Effects of reagent vibrations on chemical reactivity

F/CI + methane

 $F + CHD_3(1_1) \& CH_4(3_1)$: W. Zhang & Dr. H. Kawamata $CI + CHD_3(v_1 = 1)$: S. Yan & Y.-T. Wu $CI + CH_4(v_3 = 1)$: Dr. H. Kawamata $CI + CH_2D_2(v_1, v_6 = 1)$: S. Yan, Y.-T. Wu & Dr. J. Riedel $CI + CHD_3(v_1+v_3 = 1)$: Dr. J. Riedel & Y.-T. Wu

\$\$\$: NSC, AS, & AOARD

Three separate but related issues

- (1) How to think of mode-specific and bond-selective reactivity ?
- ****** (2) How to unveil the collective atomic motion in the transition state region ?
 - (3) How to reconcile Polanyi's rules for reactions of polyatomic molecules ?

Four H-atom abstraction reactions of the $X + CH_4$ type



Multi-mode reagent & two molecular

products

Very different energetic and barrier properties

Effects of reactant vibration & mode type?

 $CI + CH_4$: late barrier $F + CH_4$: early barrier

$F + CH_4 \rightarrow HF + CH_3$

 $\Delta H_0 = -31.85 \text{ kcal/mol} (-1.38 \text{ eV})$

 $k = 1.64 \times 10^{-10} \exp(-265/T) \ cm^3/molecule\cdotsec$ for $T = 180-400 \ K$

Energy disposal

HF : highly inverted, peaking @ v = 2, rotationally cold (Polanyi, Setser, Nesbitt,..)

 CH_3 : probing v_2 (umbrella) mode

0:1:2 = 1:0.36:0.15 (Sugawara et al., 1990)

$F + CD_4 \rightarrow CD_3 + DF$



A strong even-odd alternation in favor of odd N states

→ mainly tumbling rotation

JCP 120(2004)5863

Nuclear spin statistics

For $K \neq 0$



For K = 0 CH₃ even N : odd N = 4 : 0 CD₃ even N : odd N = 1 : 10

→ predominantly low-K excitation





What happens in the TS region?

Two molecular products with multiple internal degrees of freedom

What to measure?

Product-Pair Correlation : two birds with one stone

How to achieve that?

Conservation laws

Pair-Correlated Distribution

Joint probability matrix P(n,m)

$P(n) = \sum_{m} P(n,m)$	m ⁿ	1	2	3	P(m)
$P(m) = \sum_{n} P(n,m)$	1	0.1	0.3	0.15	0.55
	2	0.2	0.1	0	0.3
Uncorrelated: $P(n.m) = P(n) P(m)$	3	0	0.1	0.05	0.15
Strictly correlated: say n = m + i	P(n)	0.3	0.5	0.2	1.0
$P(n,m) = \delta_{m+i,n} P(n)$					

PCCP 9 (2007)17



Concerted motions at transition state

Correlated decode? product pair Two molecular products with multiple internal degrees of freedom

What to measure?

Product-Pair Correlation : two birds with one stone

How to achieve that?

Conservation laws







RSI 74(2003)2495

Time-sliced (ion) velocity-map imaging





The picture tells the story !

CDCS

State-resolved DCS of product pairs : HF(v') + CD₃(0v₂00) CD₃ is not a spectator !

Science 300 (2003) 966

What will happen if the reactant is vibrational excited ?

Polanyi's rules - Effects of barrier location; ACR 5(1972)161



Let us make an educated guess

- $F + CHD_3$ is an early-barrier reaction
 - → C-H stretch is less effective than translation How will the overall rate change at fixed E_c ? (~ the same, at least, for the DF + CHD₂ formation)
- Vibrational excitation of $CHD_3(v_1=1)$ activates the C-H bond, thus facilitating its breakage to form HF + CD_3
 - \rightarrow isotopic branching, HF > DF
- Yet, C-H is a spectator bond as F attacks the D atoms
 - → favoring $CHD_2(v_1=1)$ over $CHD_2(v=0)$

How about the other CD₃ *and* CHD₂ *states?*

$F + CHD_3(v) \rightarrow DF(v') + CHD_2(v), E_c = 3.6 \text{ kcal/mol}$



The formation of $CHD_2(v_1=1)$ is anticipated (spectator), but **unexpectedly**, the **only** detectable product (**mode-specificity**)

$F + CHD_3(v) \rightarrow DF(v') + CHD_2(v_1), E_c = 3.6 \text{ kcal/mol}$



Two product images are so much alike!

