Hydrogen Addition to Propene Tunneling Reactions in a Solid *para*-Hydrogen Matrix

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Karolina A. Haupa, Yuan-Pern Lee

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FF 08

THE UNIVERSITY OF GEORGIA

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National Chiao Tung University

Background

Gas Phase

W.J. Moore, H.S. Taylor, The mercury photosensitized hydrogenation of ethylene, propylene, and *n*-butylene, The Journal of Chemical Physics 8 (1940) 504-505.
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B.D. Darwent, R. Roberts, The reactions of hydrogen atoms with hydrocarbons, Discuss. Faraday Soc. (1953) 55-63.
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G.R. Hoey, D.J. Leroy, The mercury photosensitized hydrogenation of propylene and the activation energy of the reaction C3H7+H2 = C3H8+H, Can. J. Chem. 33 (1955) 580-588.
J.N. Bradley, H.W. Melville, J.C. Robb, The kinetics and chemistry of the interaction of alkyl radicals. III. The disproportionation and combination of propyl radicals, P. Roy. Soc. Lond. A Mat. 236 (1956) 339-342.
R.A. Back, The mercury-photosensitized decompositions of propane and ethane, Can. J. Chem. 37 (1959) 1834-1842.
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Solid Film – 77 K

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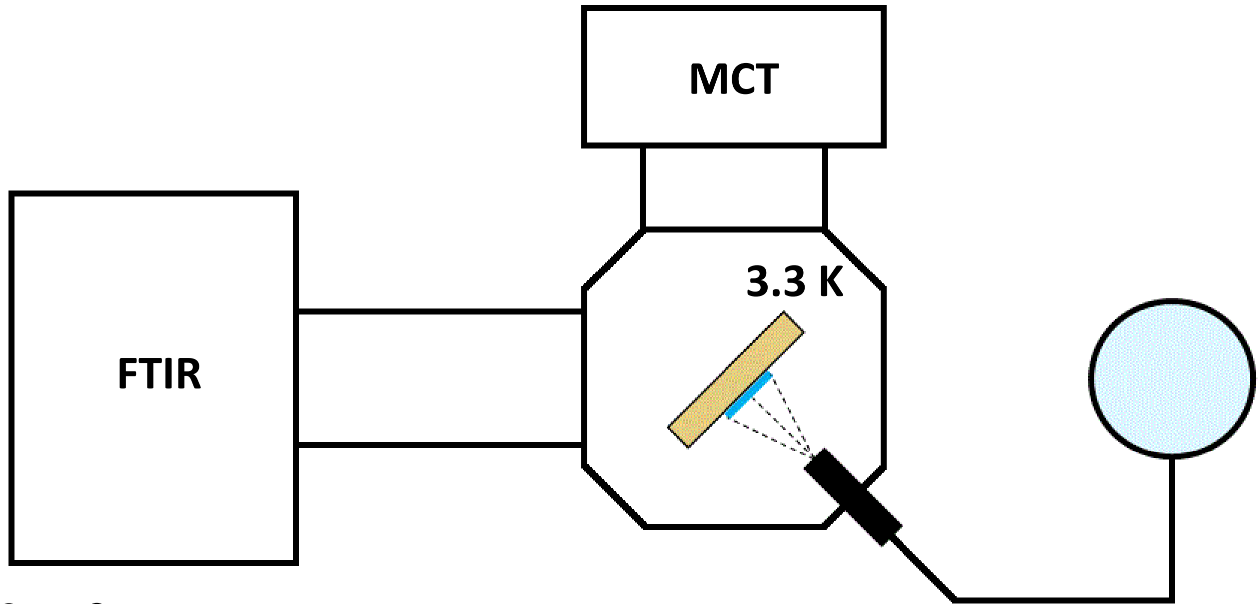
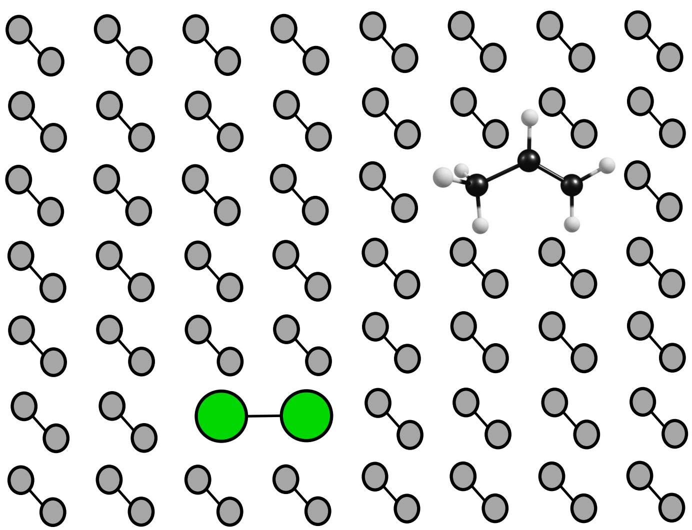
A.K. Hagopian, R.H.A. Johnsen, Reactions of thermal hydrogen atoms with propene at 77 K. Infrared heating effects in solid organics *in vacuo*, J. Chem. Soc. Chem. Comm. (1974) 837-838.

Solid Film – 10 K

K. Hiraoka, T. Sato, S. Sato, T. Takayama, T. Yokoyama, N. Sogoshi, S. Kitagawa, Study on the tunneling reaction of H atoms with a solid thin film of C_3H_6 at 10 K, J. Phys. Chem. B 106 (2002) 4974-4978.

p-H_2 Setup



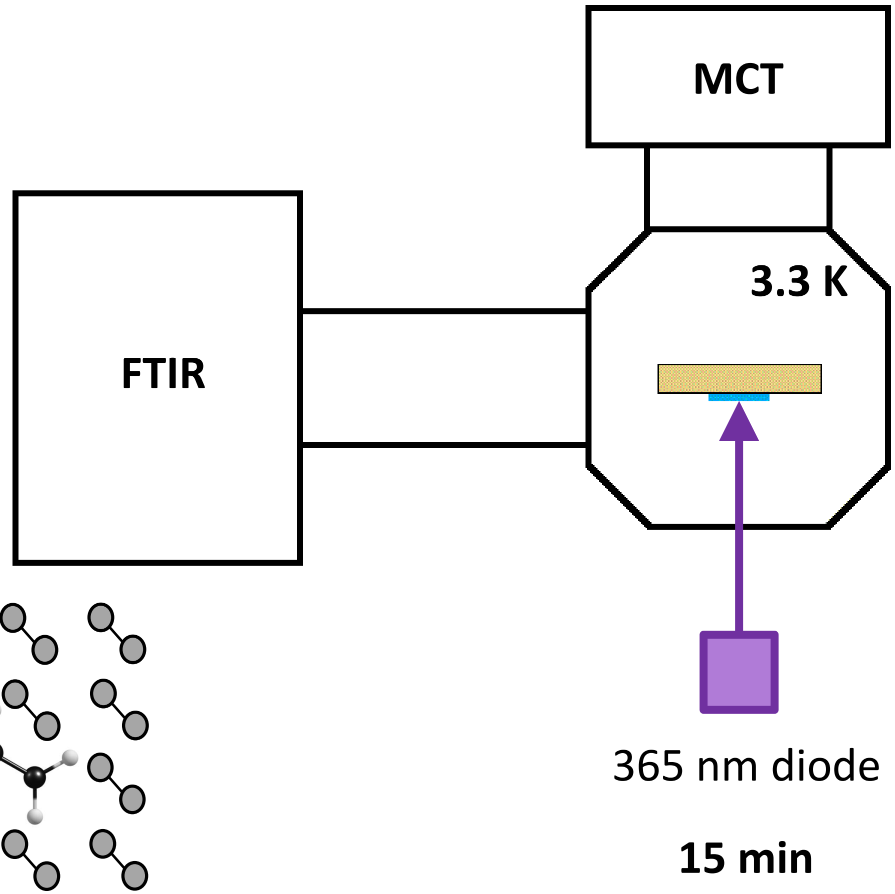


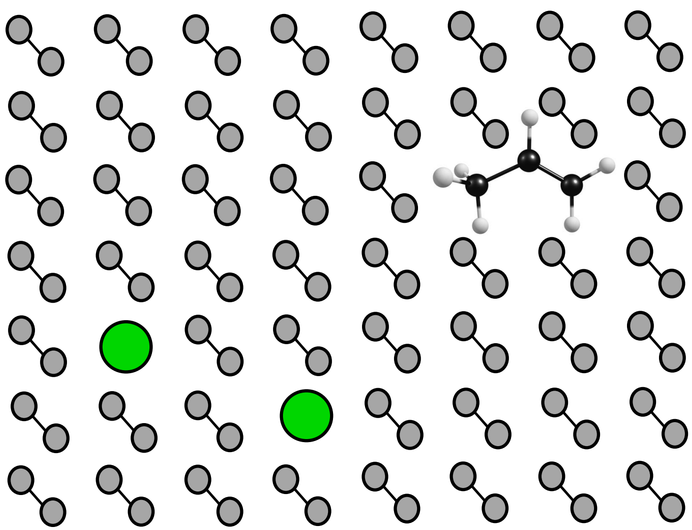
1/4/5000
Propene/Cl_2/p-H_2

5 hrs (10-13 mmol/hr)

p-H_2 Setup

$$Cl_2 \xrightarrow{365\ \text{nm}} 2\ Cl$$



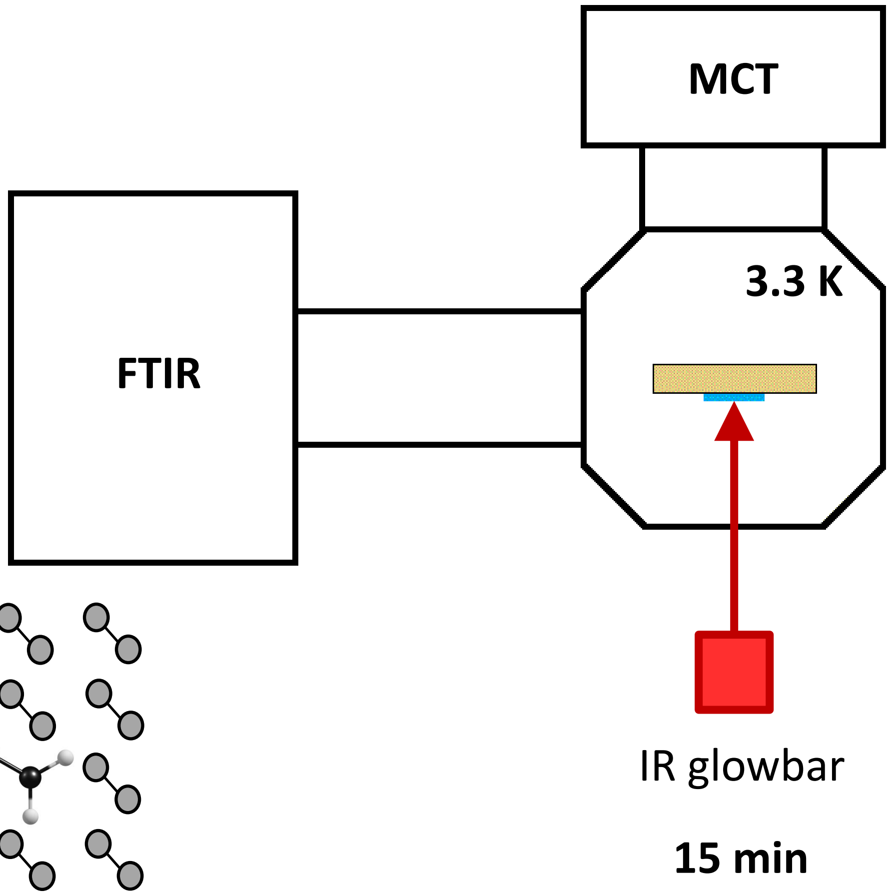


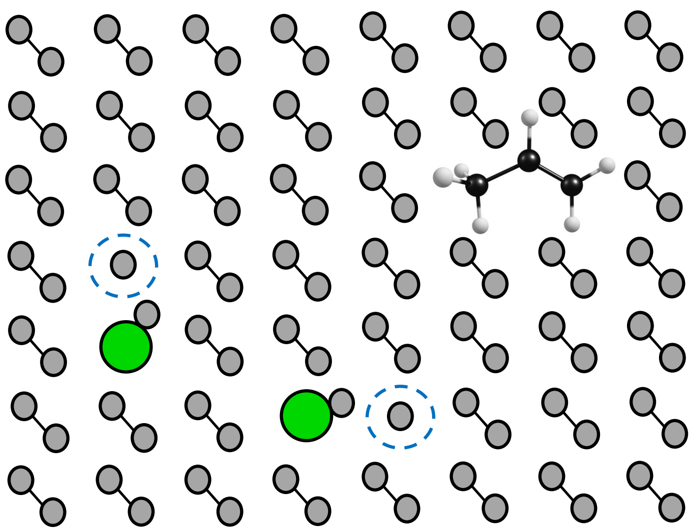
p-H_2 Setup

$$Cl_2 \xrightarrow{365\ \text{nm}} 2\ Cl$$

$$Cl + H_2 \xrightarrow{IR} HCl + H$$

$$\text{Propene} + H \rightarrow \text{Propyl}$$





p-H_2 Setup

$$Cl_2 \xrightarrow{365\ \text{nm}} 2\ Cl$$

$$Cl + H_2 \xrightarrow{\text{IR}} HCl + H$$

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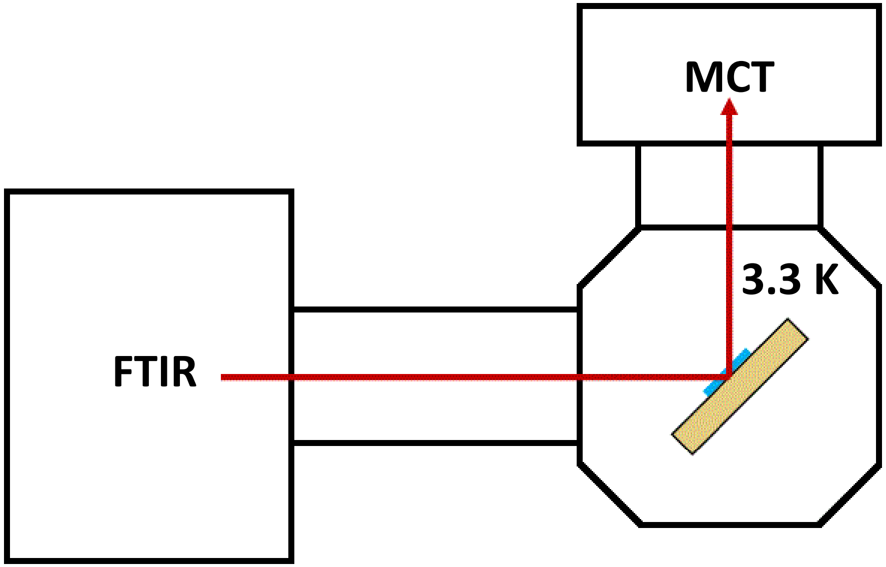
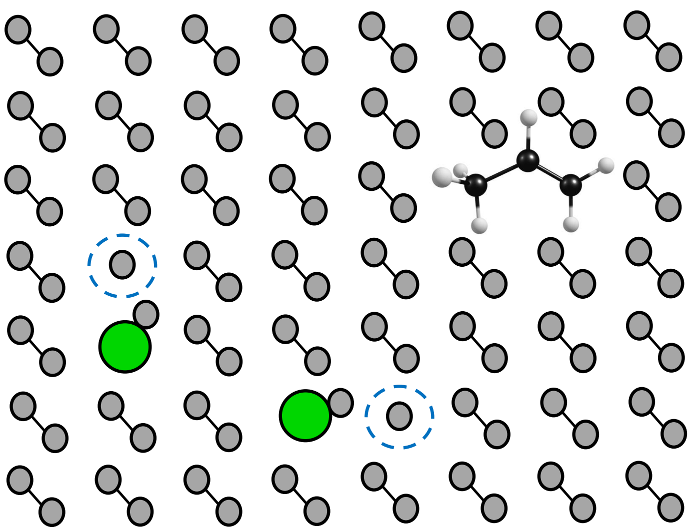
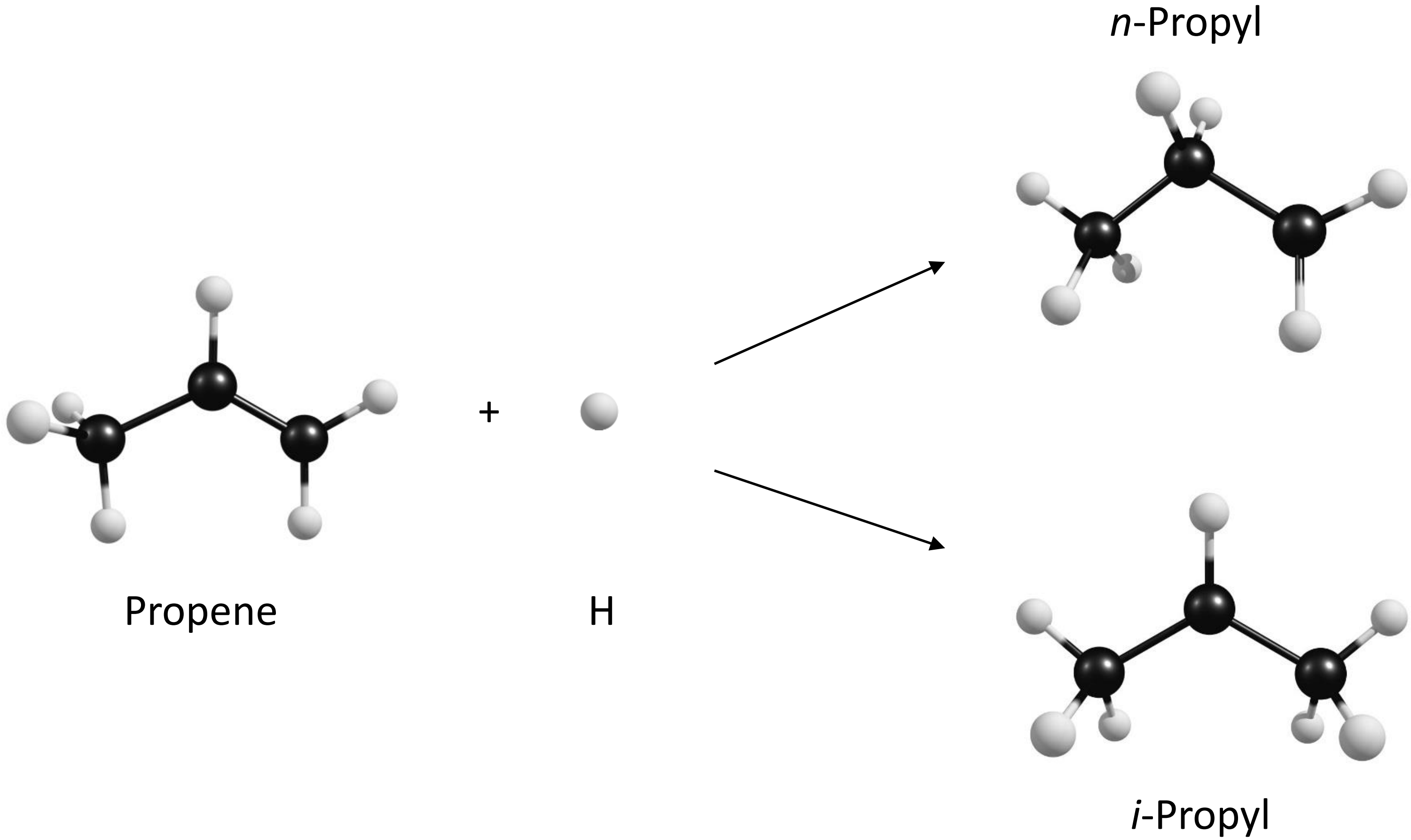




