Roaming Molecules

A Review of a Novel Reaction Mechanism

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Outline

1. Experimental Observations
    - Formaldehyde
    - Other Systems

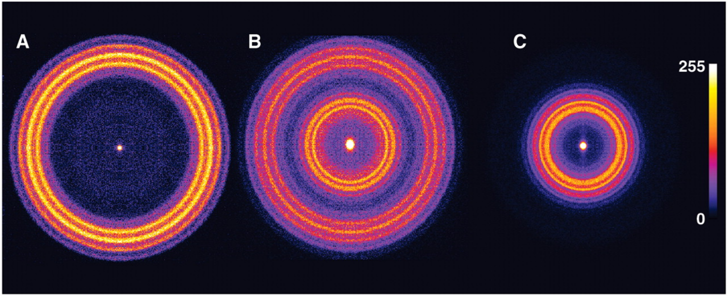
2. Theories for Explanation
    - A phase space state-counting theory of roaming
    - A Variable Reaction Coordinate Transition State Theory Approach

Experimental Observations

Formaldehyde

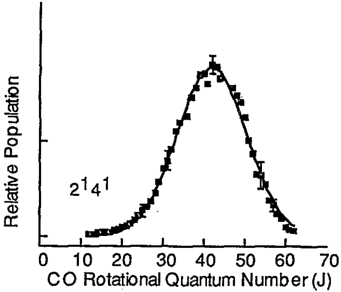
Experimental Setup

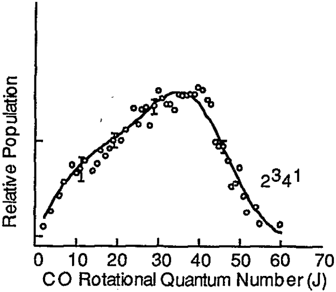
- Photolysis laser: 330 nm (30340 cm^{-1})
- H_2CO in collision-less molecular beam
- Excites and dissociates within a few picoseconds
- DC slice imaging to probe CO rotational state



An Unexpected Distribution

More energy yields an asymmetric, *colder* distribution?



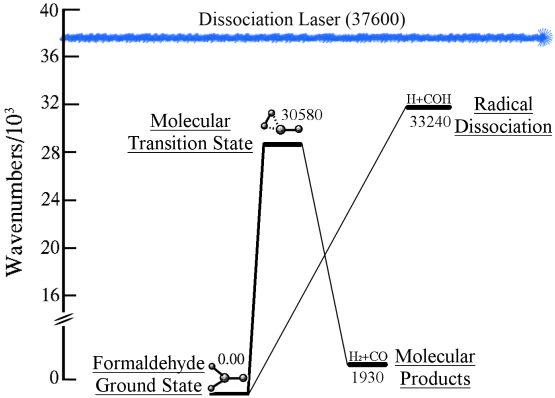


$2^1 4^1$: 800 cm^{-1} below

$2^3 4^1$: 1500 cm^{-1} *above*

the threshold for radical dissociation

Energy Scales



Other Systems

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- NO_3: roams on both D_0 and D_1 surface. Nearly *all* of the reactive flux is *via* roaming.
- Many others, 20+ at last count (see Bowman [2014])

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- multi-modal product state distributions
- Systems where a radical dissociation threshold is nearly isoenergetic to a transition state to molecular products
- All systems which include a radical-radical abstraction reaction (most alkanes)

Theories for Explanation

Jordan and Kable

A phase space state-counting theory of roaming

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On the other hand, posits that radical dissociation and the roaming pathway *are* linked and therefore the rates *must* be calculated together. This is their point of attack.

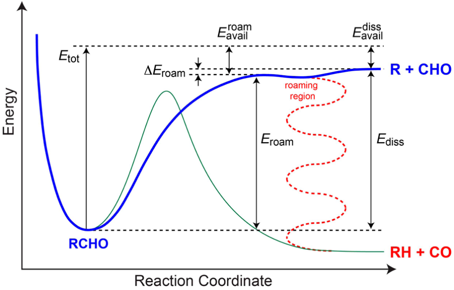
Jordan and Kable

Partitions the results of a phase-space volume summation based on the energy available to roam or dissociate. The phase space theory (Chesnavich and Bowers [1977]) treats the fragments as non-interacting in the roaming region.

Jordan and Kable

Requires 2 parameters:

- ΔE_{roam}, the energy difference between bond dissociation threshold and roaming threshold
- P_{roam}, the probability that states that may roam do rather than recombine to form reactants.