Science 325 (2009) 303

$F + CHD_3(v) \rightarrow DF(v') + CHD_2(v_1), E_c = 1.2 \text{ kcal/mol}$



One-quantum excitation of C-H bond in the CHD_3 reactant affects the correlated DF vib. distribution as the F attacks the unexcited C-D bond, but exerts little effect on correlated DCS

C-H bond excitation, not a mere spectator

$F + CHD_3(v) \rightarrow DF(v') + CHD_2(v_1), E_c = 3.6 \text{ kcal/mol}$



Two product images are so much alike! energetics \rightarrow ring size; **similar pathways** $\rightarrow I(\Theta)$

$F + CHD_3(v) \rightarrow DF(v') + CHD_2(v_1)$



Vibrational excitation of the C-H bond in CHD_3 reactant not only prohibits the cleavage of the CH bond, but also slows down the rate of formation of DF + CHD_2

Scoreboard of the "conventional wisdom"

• $F + CHD_3$ is an early-barrier reaction

- → C-H stretch is less effective than translation V How will the overall rate change at fixed E_c ? (~ the same, at least, for the DF + CHD₂ formation)
- Vibrational excitation of CHD₃(v₁=1) activates the C-H bond, thus facilitating its breakage to form HF + CD₃
 - \rightarrow isotopic branching, HF > DF
- Yet, C-H is a spectator bond as F attacks the D atoms
 - → favoring $CHD_2(v_1=1)$ over $CHD_2(v=0)$ V

How about the other CD₃ and CHD₂ states?

"CH Stretching Excitation in the Early Barrier F + CHD₃ Reaction Inhibits CH Bond Cleavage" Zhang et al., Science 325 (2009) 303

C&E News, Vol. 87, No. 29, p. 16 (July 20, 2009)

A New Molecular Dynamic Frontier

 $F + HCD_3 \longrightarrow F + [H - CD_3] \longrightarrow DF + HCD_2$

Although the C–H bond in this reaction is excited, **it unexpectedly does not break**. Rather, the reaction products favor DF + CHD₂.

Nature Chemistry, Vol. 1, No. 7, p. 336 (online July 31, 2009)

Chemical Dynamics: Stretching Stops Scission

Crossed-beam experiments have shown that, counterintuitively, breaking the C–H bond during the F + CHD_3 reaction is **impeded by its vibrational excitation**.

(RSC) Chemistry World, Vol. 6, No. 7 (July 16, 2009)

Strange Vibrations

Claire Vallance, at Univ. of Oxford, says "This is probably the best example I have seen of using light to control and steer a chemical reaction, and **is unique in its simplicity - they have succeeded where vastly more complex approaches have failed**. ..."

Four H-atom abstraction reactions of the $X + CH_4$ type



Multi-mode reagents & two molecular products

Very different energetic and barrier properties

Effects of reactant vibration & mode type?

CI + CH₄: late barrier F + CH₄: early barrier

Product-Pair Correlation in CI + $CHD_3 \rightarrow HCI + CD_3$



Science 316 (2007) 1723

80

How about correlated vibrational branching?

 $\sigma_{s}^{V=1}/\sigma_{s}$ 9000 HCI (v'=1) branching 0.4 σg Ισα **x10** 0.2 1.34 9.97 0.0 15 20 5 0 10 $\mathsf{E}_{\mathbf{C}}(\mathbf{kcal/mol})$

Stretch vs. Ground

Reaction with *C-H* stretch-excited CHD₃ yields a 20-fold increase in the coincidently formed *HCI(v'=1)* products.

Reaction with *groundstate CHD*₃ yields predominantly groundstate product pair; the same for *bend-excited reactants*.

Science 316(2007)1723

How to decode the pair-correlation information ?

Responses of CH_4 vibrations to the approaching CI atom – Reaction Path Hamitonian by Miller et at, JCP 92(1980)99



Duncan et al, JCP 103(1995)9642

Corchado et al, JCP 112 (2000)9375



It takes two to tango!

Visualizing collective nuclear motions in the TS region

Ground-State Reaction

A vibrationally *adiabatic* process

Bend-Excited Reactants

A *non-adiabatic* pathway, funneling bending energy into product rotation and translation

C-H Stretch-Excited CHD₃

Bifurcated pathways: one *direct* path mediated by couplings to *S*, and the other complex-forming path governed by *Feshbach (reactive) resonance*

PNAS 105(2008)12667

Transition State (TS)



- Energetic
- Vibrational Frequencies

Static properties

State-correlation of product-pair → dynamical aspect (or nuclear motions) of TS

PNAS 105(2008)12667

Summary of $F/CI + CHD_3(v_1=1)$

- (1) Vibrational enhancement is seen in Cl + CHD₃, but no more efficient than translation; the same vibr.
 excitation in F + CHD₃ slows down the overall reaction rate by at least 20-fold.
- (2) In CI + CHD₃, the C-H stretching excitation facilitates the C-H bond cleavage; but it essentially shuts down the H-atom transfer channel in $F + CHD_3^{\neq}$.
- (3) **Numerous** product channels are populated with copious amounts in $CI + CHD_3^{\neq}$; but in $F + CHD_3^{\neq}$ only the "spectator" state $CHD_2(v_1=1)$ is detected; yet the initial C-H excitation is **not** just a spectator.

the barrier location is important, but is it all ?