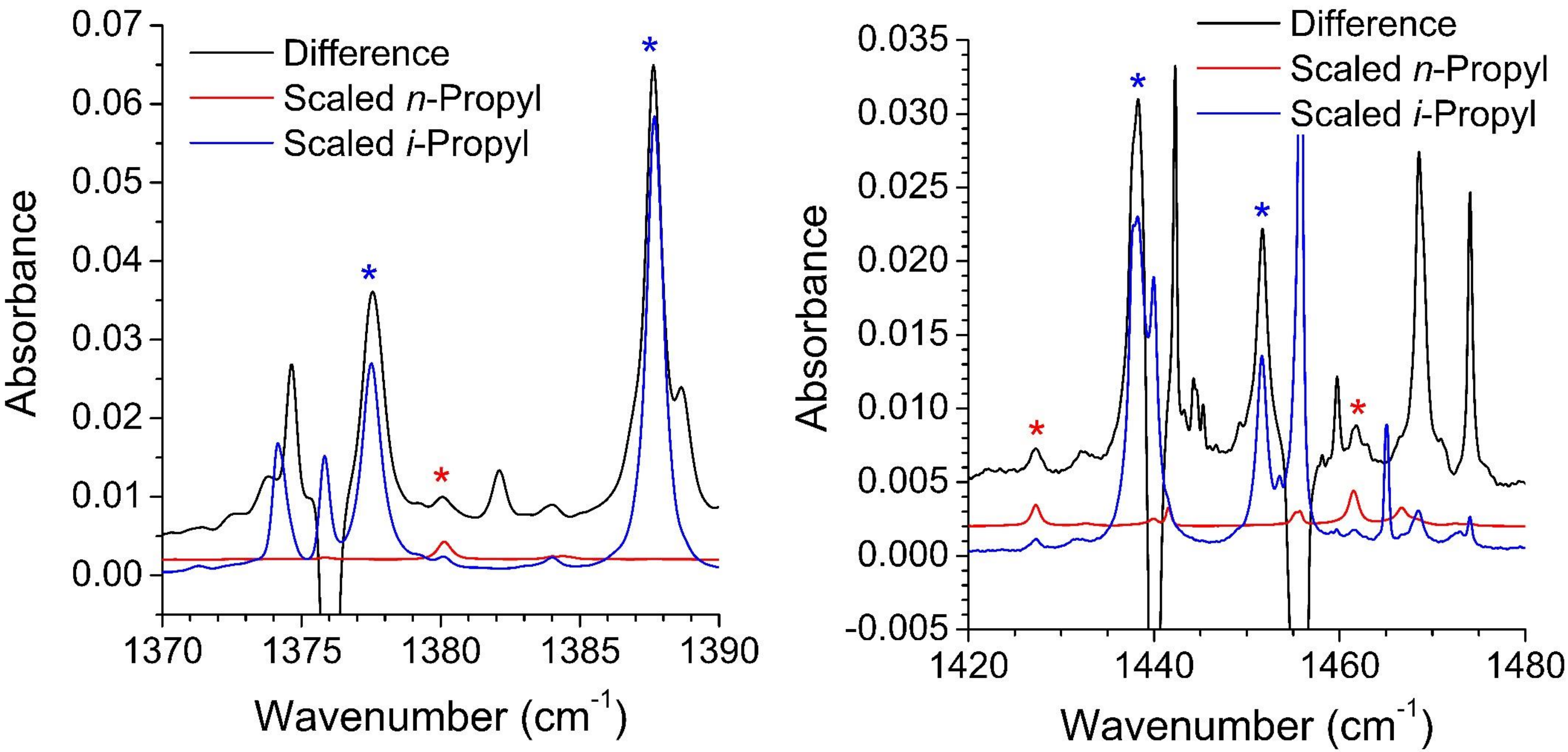
200 scans (0.25 cm^{-1} resolution)