Jordan and Kable

Use a phase space state count, w, for fixed total energy, E and total angular momentum, J. Classically, with n degrees of freedom, w of the form:

$$w \propto \frac{1}{h^n} \int_{E,J} d\vec{p}\, d\vec{q} \tag{1}$$

Roaming fragments are *independent* from each other so their contributions can be computed from their individual spectroscopic constants.

Jordan and Kable

Can partition energy into fragment, relative translational, E_{trans}, and internal energy. Roaming states have:

$$E_{\mathrm{trans}} \leq \Delta E_{\mathrm{roam}}$$

Dissociative states have:

$$E_{\mathrm{trans}} > \Delta E_{\mathrm{roam}}$$

Estimate an upper bound for the branching ratio for roaming compared to dissociative products, $f^{\mathrm{U.B.}}_{\mathrm{roam}}$, as the ratio of state counts as a function of energy, E:

$$f^{\mathrm{U.B.}}_{\mathrm{roam}}(E) = \frac{w_{\mathrm{roam}}(E)}{w_{\mathrm{roam}}(E) + w_{\mathrm{diss}}(E)} \tag{2}$$

Jordan and Kable

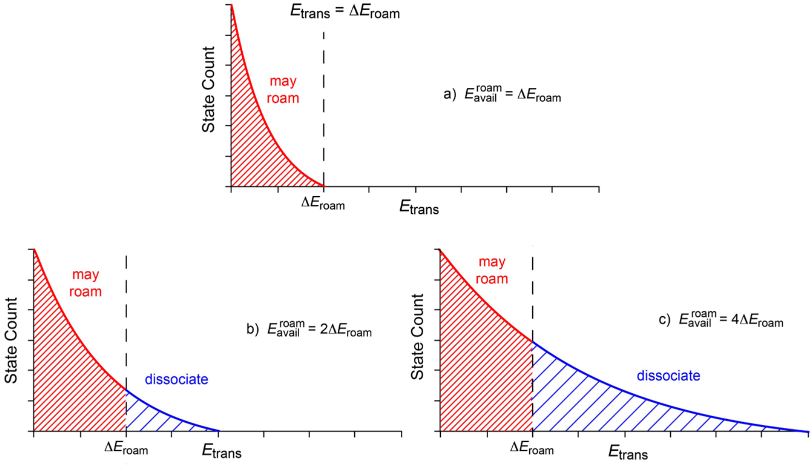
$f_{\mathrm{roam}}^{\mathrm{U.B.}}(E)$ is almost certainly an upper bound because

- A free rotor estimate of w_{roam} will over-count the available states
- Some roaming states may not lead to molecular products—they may re-combine to reactants

The impact of these effects are combined in P_{roam}. The revised estimate is $f_{\mathrm{roam}} = P_{\mathrm{roam}} \cdot f_{\mathrm{roam}}^{\mathrm{U.B.}}$:

$$f_{\mathrm{roam}}(E) = P_{\mathrm{roam}} \frac{w_{\mathrm{roam}}(E)}{w_{\mathrm{roam}}(E) + w_{\mathrm{diss}}(E)} \tag{3}$$

Jordan and Kable



Jordan and Kable: H_2CO

Dissociation pathways for H_2CO:

$$
\begin{aligned}
\mathrm{H_2CO} \longrightarrow\ & \mathrm{H_2 + CO} && (4)\\
& \text{(TS channel, 28150 cm}^{-1}\text{)} \\
\longrightarrow\ & \mathrm{H_2 + CO} && (5)\\
& \text{(roaming channel, 30180 cm}^{-1}\text{)} \\
\longrightarrow\ & \mathrm{H + HCO} && (6)\\
& \text{(dissociation channel, 30328 cm}^{-1}\text{)} \\
\longrightarrow\ & \mathrm{H + HCO} && (7)\\
& \text{(triplet channel, 31450 cm}^{-1}\text{)} \\
\longrightarrow\ & \mathrm{H + H + CO} && (8)\\
& \text{(triple fragmentation, 35370 cm}^{-1}\text{)}
\end{aligned}
$$

