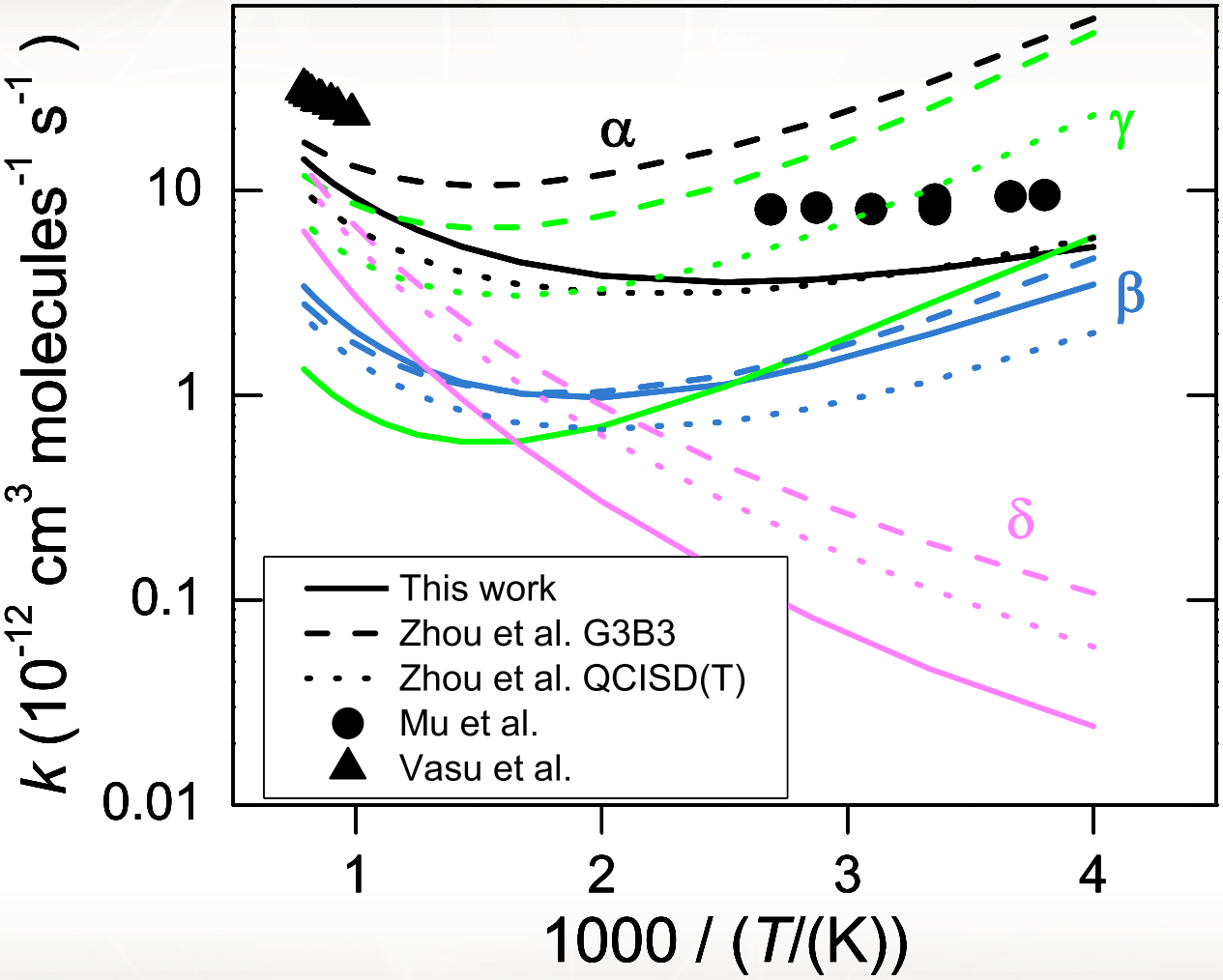




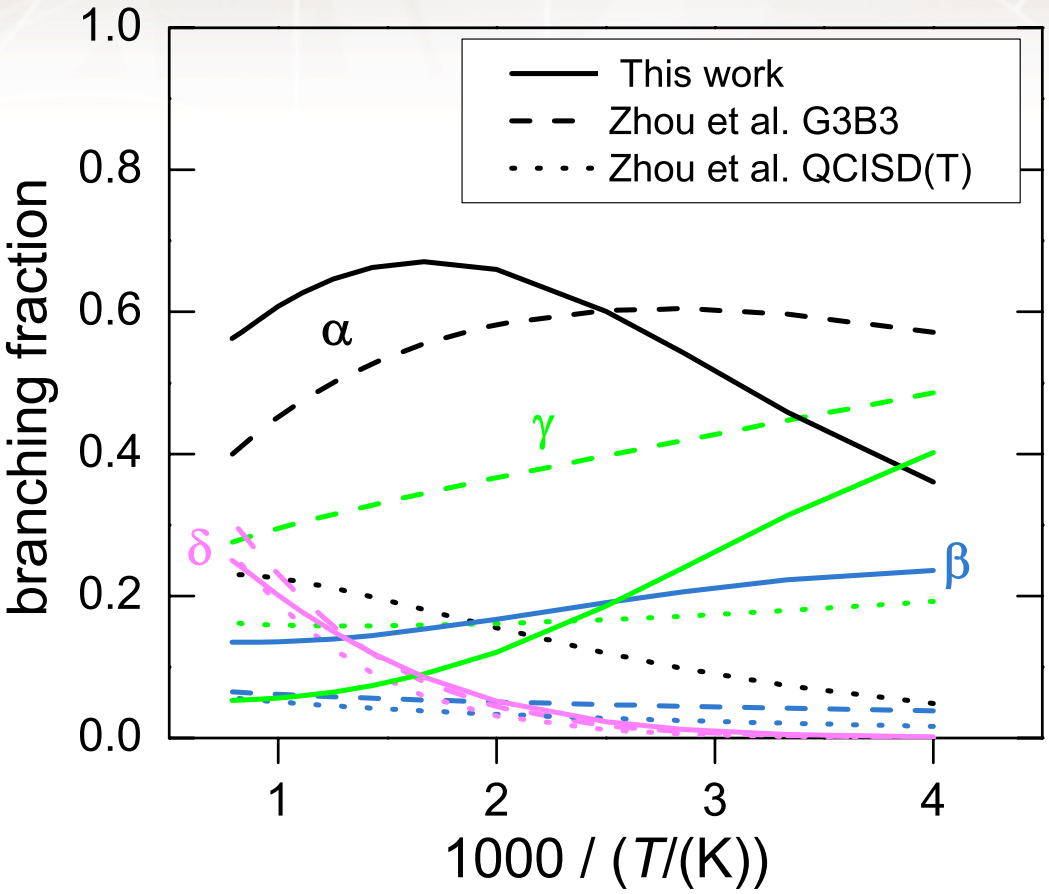
+0.7 kcal mol^{-1}

A fully harmonic model (i.e. no HR's in either reactants or TS's) suggests that it is possible.