Every 30 min for 12 hours

Hydrogen Addition to Propene

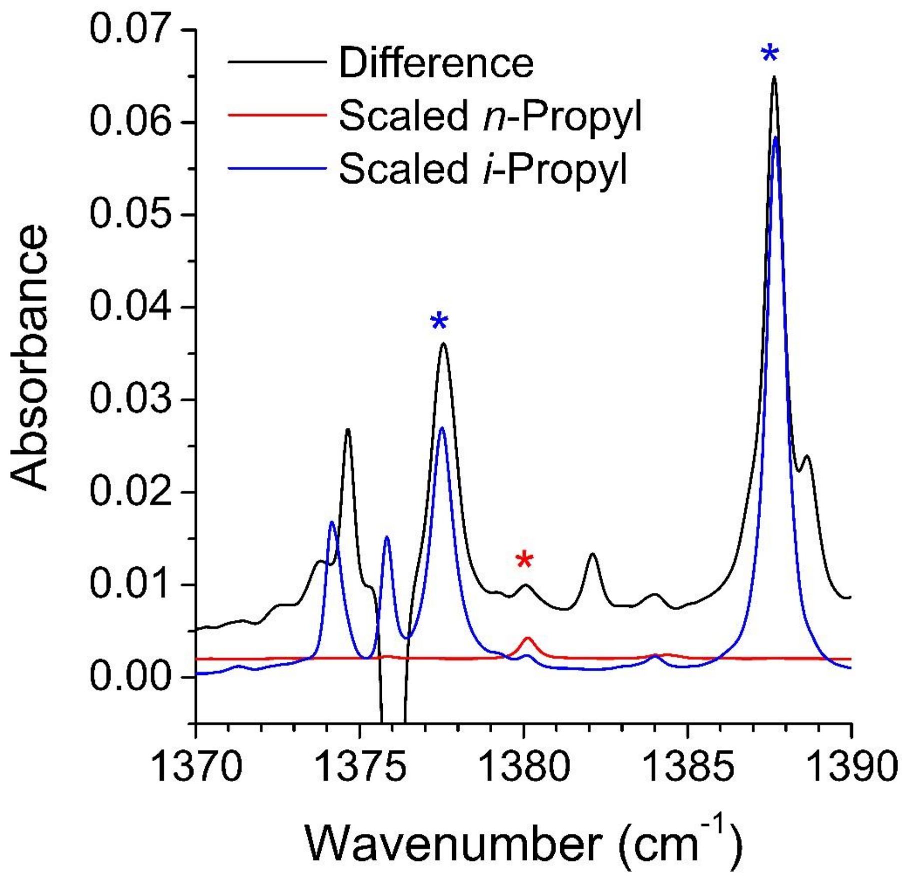


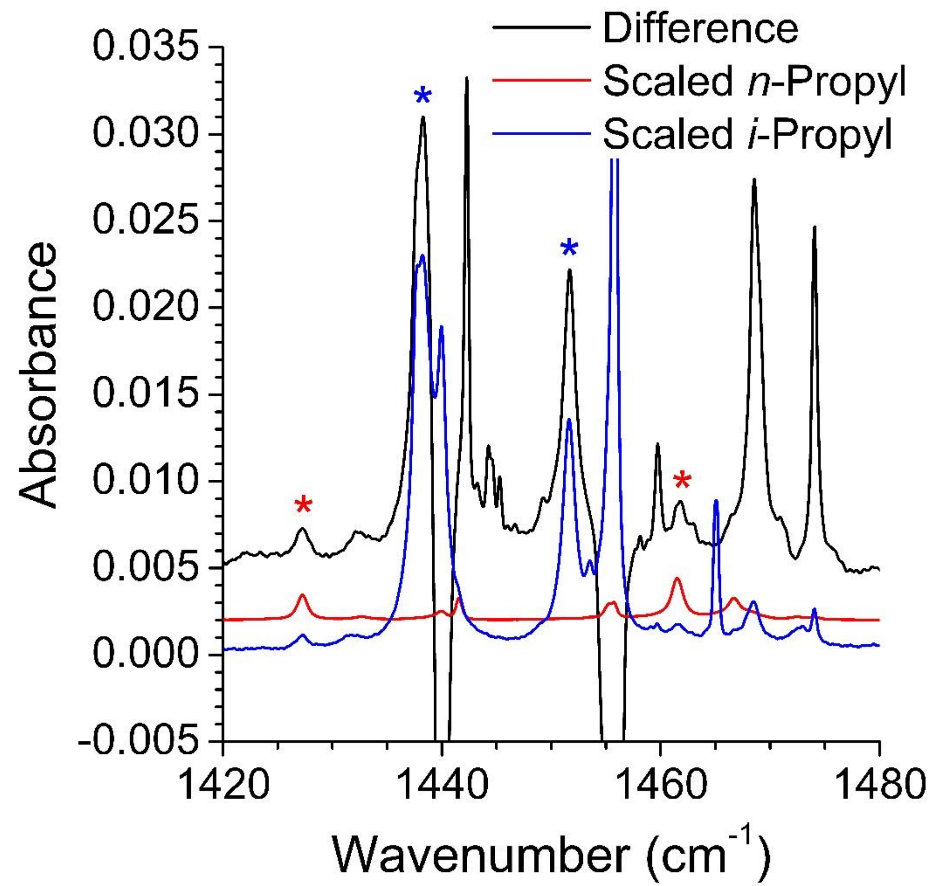
Hydrogen Addition to Propene



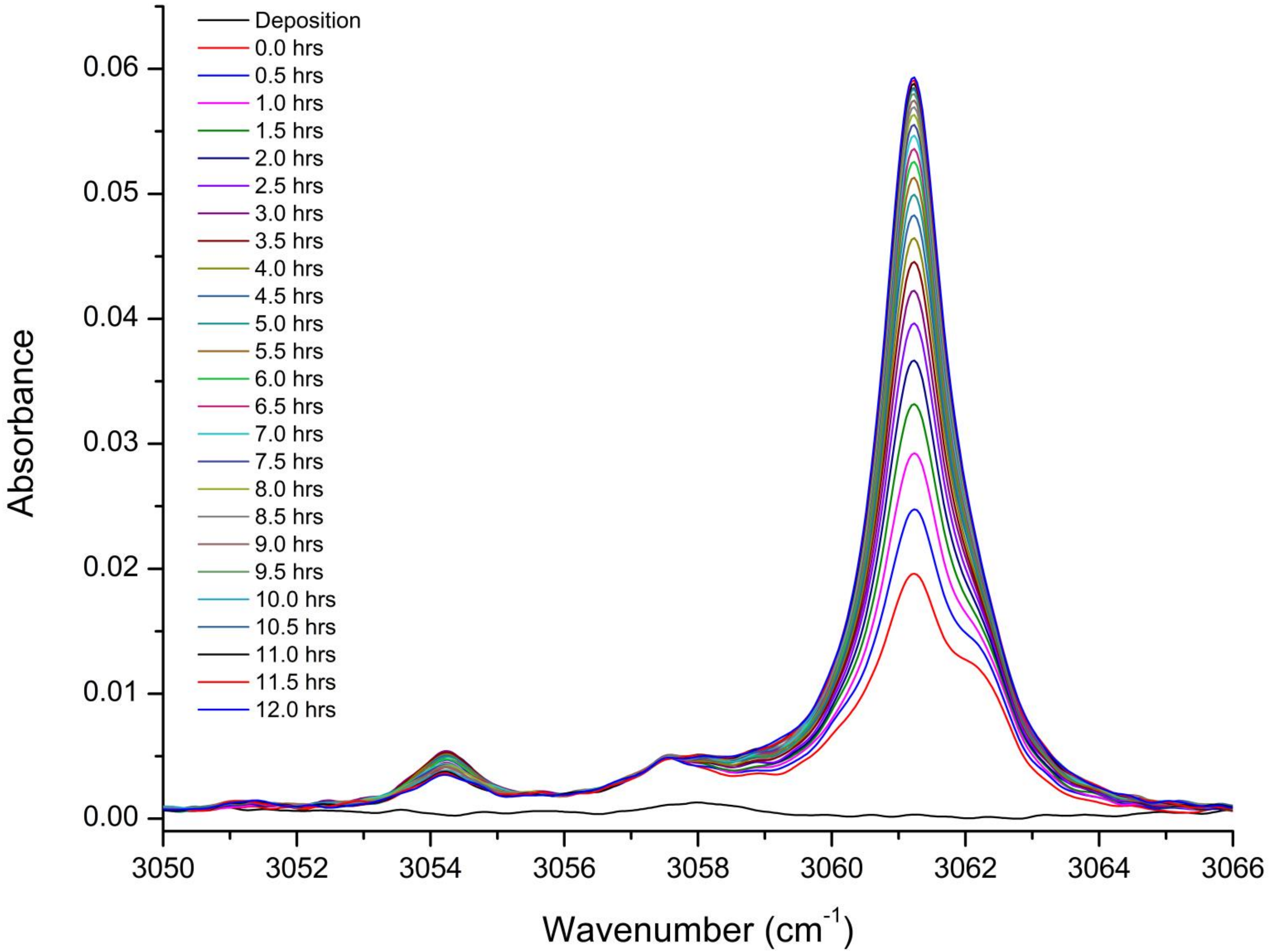
Hydrogen Addition to Propene

$$\frac{i-\text{propyl}}{n-\text{propyl}} \approx \frac{9}{1}$$



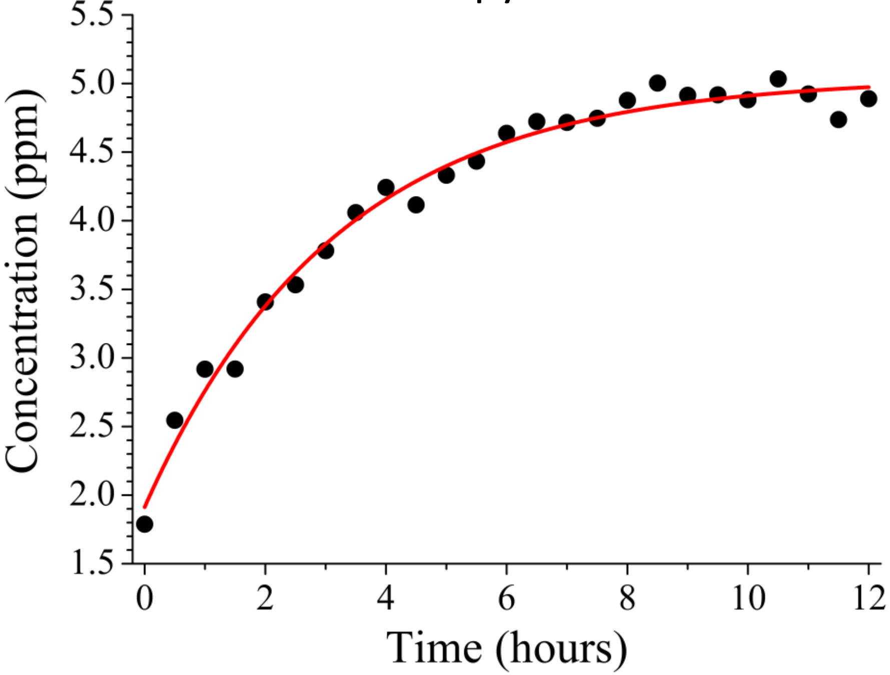


Hydrogen Addition to Propene – Kinetics

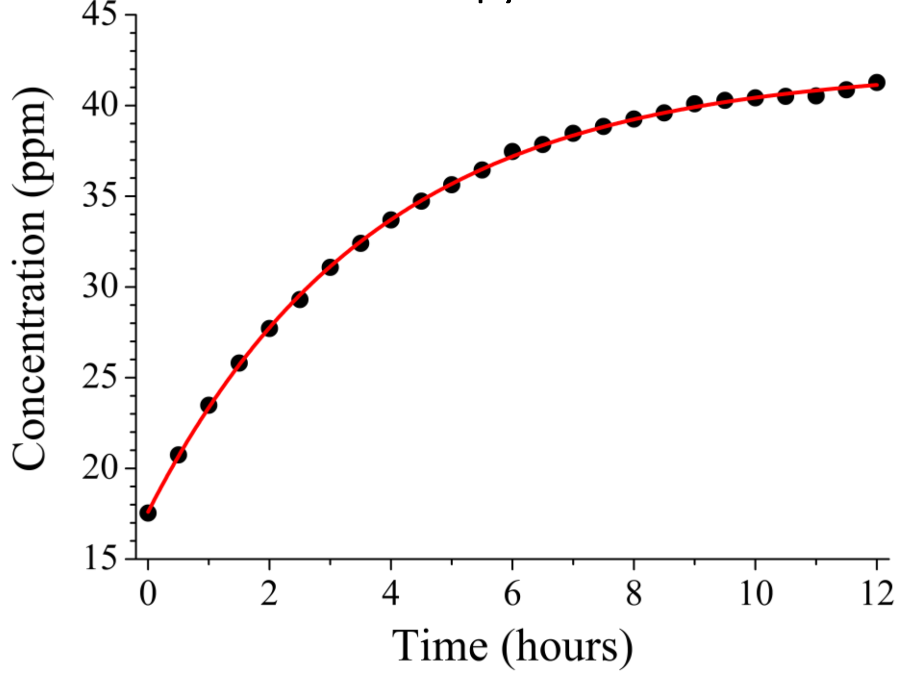


Hydrogen Addition to Propene – Kinetics

n-Propyl

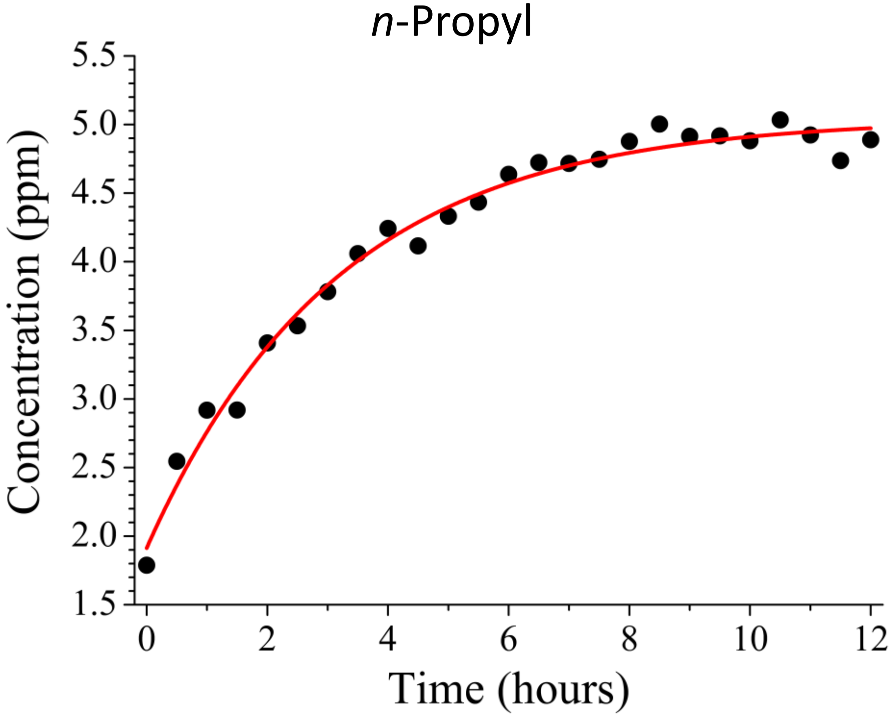


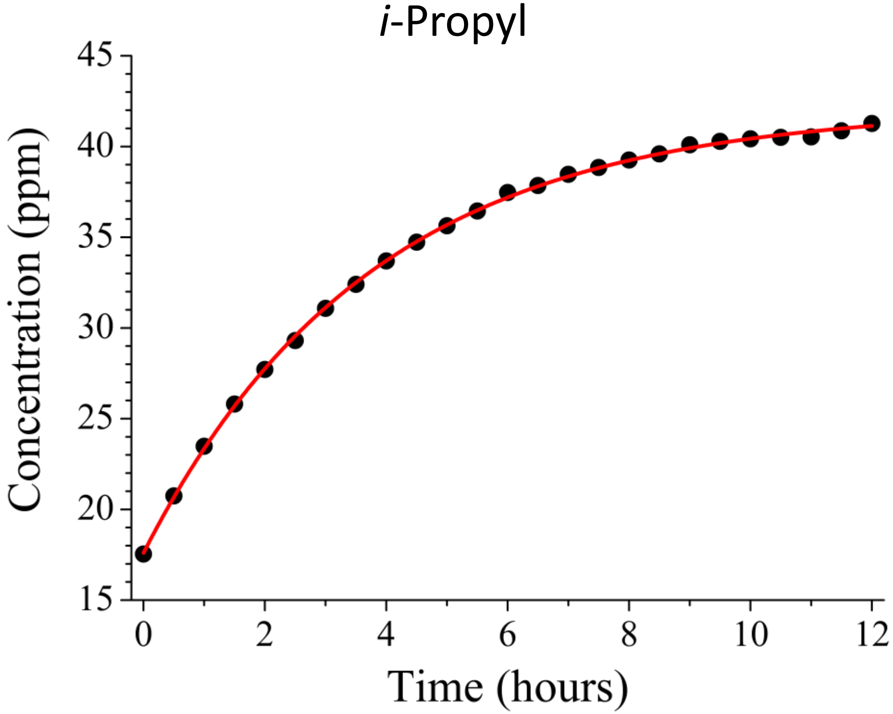
i-Propyl



Hydrogen Addition to Propene – Kinetics

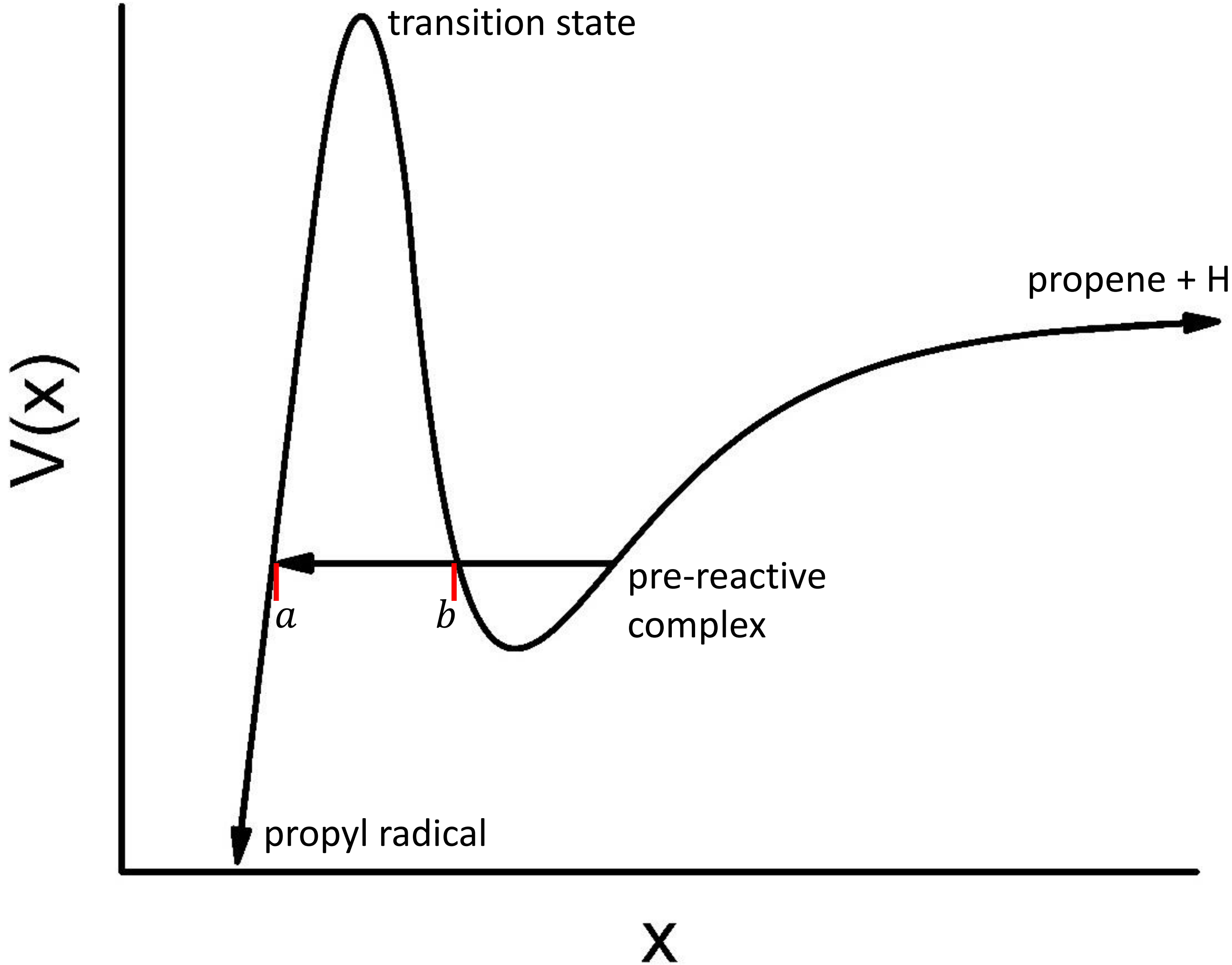
$$\frac{i-\text{propyl}}{n-\text{propyl}} \approx \frac{8.4}{1}$$



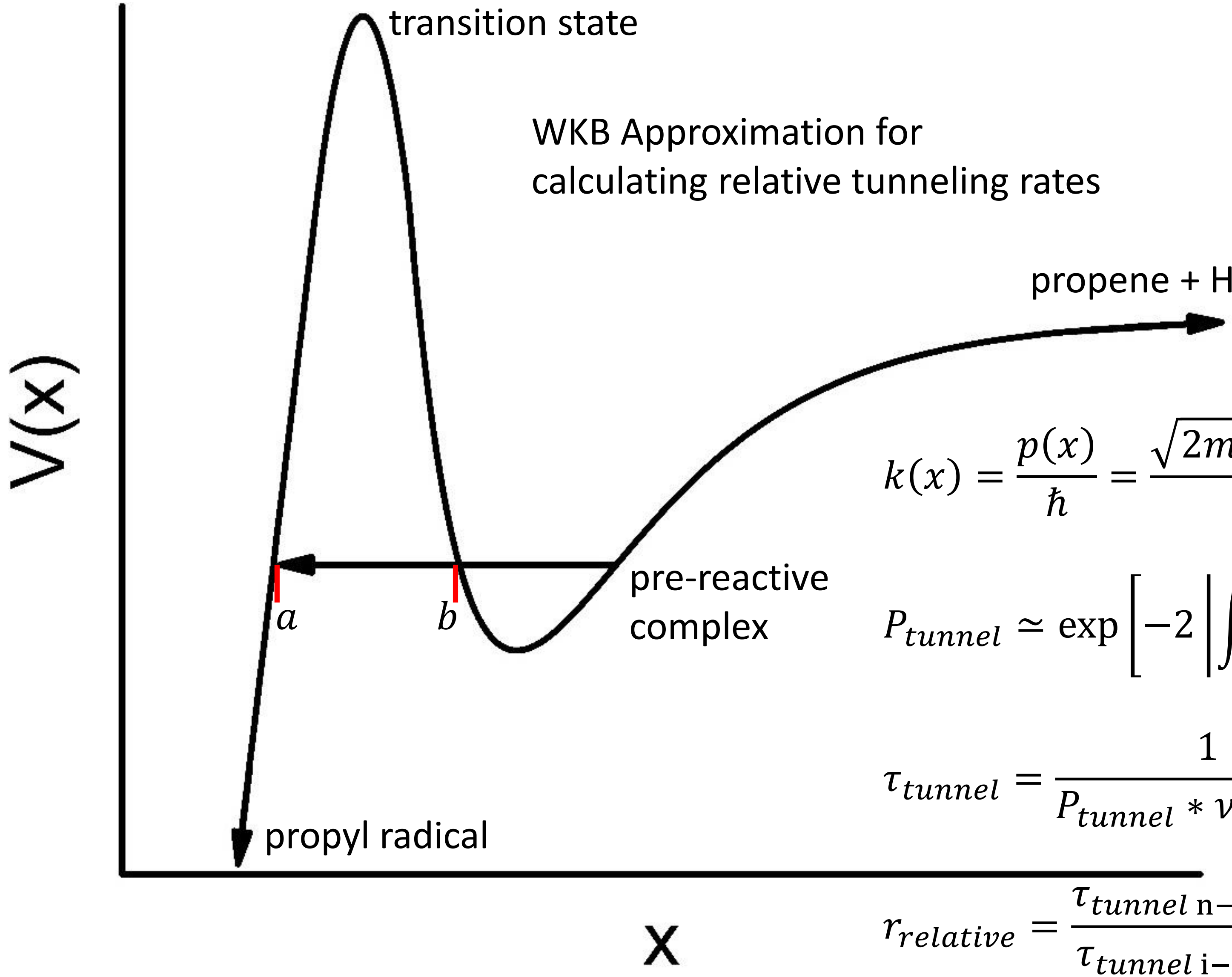


$k \approx (4-5)\times 10^{-3}\ \text{min}^{-1}$ $\tau \approx 200 - 250\ \text{min}$