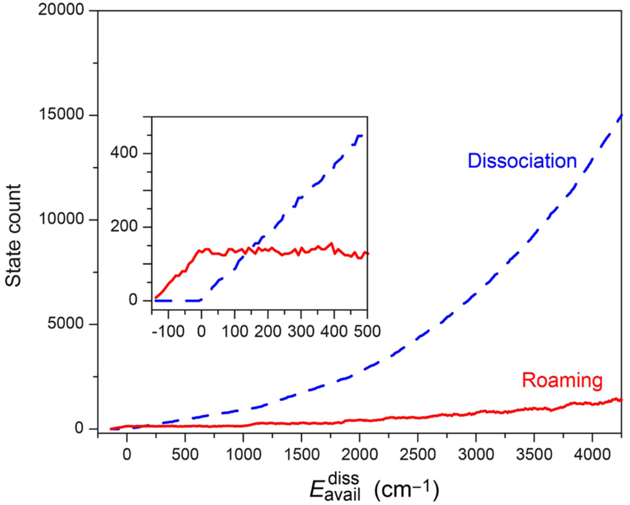
Jordan and Kable: H_2CO

If $F(E)$ is the overall branching fraction for each of these pathways as a function of energy,

$$f_{\mathrm{roam}}(E) = \frac{F_{\mathrm{roam}}(E)}{F_{\mathrm{roam}}(E) + F_{\mathrm{rad}}(E)} \tag{9}$$

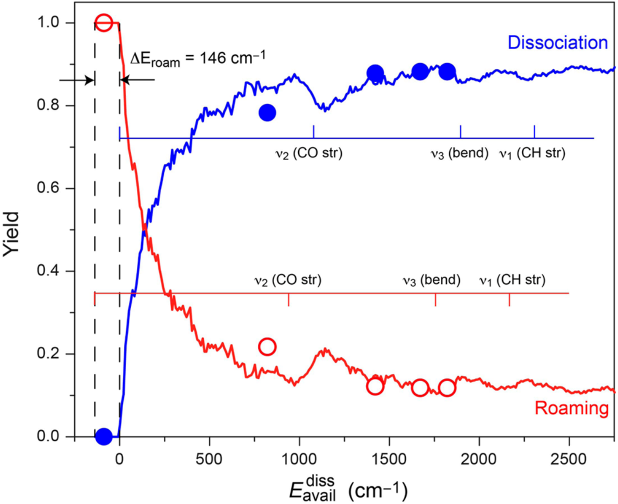
Use the midpoint of experimental values for $\Delta E_{\mathrm{roam}} = 146\mathrm{cm}^{-1}$ and set $P_{\mathrm{roam}} = 1$.

Jordan and Kable: H_2CO



$w_{\mathrm{roam}}(E)$ and $w_{\mathrm{diss}}(E)$ for H_2CO

Jordan and Kable: H_2CO



Jordan and Kable: Conclusions

- In 3 systems, found reasonable agreement when taking P_{roam} to be an adjustable parameter: H_2CO, $P_{\mathrm{roam}} = 0.99$; NO_3, $P_{\mathrm{roam}} = 0.0075$; CH_3CHO, $P_{\mathrm{roam}} = 0.21$
- There are few experiments available for direct comparison.
- While the fitted model does give roaming fractions in reasonable agreement with experiment, it provides no way to construct P_{roam} or ΔE_{roam} from the properties of the energy landscape. Also, gives no information about products formed *via* conventional pathway.

Klippenstein and Harding

A Variable Reaction Coordinate Transition State Theory Approach

Klippenstein and Harding

Klippenstein et al. [2011]:

- Assuming that the roaming and direct dissociation pathways are dynamically separated

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- Assuming that the roaming and direct dissociation pathways are dynamically separated
- Describes a transition state theory for computing branching ratio between radical dissociation and roaming.

Klippenstein and Harding

Assumes decomposition can be broken into a sequence of steps:

1. Partial decomposition into two weakly interacting fragments

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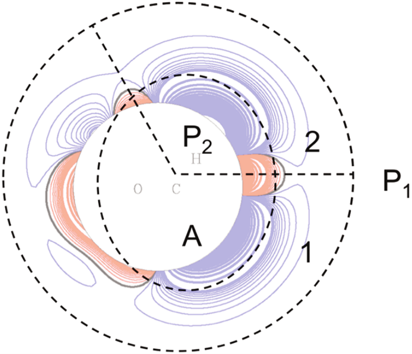
Steady-state kinetics using transition state fluxes for each process then give the relative branching ratios.

Klippenstein and Harding

Regions of the energy surface:

A	H_2CO	reactant
P_1	$HCO + H$	products, radical
P_2	$CO + H_2$	products, molecular
1	HCO···H	intermediate
2	H···HCO	intermediate



Blue contours are attractive, red are repulsive. Dashed lines represent dividing surfaces.