Channel specific rate coefficients



Branching fractions

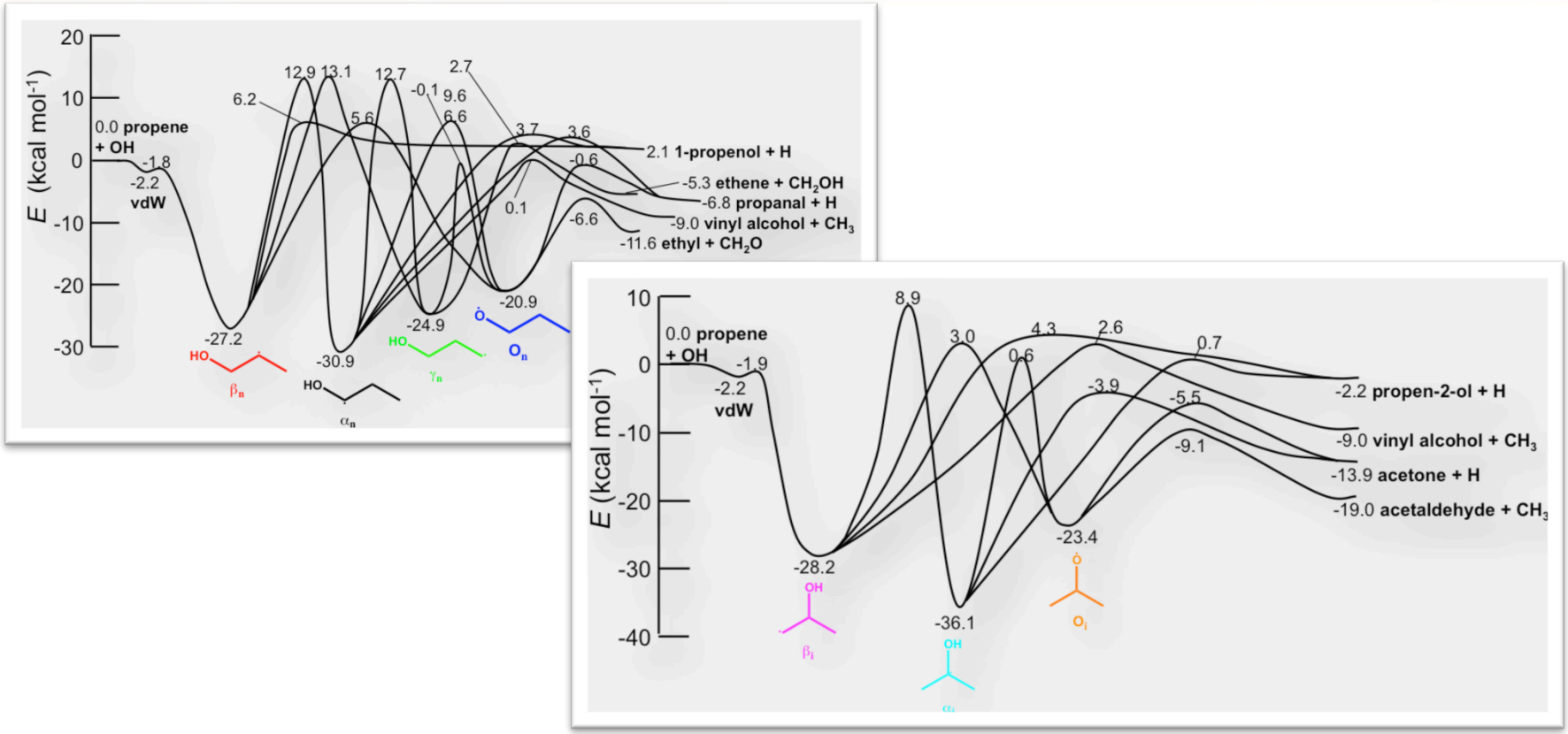


The largest uncertainty is attributed to the γ channel due to the strongly coupled HR's and the barrier height not appearing in the propanol + OH system.

The other channels are expected to be more reliable based on the propanol system.