Relative Addition Rate Calculations



Relative Addition Rate Calculations



WKB Approximation for
calculating relative tunneling rates

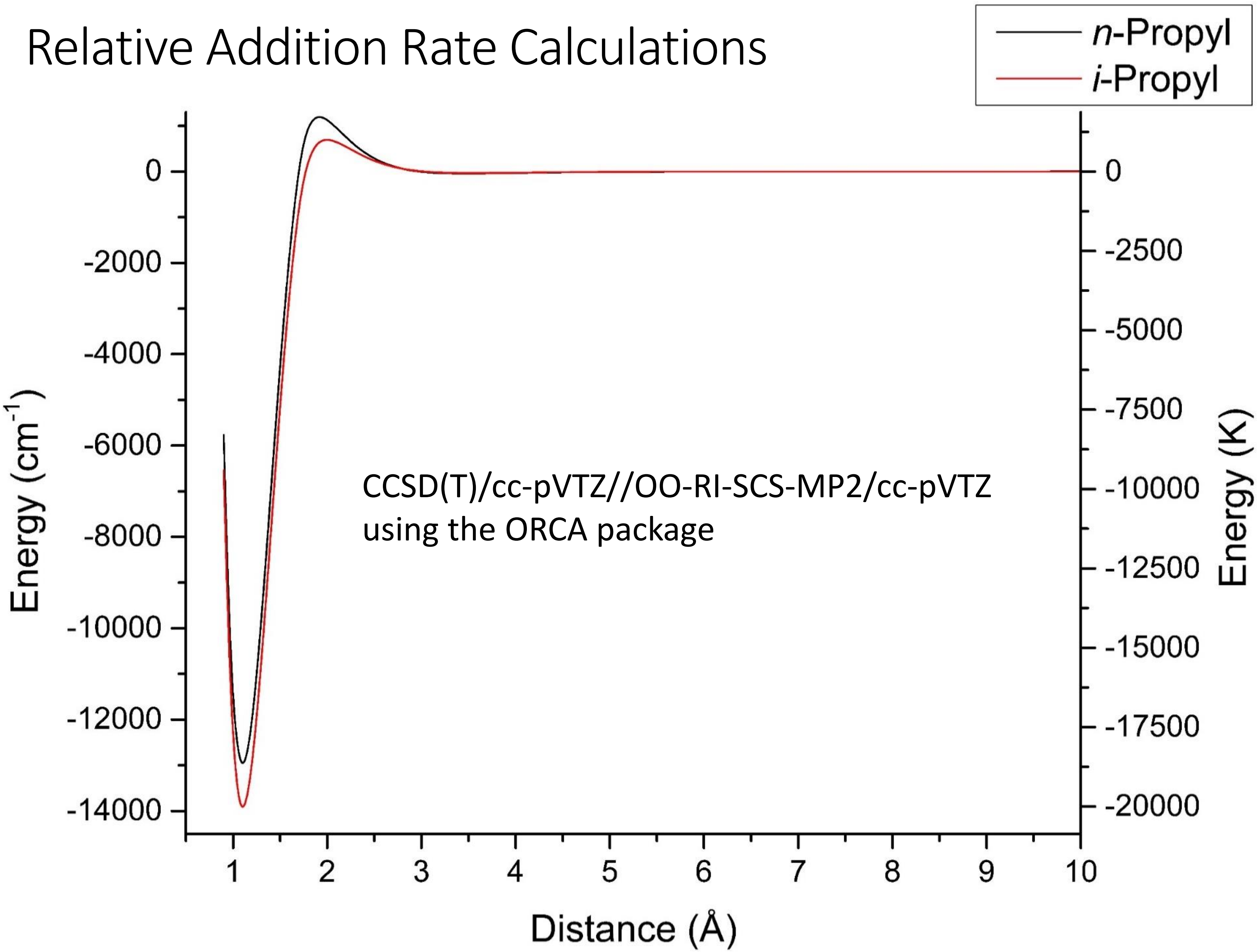
$$k(x) = \frac{p(x)}{\hbar} = \frac{\sqrt{2m[E - V(x)]}}{\hbar}$$

$$P_{tunnel} \simeq \exp\left[-2\left|\int_a^b k(x)\,dx\right|\right]$$

$$\tau_{tunnel} = \frac{1}{P_{tunnel} * \nu_{complex}}$$

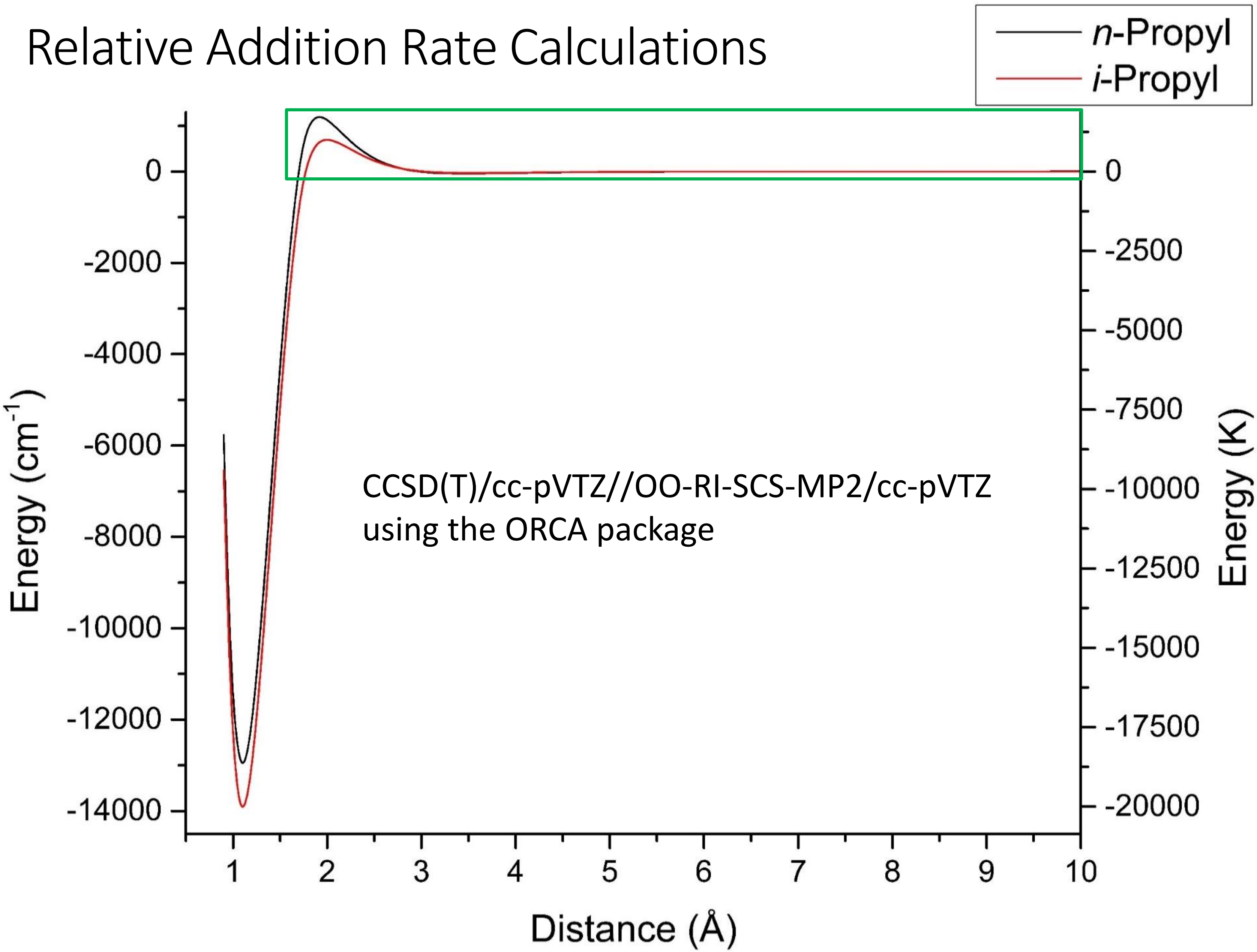
$$r_{relative} = \frac{\tau_{tunnel\ \mathrm{n}-Propyl}}{\tau_{tunnel\ \mathrm{i}-Propyl}}$$

Relative Addition Rate Calculations



CCSD(T)/cc-pVTZ//OO-RI-SCS-MP2/cc-pVTZ
using the ORCA package

Relative Addition Rate Calculations



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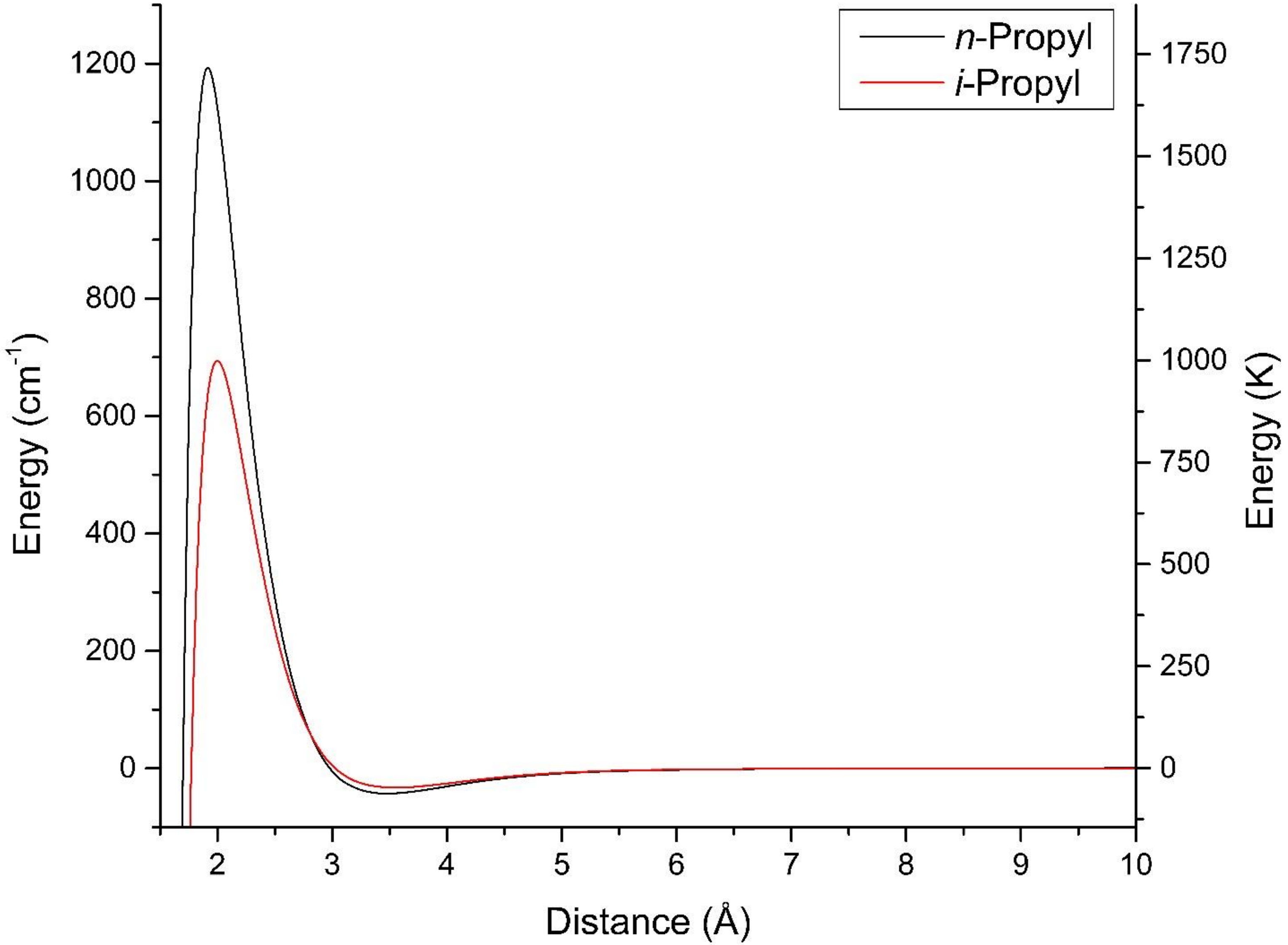
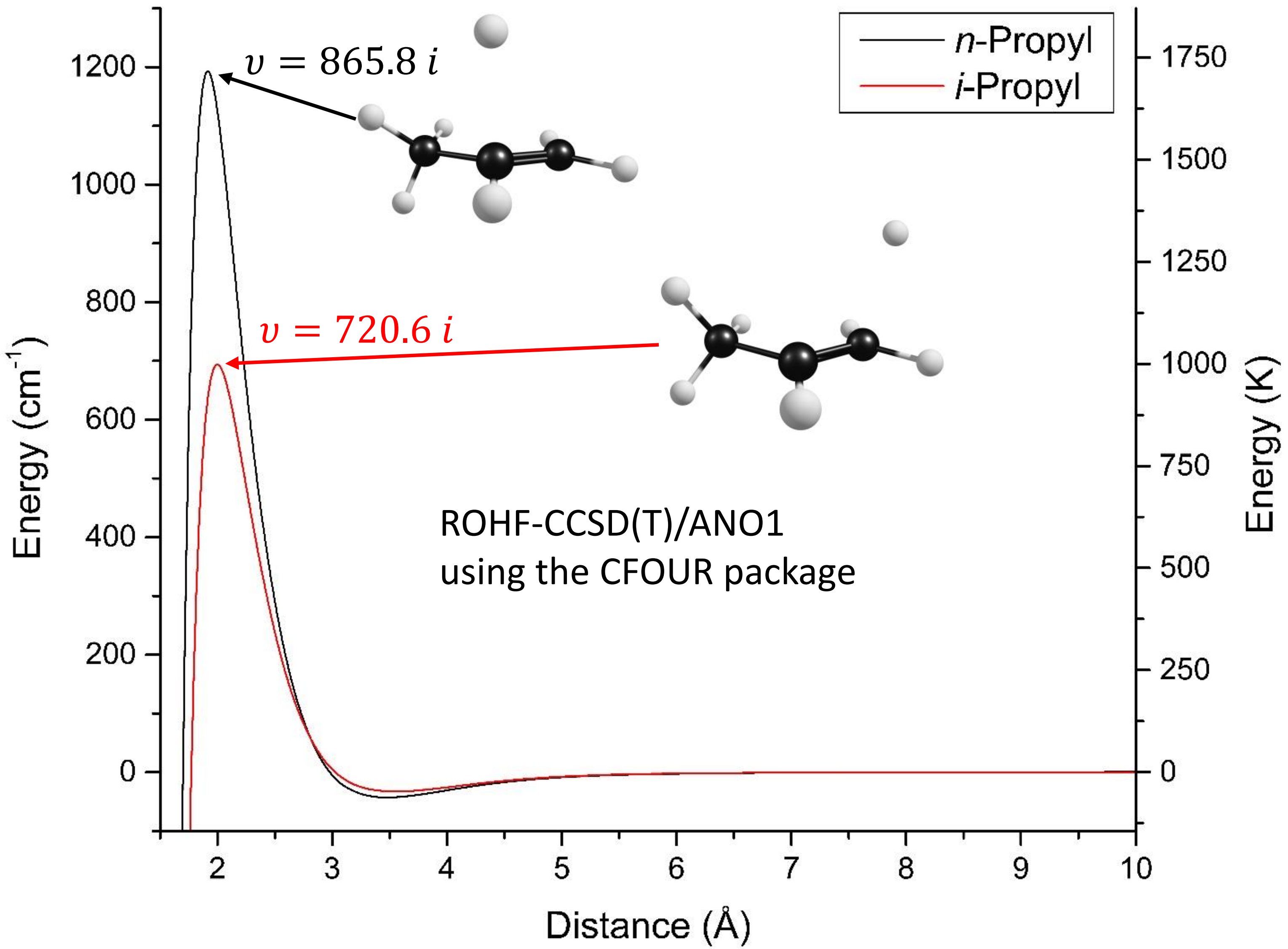
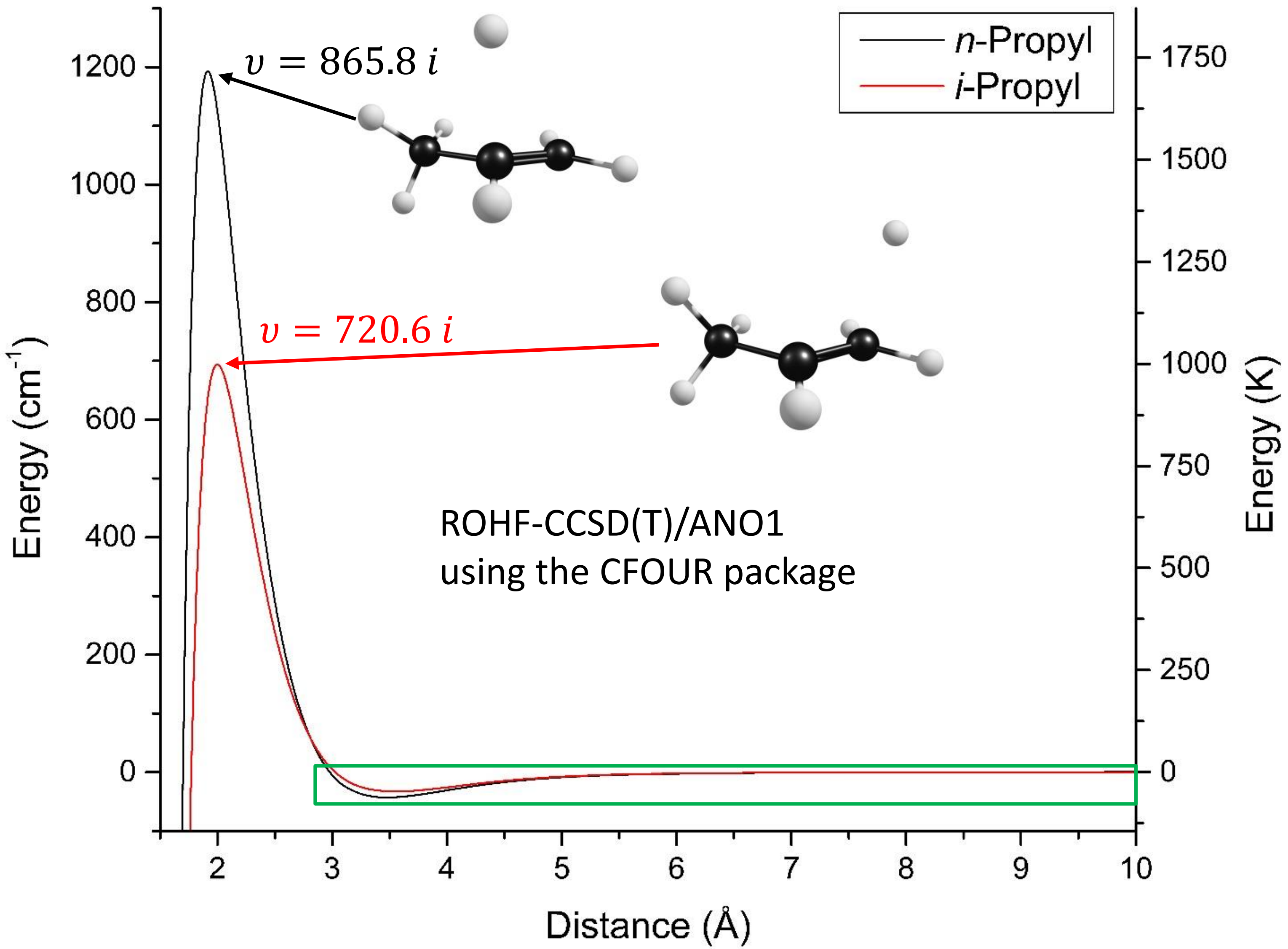
Relative Addition Rate Calculations