Klippenstein and Harding: Steady State Kinetics

$$d[A]/dt = k_{1,A}[1] - k_{A,1}[A]$$

$$d[1]/dt = k_{A,1}[A] + k_{2,1}[2] - (k_{1,A} + k_{1,2} + k_{1,P_1})[1]$$

$$d[2]/dt = k_{1,2}[1] - (k_{2,1} + k_{2,P_1} + k_{2,P_2})[2]$$

$$d[P_1]/dt = k_{1,P_1}[1] + k_{2,P1}[2]$$

$$d[P_2]/dt = k_{2,P_2}[2]$$

Where $k_{i,j}$ is the rate coefficient for $i- > j$.

Klippenstein and Harding: Steady State Kinetics

Assuming steady state for the two intermediates, 1 and 2, yields the following branching ratio between roaming, P_2, and simple dissociation, P_1:

$$\frac{k_{P_2}}{k_{P_1}} = k_{2,P_2} / \left[k_{2,P_1} \left(1 + \frac{k_{1,P_1}}{k_{1,2}} \right) + k_{1,P_1} \left(\frac{k_{2,1} + k_{2,P_2}}{k_{1,2}} \right) \right] \tag{10}$$

Klippenstein and Harding: Steady State Kinetics

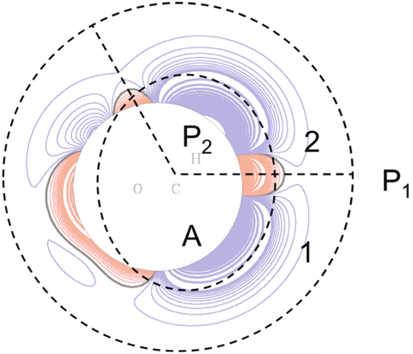
The rate coefficients may also be expressed in terms of reactive fluxes, $N_{i,j} = k_{i,j}(h\rho_i)$, where ρ_i is the density of states for species i. The $\{N_{i,j}\}$ will be evaluated according to transition state theory as the number of reactive trajectories crossing the dividing surfaces shown earlier.

$$\frac{k_{P_2}}{k_{P_1}} = N_{2,P_2} / \left[N_{2,P_1}\left(1 + \frac{N_{1,P_1}}{N_{1,2}}\right) + N_{1,P_1}\left(1 + \frac{N_{2,P_2}}{N_{1,2}}\right)\right] \qquad (11)$$

Note that as a consequence of microscopic reversibility, $N_{i,j} = N_{j,i}$.

Klippenstein and Harding: And they're off to the races

To evaluate the fluxes, the authors must treat both spherical and planar dividing surfaces.
They do this by using variable reaction coordinate transition state theory, a sum of states in configuration space.



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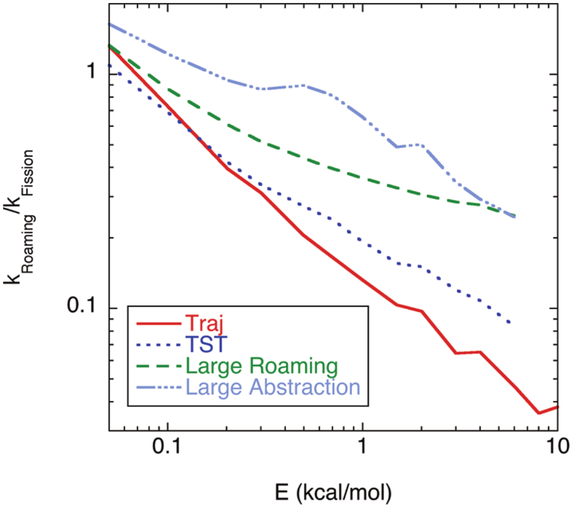

Klippenstein and Harding: Conclusions

Compares quite favorably to reduced dimension trajectories at energies of less than 1 kcal/mol above the radical asymptote.

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Does systematically less well at higher energies or when radical and roaming fluxes are approximately equal.

Questions

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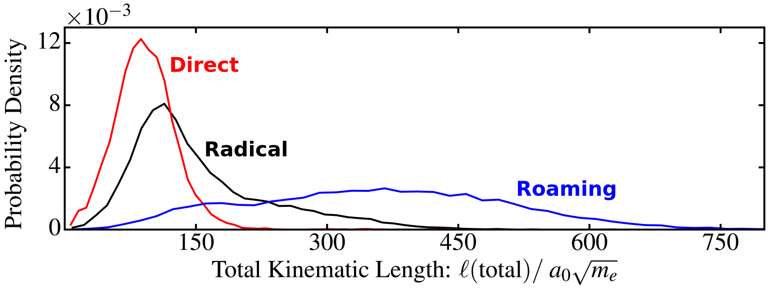
Some of our results



References

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