Unimolecular dissociation of the hydroxyalkyl and alkoxy radicals

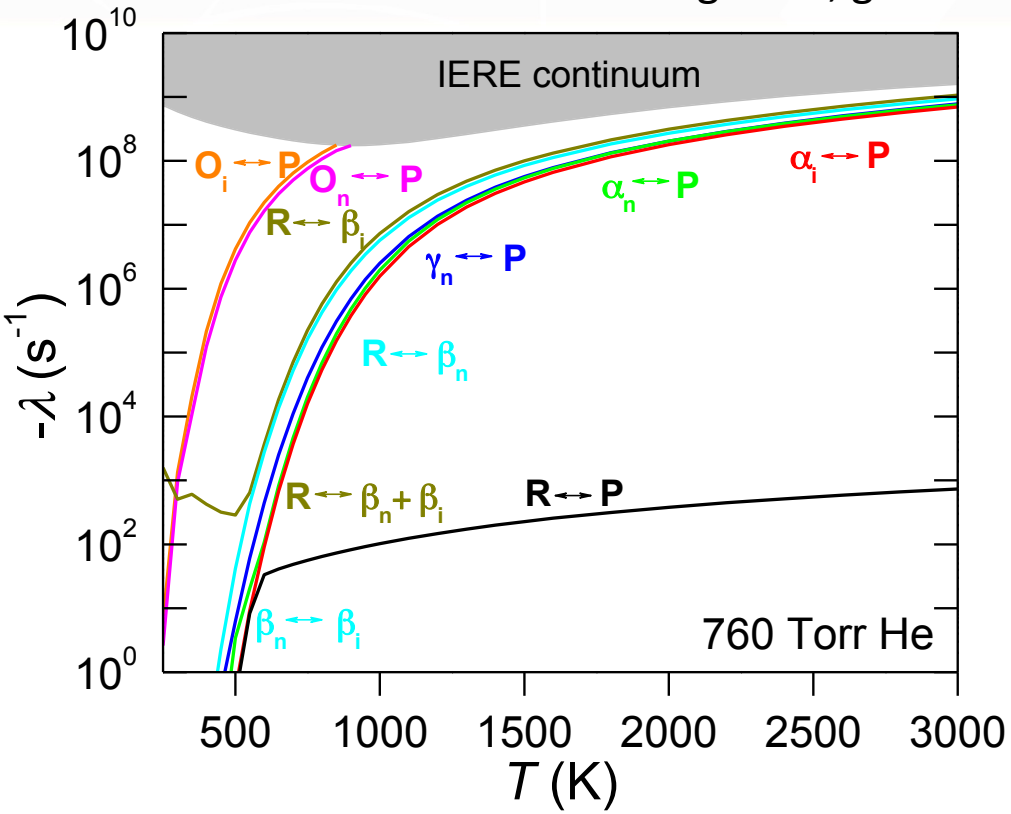
The propene + OH potential energy surface contains all relevant species.



The propene + OH kinetics was previously tested successfully against a large number of experimental data in a wide *P* and *T* range.

The calculation of the rate coefficients require the analysis of the eigenvalues.

Rate coefficients are calculated using a ME, given in the form: $\frac{d|w(t)\rangle}{dt} = \mathbf{G}|w(t)\rangle$