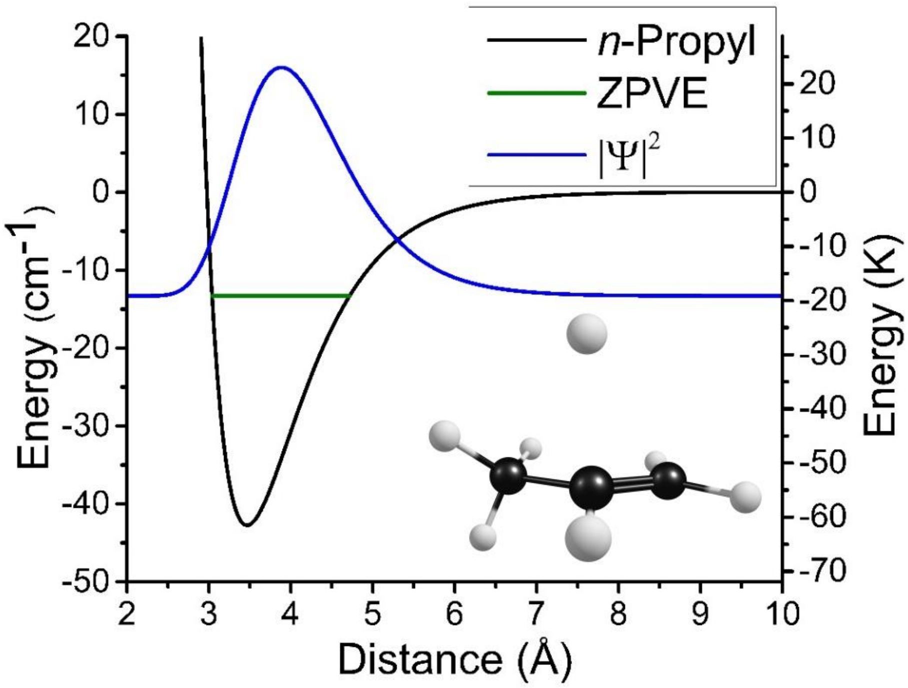
Relative Addition Rate Calculations

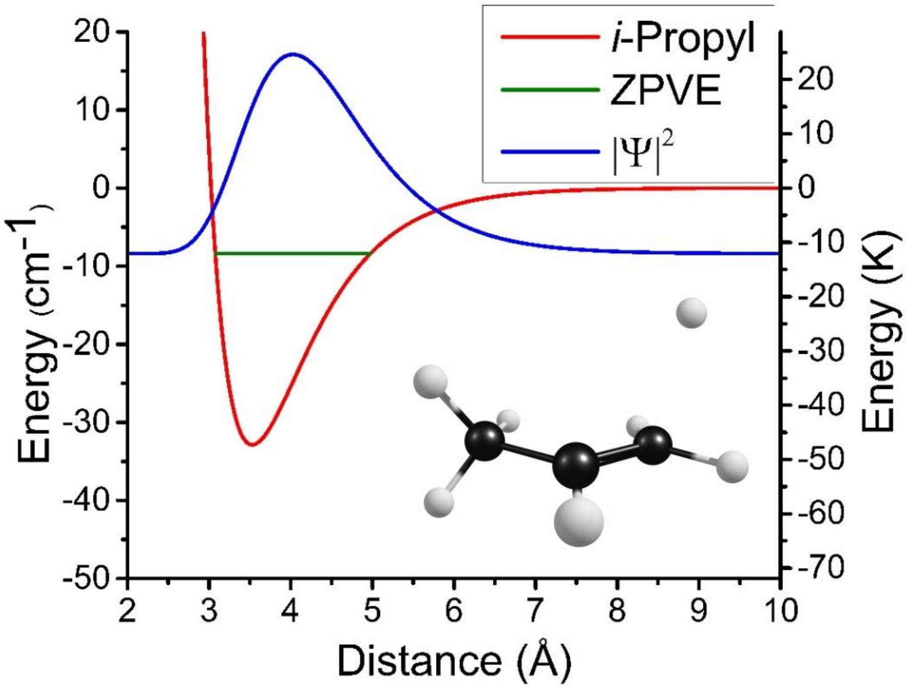


Relative Addition Rate Calculations



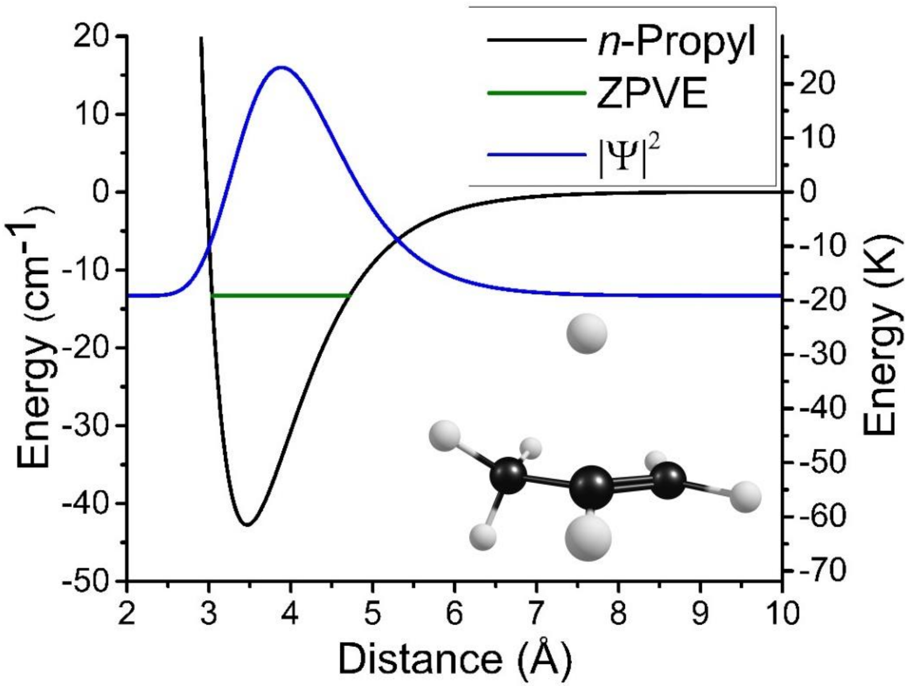
Relative Addition Rate Calculations

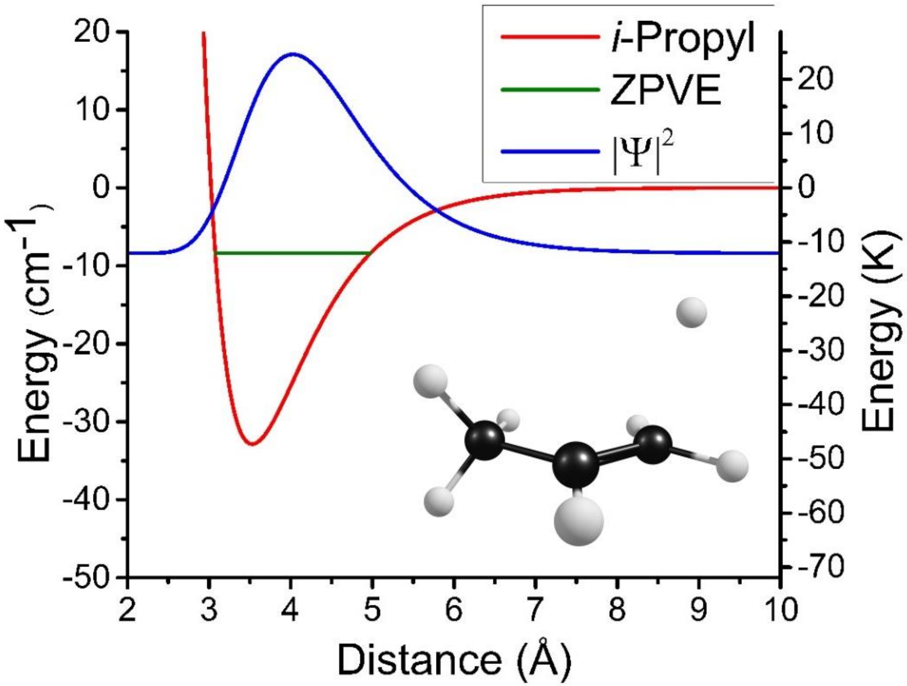




Relative Addition Rate Calculations

$$\text{Experimental}\left(\frac{i-\text{propyl}}{n-\text{propyl}}\right) \approx \frac{8\ or\ 9}{1} \qquad \text{Theoretical}\left(\frac{i-\text{propyl}}{n-\text{propyl}}\right) \approx \frac{17}{1}$$





Conclusions

- We measured the hydrogen addition to propene tunneling rates in a *p*-H_2 matrix
- We used the WKB approximation to calculate theoretical predictions for the relative tunneling rates
- Theoretical predictions for the relative tunneling rates mostly agree with experimental measurements

Funding/Support

U.S. DEPARTMENT OF ENERGY

Office of International Education
UNIVERSITY OF GEORGIA

Graduate School
UNIVERSITY OF GEORGIA

科技部
Ministry of Science and Technology

國立交通大學
National Chiao Tung University

MINISTRY OF EDUCATION 教育部

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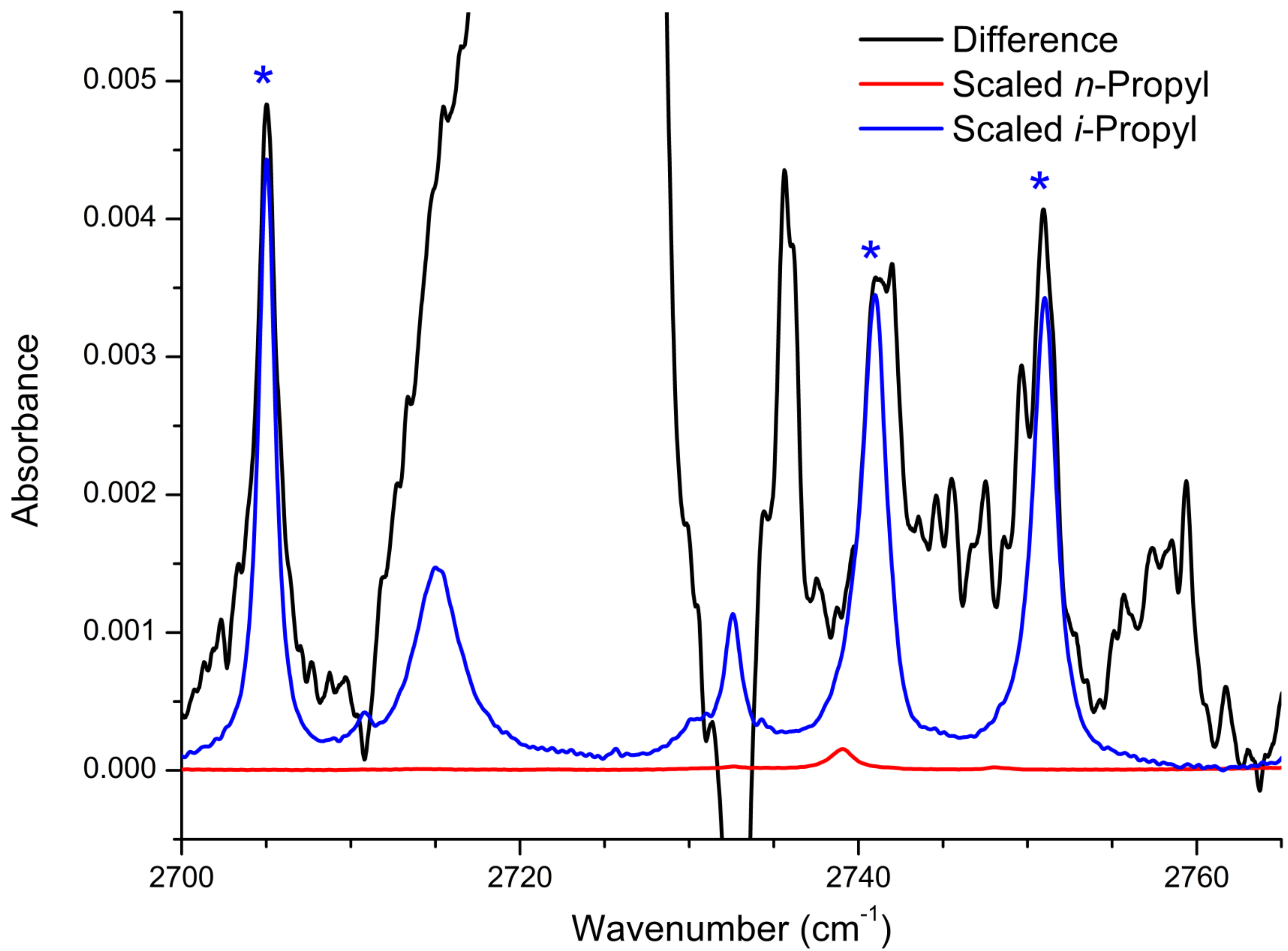
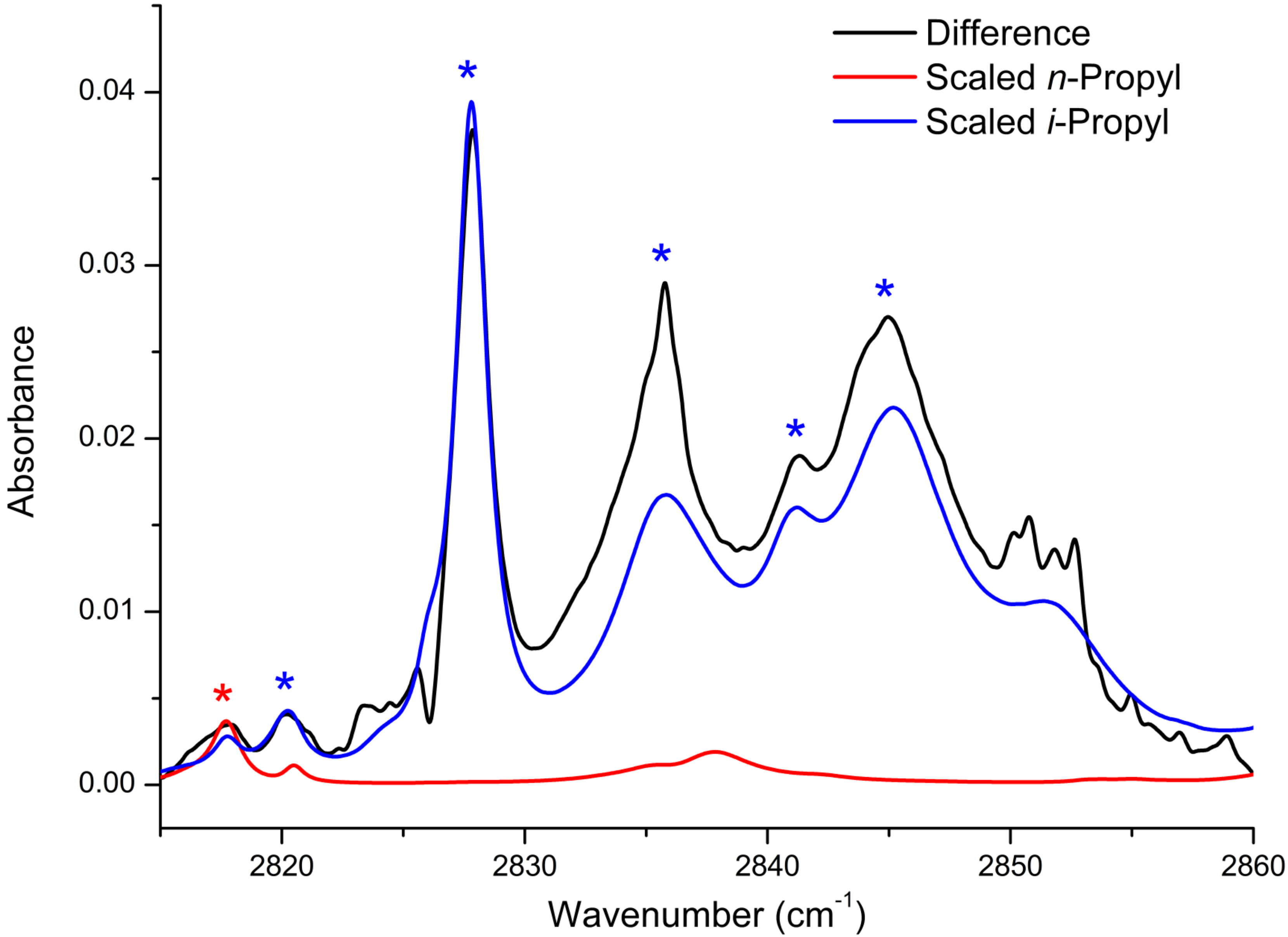
The rest of the Douberly group

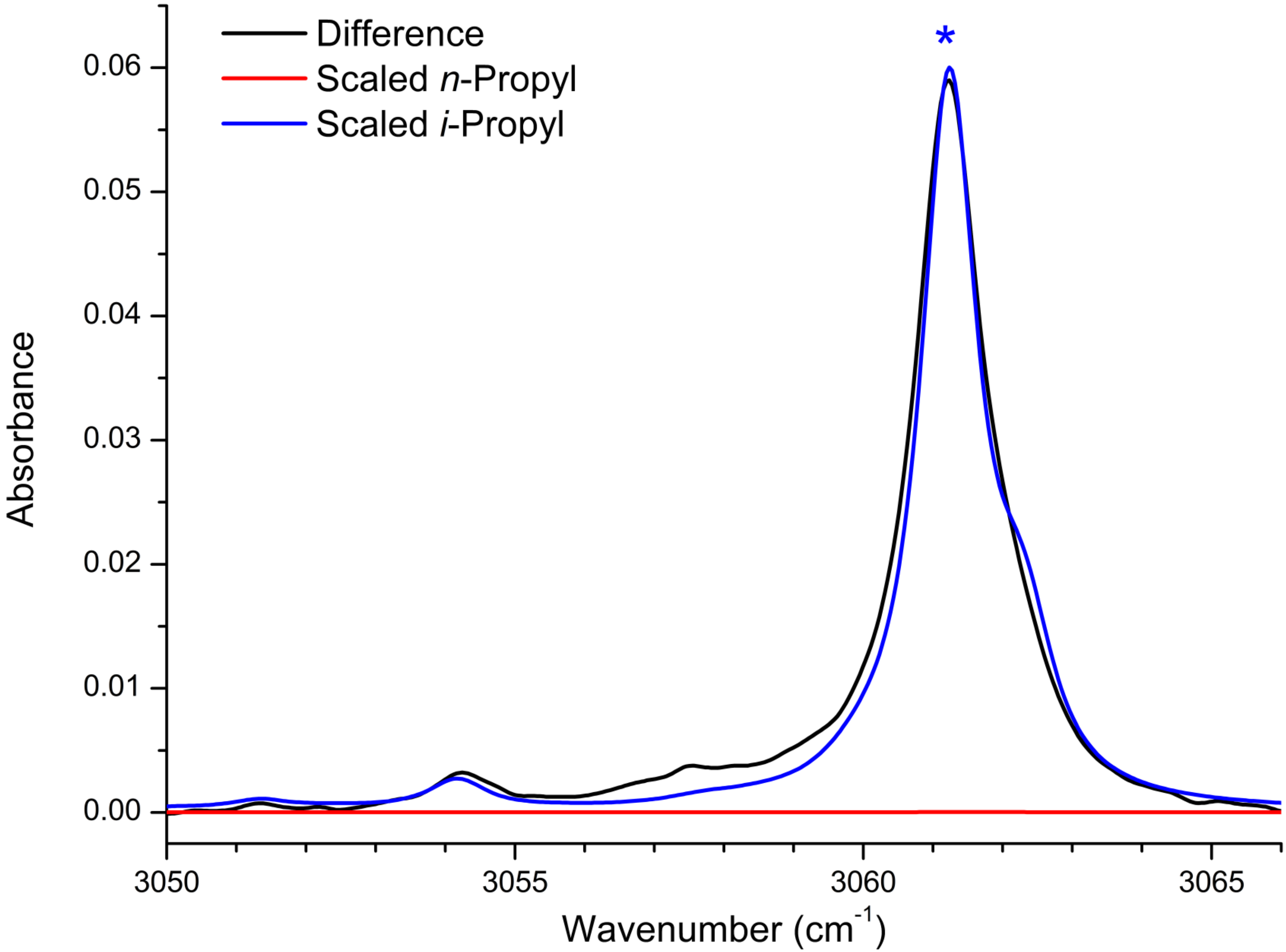
Thank you for your attention



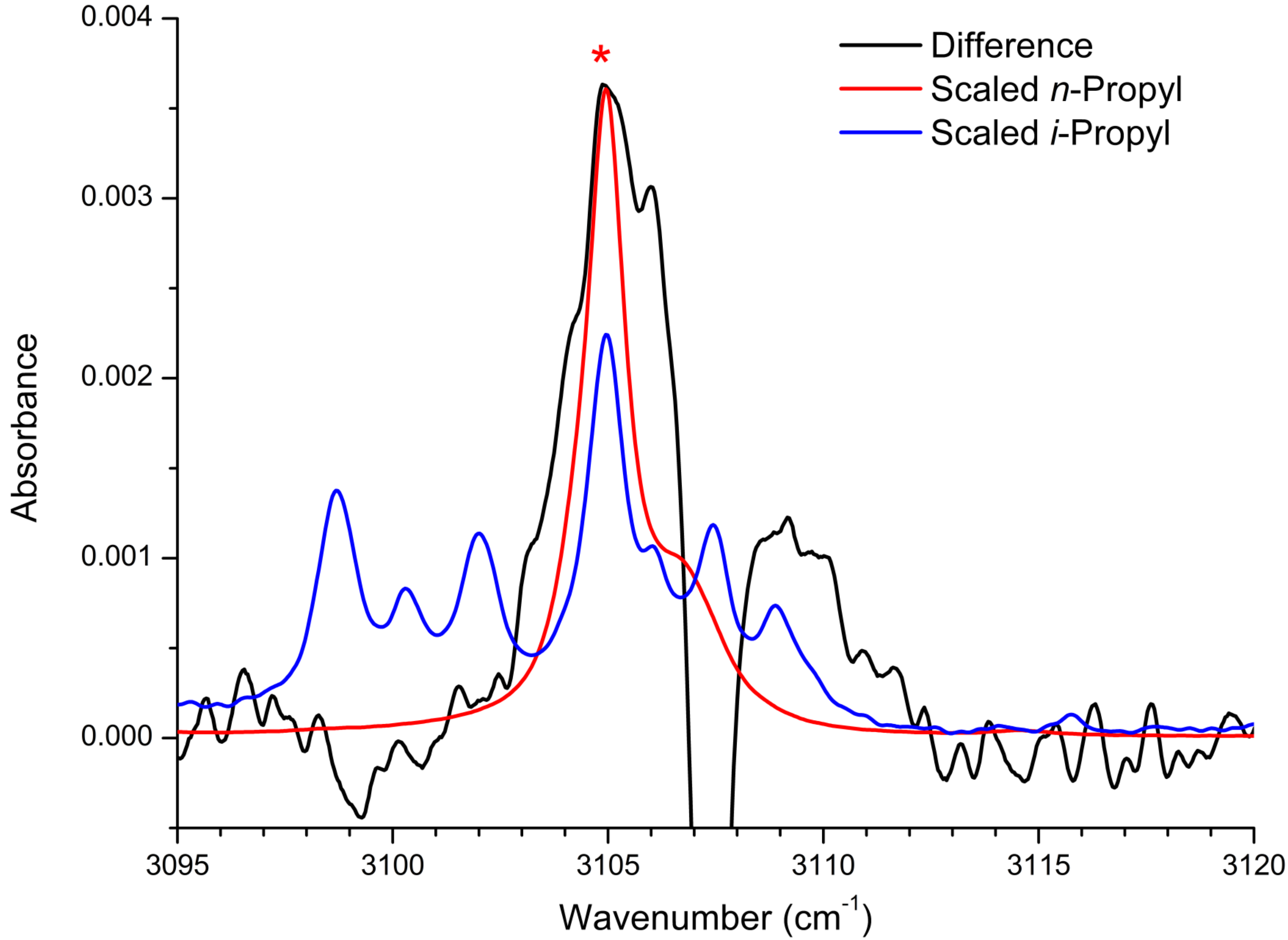
Difference
Scaled n-Propyl
Scaled i-Propyl
*
*
*
0.005
0.004
0.003
0.002
0.001
0.000
Absorbance
2700
2720
2740
2760
Wavenumber (cm-1)



Difference
Scaled *n*-Propyl
Scaled *i*-Propyl
Absorbance
0.00
0.01
0.02
0.03
0.04
2820
2830
2840
2850
2860
Wavenumber (cm^{-1})

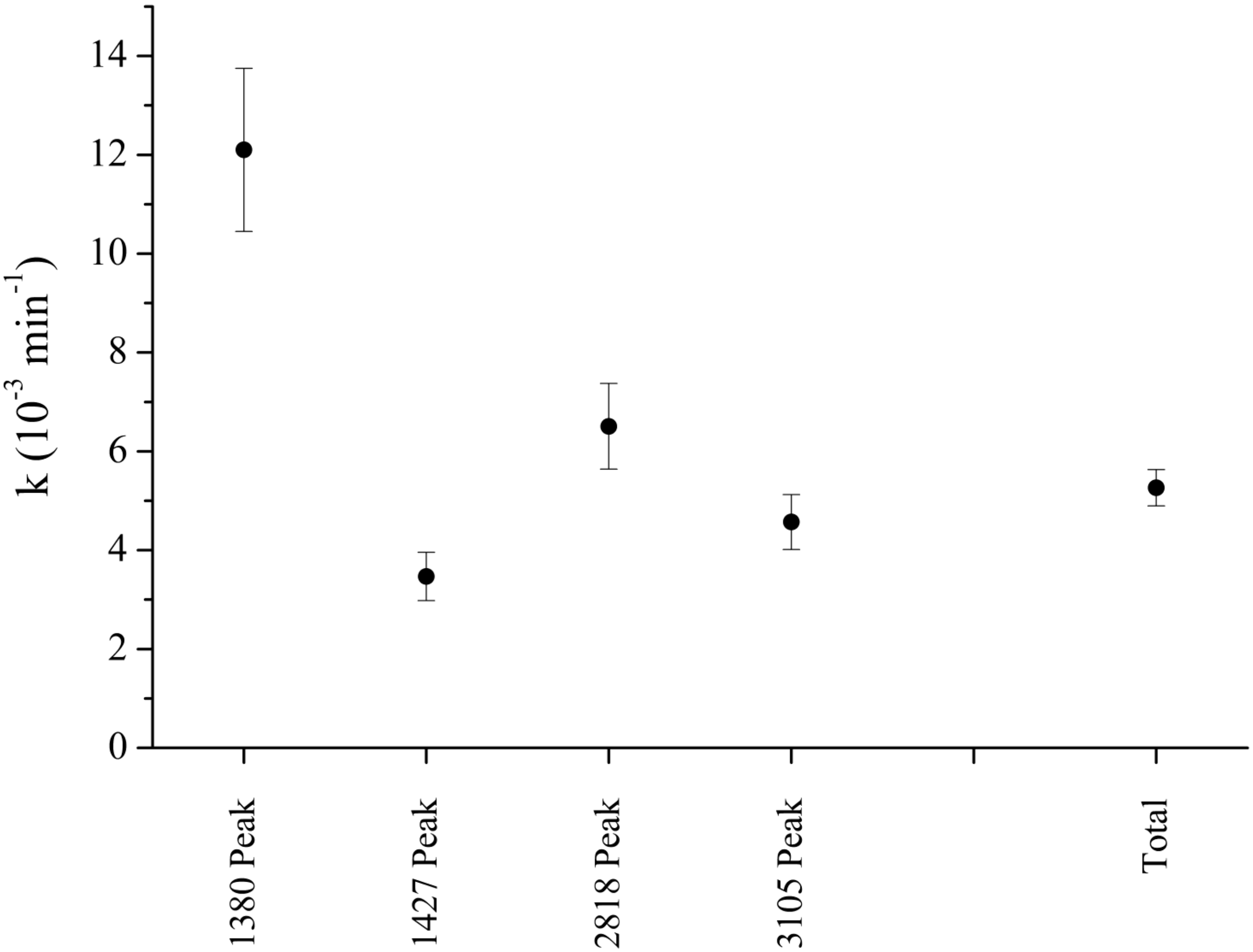


Difference
Scaled n-Propyl
Scaled i-Propyl
*
0.06
0.05
0.04
0.03
0.02
0.01
0.00
Absorbance
3050
3055
3060
3065
Wavenumber (cm-1)

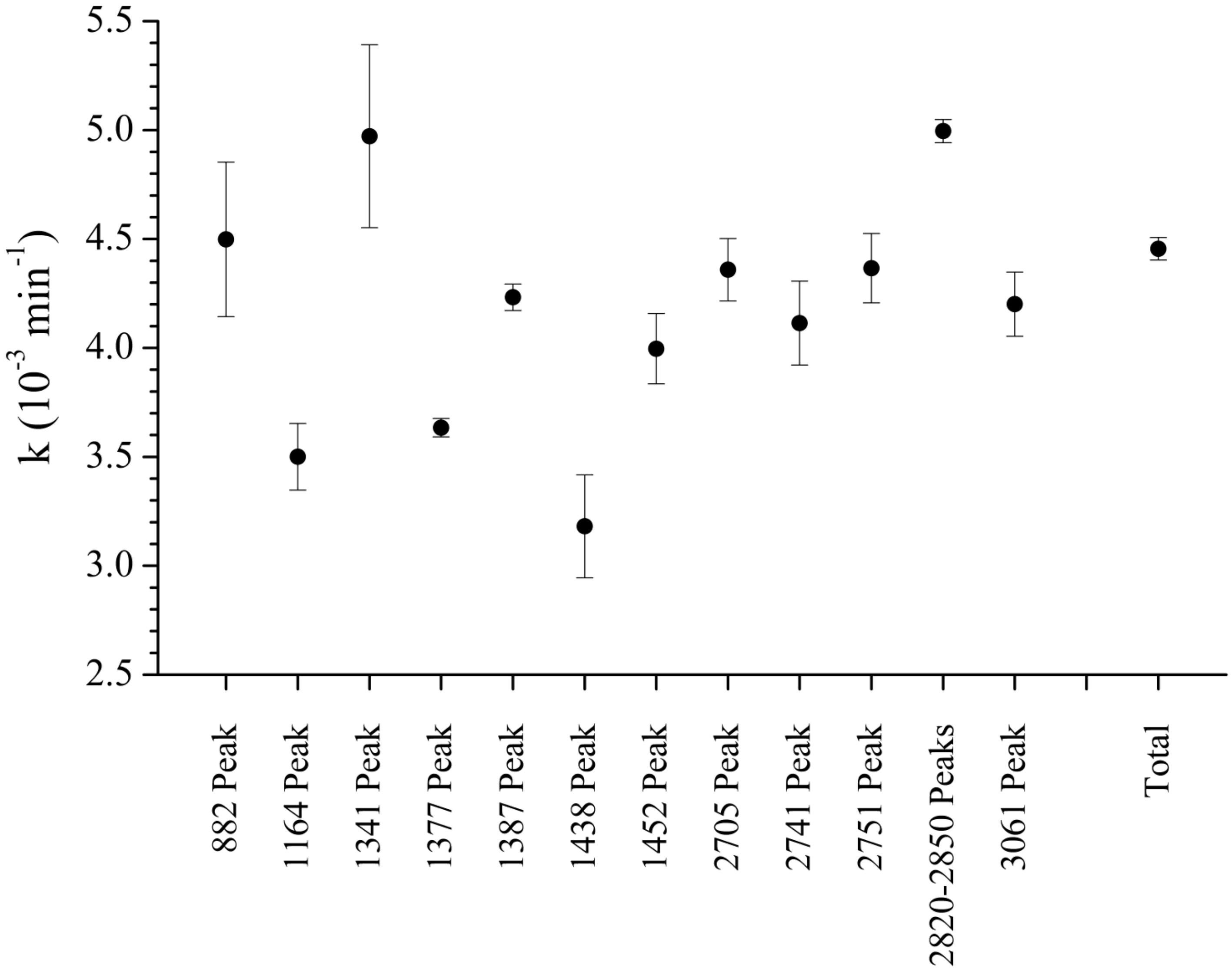


Difference
Scaled *n*-Propyl
Scaled *i*-Propyl
*
Absorbance
0.004
0.003
0.002
0.001
0.000
3095
3100
3105
3110
3115
3120
Wavenumber (cm^{-1})