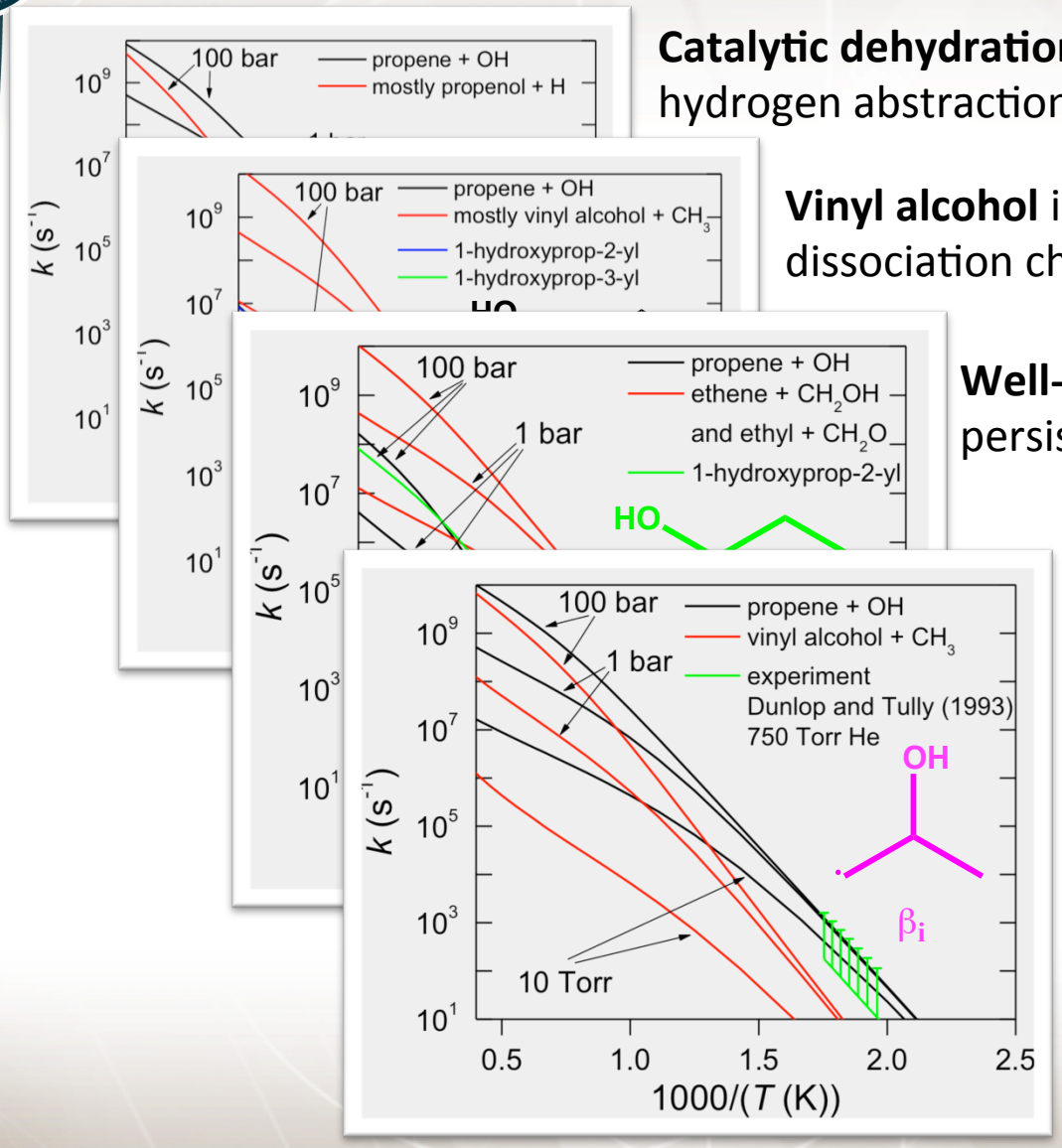


Long-time method:
IERE > CSE

Initial-rate method:
IERE >> CSE

When one or more CSE's merge into the IERE's, rate coefficients related to the unmerged CSE's can be only obtained by reducing the number of chemical species in the problem by merging equilibrating species into a "superspecies".

Pressure and temperature dependent results



Catalytic dehydration of *n*/*i*-propanol via β-hydrogen abstraction by OH.

Vinyl alcohol is formed from various dissociation channels.

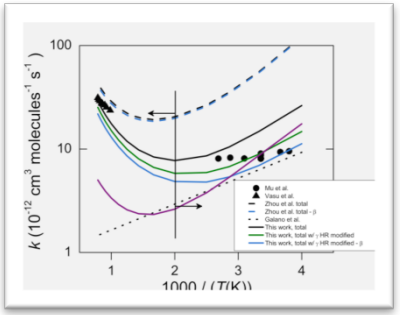
Well-skipping (formally direct) channels persist even at high pressures.

Comparison to experiment is limited.

Conclusions and challenges

Abstraction rate coefficients form alcohols for propanols and *n*-butanol were determined. In the case of the secondary γ channel the uncertainty is large, mainly because:

- uncertainty in barrier height
- strongly coupled HR's



However, up to date our calculations are the only ones, which give satisfactory agreement between experiments and theory in the whole temperature range.

Calculation of the dissociation pathways requires a rigorous ME treatment.

We calculated all possible dissociation channels for C_3H_7O radicals as a functions of pressure and temperature.