n-Propyl Growth Rate Constants



i-Propyl Growth Rate Constants



Kinetics Fitting Parameters

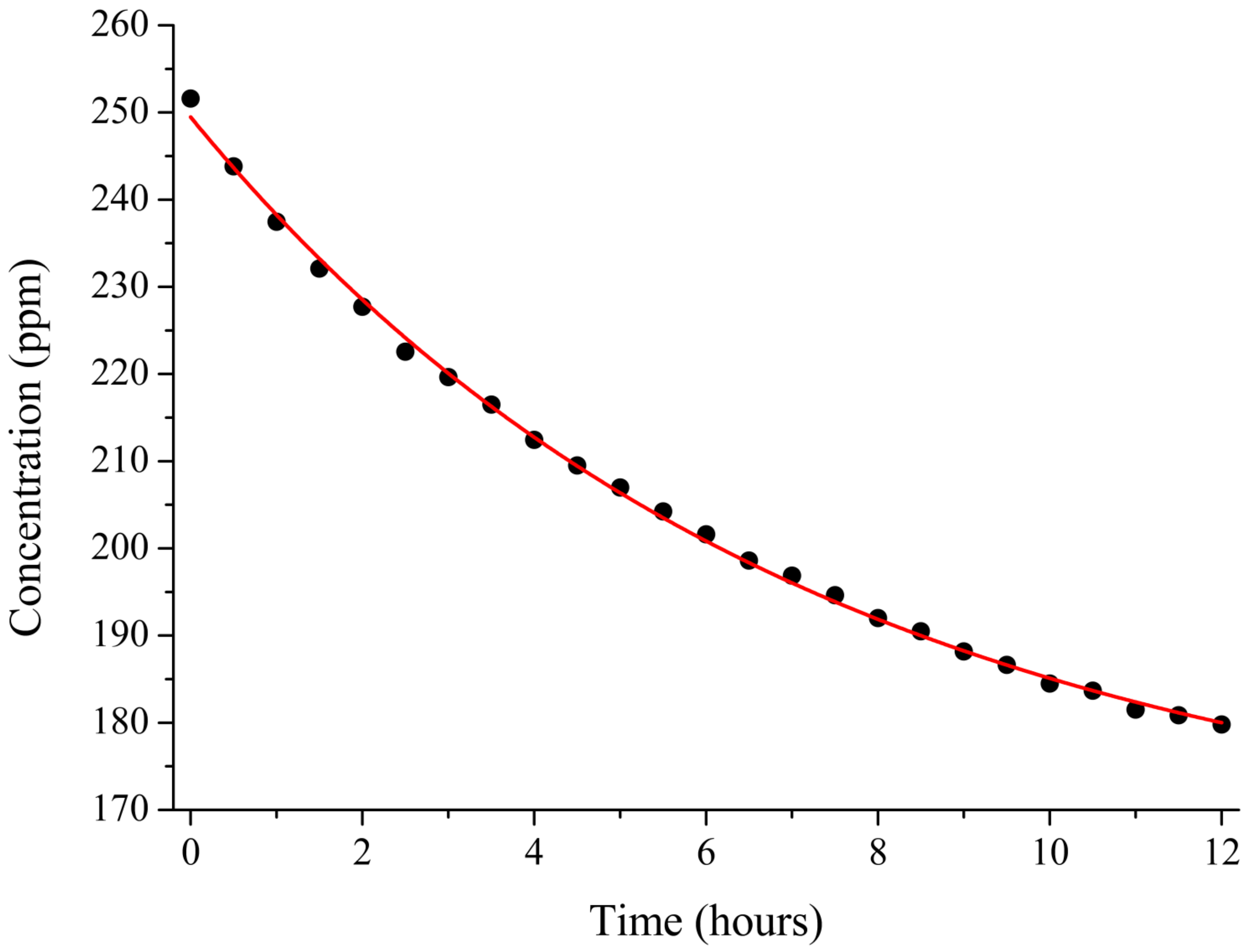
	***n*-Propyl**	***i*-Propyl**
$[X]_0$	(1.91 ± 0.10) ppm	(17.60 ± 0.13) ppm
$[X]_\infty$	(5.044 ± 0.058) ppm	(42.124 ± 0.085) ppm
A	(3.131 ± 0.082) ppm	(24.521 ± 0.098) ppm
k	(5.26 ± 0.37) × 10^{-3} min^{-1}	(4.455 ± 0.052) × 10^{-3} min^{-1}

Growth fitting function: $[X] = [X]_0 + A[1 - \exp(-kt)]$

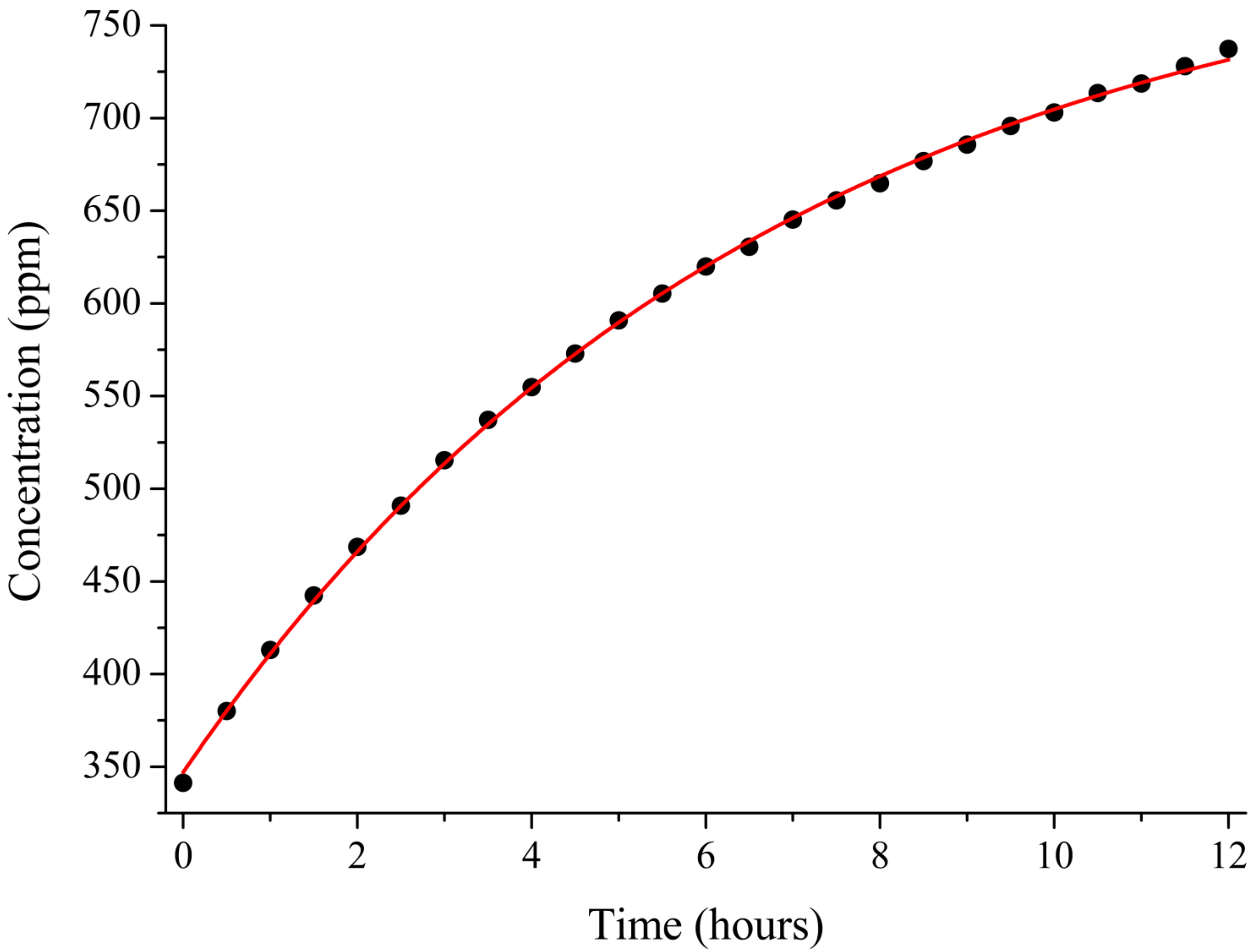
Decay fitting function: $[X] = [X]_\infty + A\exp(-kt)$

	Propene	**HCl**	**Propane**
$[X]_0$	(249.5 ± 2.0) ppm	(347.0 ± 5.8) ppm	(11.72 ± 0.65) ppm
$[X]_\infty$	(164.4 ± 1.5) ppm	(808.3 ± 4.4) ppm	(47.38 ± 0.49) ppm
A	(85.1 ± 1.3) ppm	(461.3 ± 3.7) ppm	(35.66 ± 0.42) ppm
k	(2.354 ± 0.087) × 10^{-3} min^{-1}	(2.490 ± 0.051) × 10^{-3} min^{-1}	(2.320 ± 0.067) × 10^{-3} min^{-1}

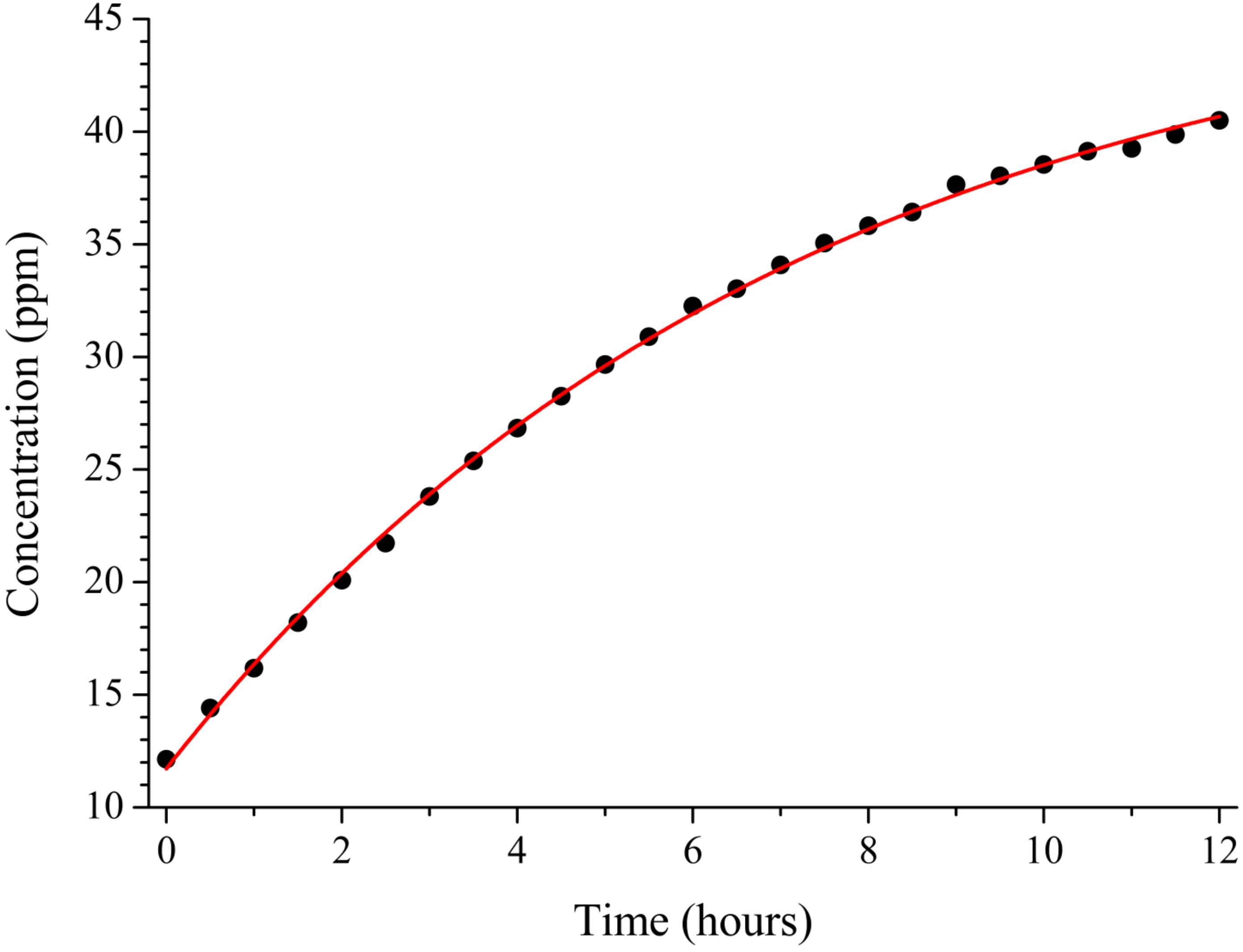
Propene Decay Kinetics



HCl Growth Kinetics



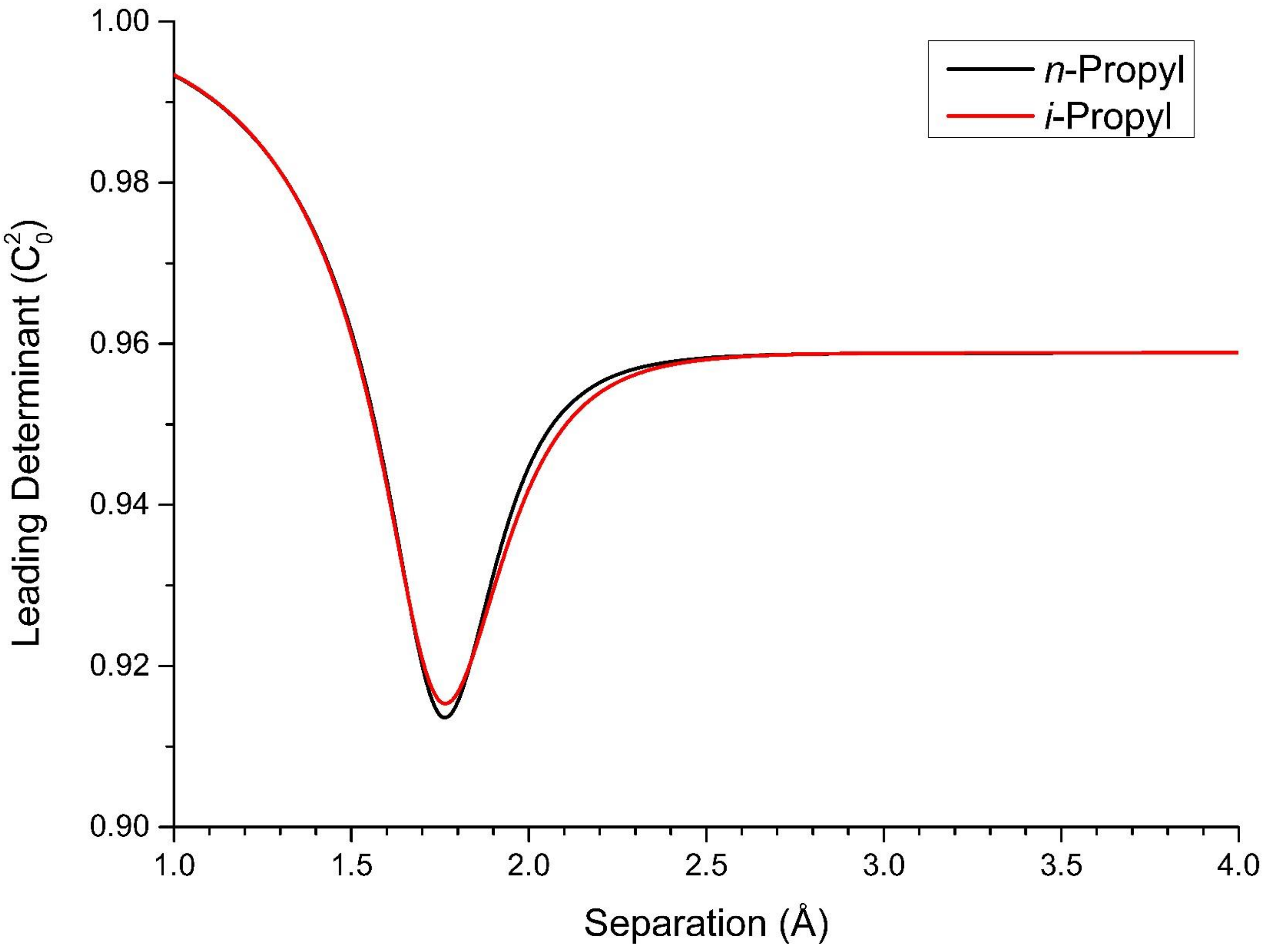
Propane Growth Kinetics



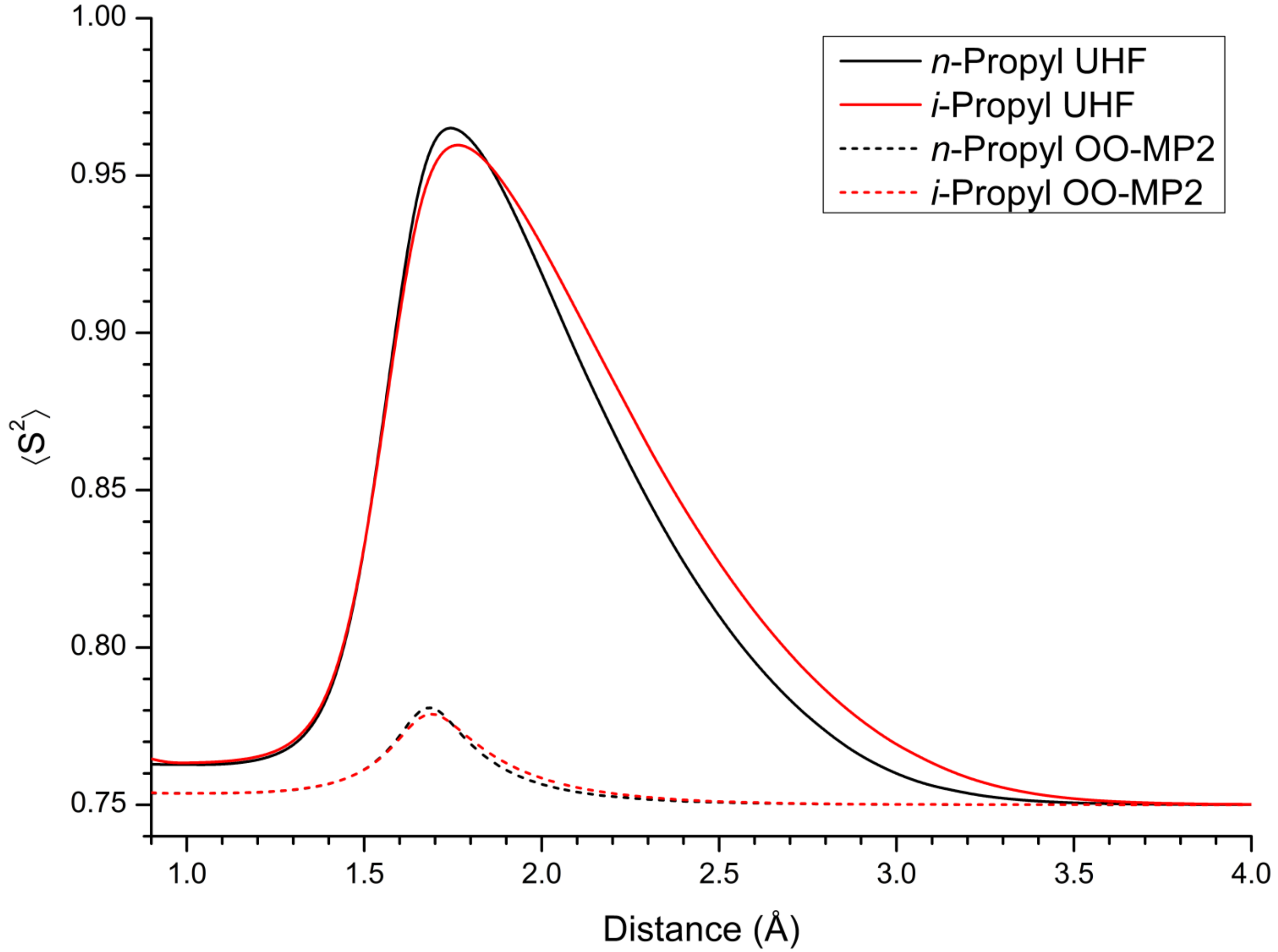
Potential Energy Scan Results

	***n*-Propyl**	***i*-Propyl**
Radical Bond Distance	1.10 Å	1.10 Å
Radical Energy	-12,949.8 cm^{-1}	-13,905.1 cm^{-1}
Transition State Bond Distance	1.92 Å	2.00 Å
Transition State Energy	1193.4 cm^{-1}	693.5 cm^{-1}
Transition State Frequency	865.8 *i* cm^{-1}	720.6 *i* cm^{-1}
Complex Bond Distance	3.46 Å	3.53 Å
Complex Energy	-42.9 cm^{-1}	-32.9 cm^{-1}
Complex ZPVE	-13.0 cm^{-1}	-8.4 cm^{-1}
Complex Frequency	2.32 THz	1.96 THz
Tunneling Probability	1.88 x 10^{-6}	3.79 x 10^{-5}
Tunneling Time Constant	229.7 ns	13.5 ns

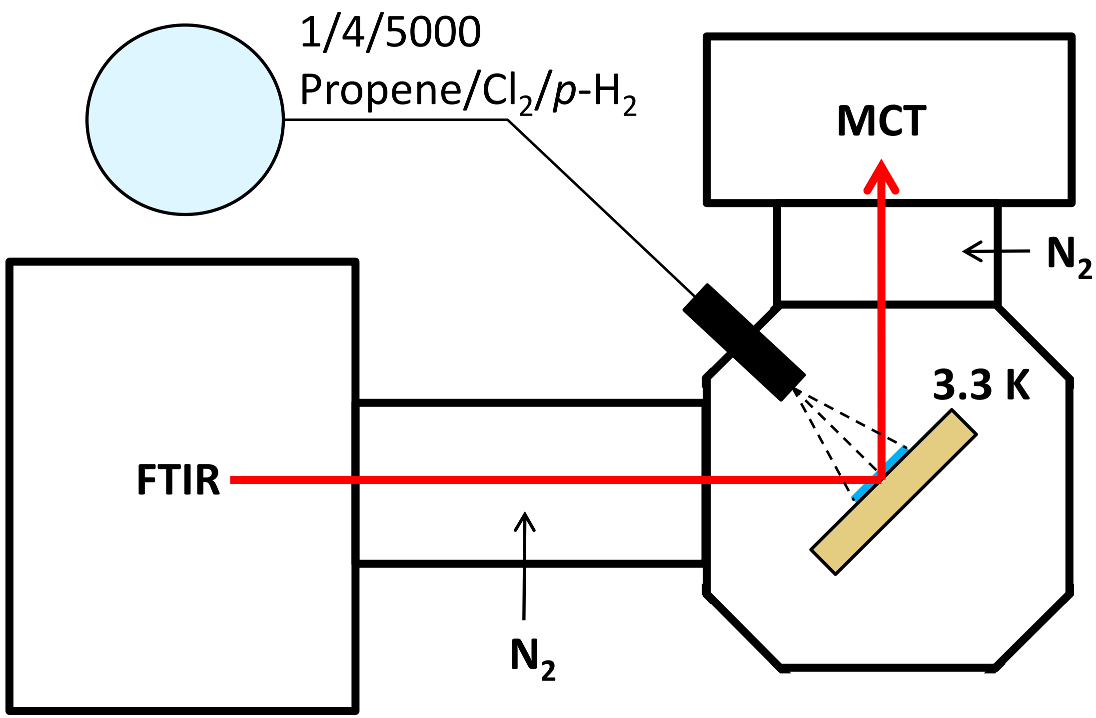
Potential Energy Scan Multireference Character



Potential Energy Scan Spin Contamination



p-H_2 Matrix Isolation Experimental Details



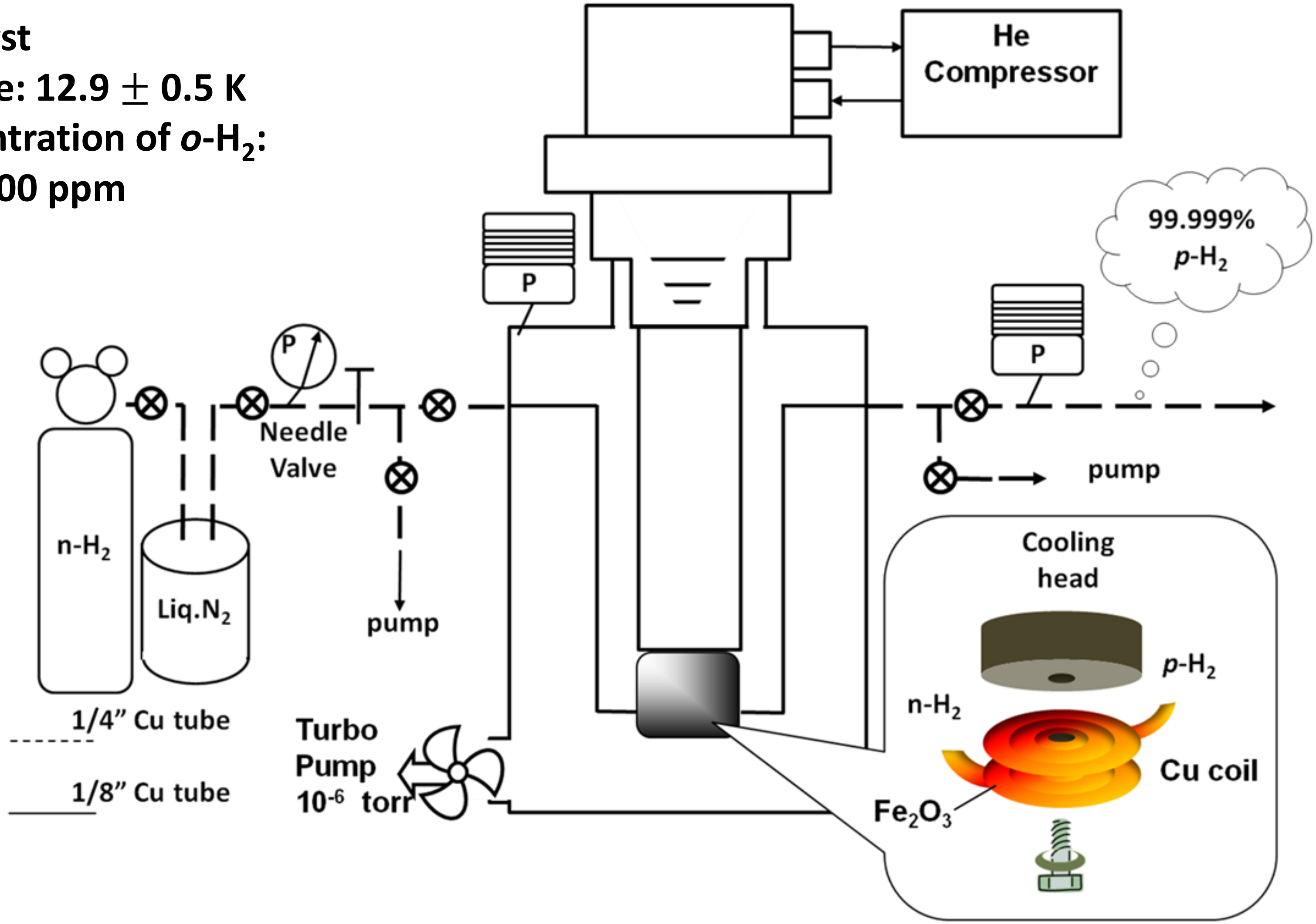
Bruker Vertex 80v FTIR
KBr Beamsplitter
Range: 4000 – 400 cm^{-1}
Resolution: 0.25 cm^{-1}
200 scans

L-N_2 cooled MCT detector

Matrix mirror: 1 in diameter gold coated copper plate
Deposition time: 5 hr
Gas flow rate: ~4 sccm (10 - 13 mmol/hr)

Production of p-H_2 Details

Fe_2O_3 catalyst
Temperature: 12.9 $\pm$ 0.5 K
Final concentration of o-H_2:
$\sim$400 – 600 ppm

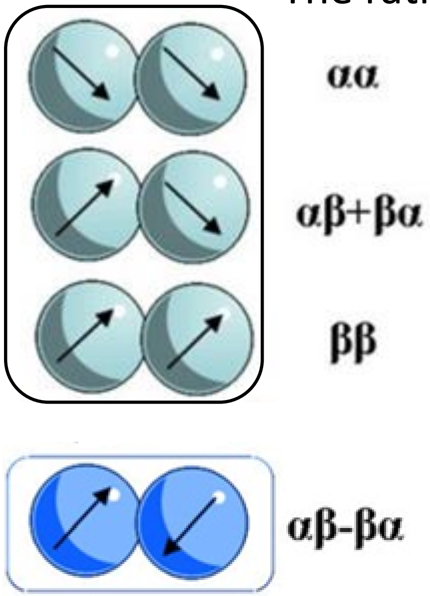


Basic quantum physics of solid p-H_2

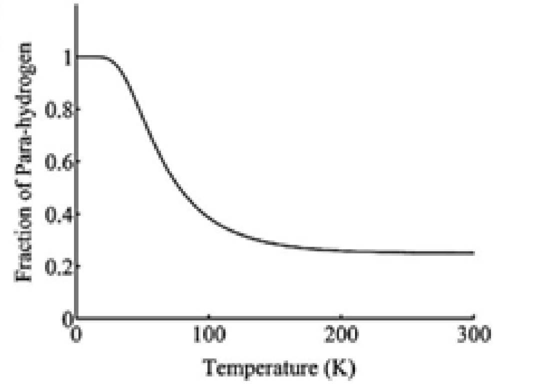
Fermion (^{1}H Nuclear spin I = $\frac{1}{2}$) ➡ ψ_{total}: anti-symmetric

$$\psi_{total} = \psi_e\, \psi_v\, \psi_r\, \psi_n$$

ψ_r	ψ_n
Odd J Anti-symmetric Ground State: $J = 1$	Symmetric ***ortho*-H₂**
Even J Symmetric Ground State: $J = 0$	Anti-symmetric ***para*-H₂**



The ratio of o-H_2:p-H_2 is 3:1 @ R.T. and 0:1 @ 0 K

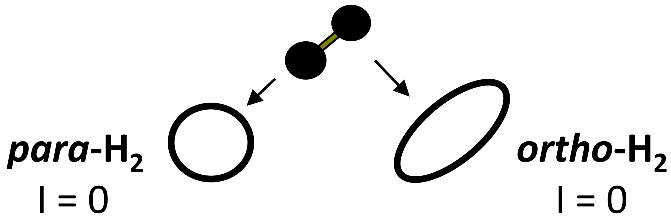


1. Equilibrium fraction of para-hydrogen as a function of temperature.

Benefits of p-H_2 as Matrix Host

No dipole moment

J = 0 rotational state is occupied
spherically symmetric charge distribution



Ar and Ne have fcc and hcp crystal structures

p-H_2 only has an hcp crystal structure

The host-guest interaction in p-H_2 is weaker than in rare gas matrices

	p-H_2	Ne	Ar
Lattice Constant (Å)	3.78	4.47	5.31
Zero-Point Amplitude Motion	18%	9%	5%
Zero-Point Lattice Vibration (Å)	0.68	0.42	0.27

p-H_2 has a high thermal conductivity

	p-H_2	Fe	Ar
Thermal Conductivity (W cm^{-1} K^{-1})	0.72	0.68	0.04

Benefits of large ZP vibrational motion in *p*-H_2

	***p*-H_2**	**Ne**	**Ar**
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The amplitude of the zero-point lattice vibrations of *p*-H_2 is a substantial fraction of the spacing between nearest H_2 molecules.

The matrix is considered to be ***'soft'***.

Crystal defects around guest species are expected to be repaired automatically.

Brings homogeneity to *p*-H_2 matrix.

Reduces the possibility of having *multiple trapping sites* and leads to reduced *inhomogeneous broadening of lines* of the guest molecules.

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Some guest molecule rotation possible

CO, CH_4, H_2O, and HCl: slightly hindered rotation in solid *p*-H_2

Larger species:

Some internal rotation (torsion) feasible: CH_3OH

Some rotation about a single axis: CH_3F

Such rotations not observed in noble-gas matrices