



Ultrafast Studies of Methyl Sulfonyl Unimolecular Dissociation Dynamics

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Abstract

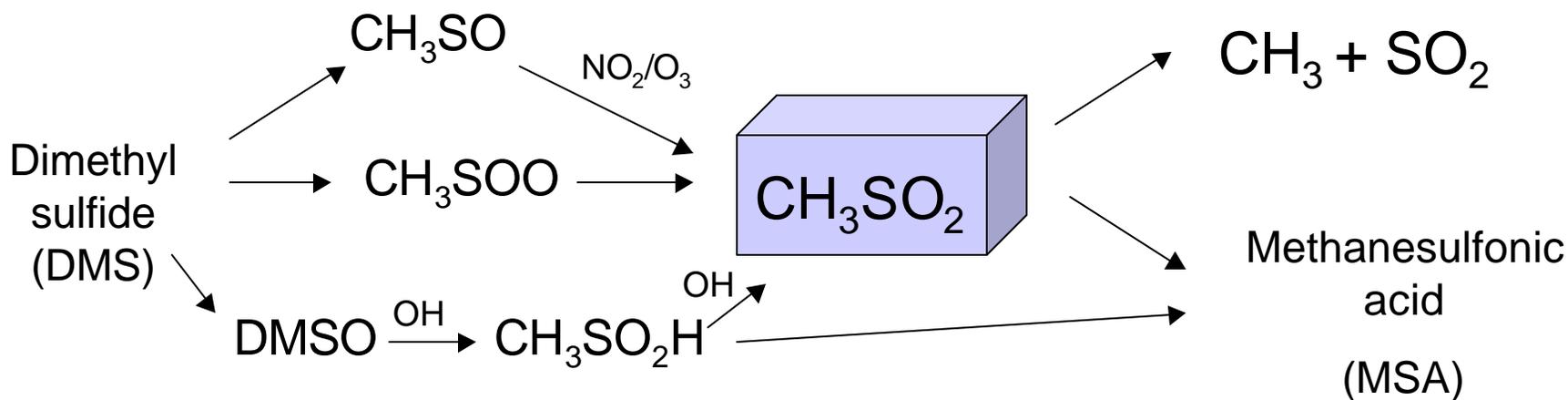
Ultrafast deep uv, mass-resolved photoionization spectroscopy has been used to study the unimolecular dissociation of methyl sulfonyl following the 193 nm photodissociation of methyl sulfonyl chloride (MSC) and methyl sulfonyl ethanol (MSE). In both cases, the parent excited state lifetime is instrument-limited (<200 fs). The unimolecular decomposition lifetimes measured for methyl sulfonyl radical from MSC and MSE are 0.34 ps and 1.2 ps, respectively. The fractions of undissociated intermediate are <0.02 and 0.40, respectively. These results are remarkably well reproduced by RRKM calculations assuming an impulsive energy partitioning.



Methyl Sulfonyl Radical

CH_3SO_2 (MS) - key intermediate in atmospheric sulfur chemistry:

- Oxidation of DMS to MSA - cloud condensation nuclei
- Thermal decomposition may contribute to T dependence of branching ratio (Barone, 1995; Ayers et al. 1996)
- May be most important intermediate in forming SO_2 (Saltelli and Hjorth, 1995)



- Kinetics of CH_3SO_2 : only *product* studies - not as reactant
- Reliable method to produce MS useful for kinetics



Methyl Sulfonyl Spectroscopy and Dynamics

- Spectroscopy and dynamics: few studies - not well characterized
 - ▶ Absorption spectra in gas and solution
 - ▶ Calculations of structures, energetics and vibrational frequencies (Davis, 1993; Franck and Turecek, 1999; Chatgialloglu et al., '87 & '94)
 - ▶ No photodissociation product studies (or other direct dynamics/kinetics)
- Methyl Sulfonyl - fs study of unimolecular dissociation dynamics
 - ▶ Does any MS survive photodissociation of precursor near 195 nm?
 - ▶ Sulfur analog of acetyl
 - ▶ fs studies of acetyl unimolecular dissociation dynamics
 - acetone photodissociation: acetyl unimol. decomp is nonRRKM (Kim and Zewail, 1996; Owrutsky and Baronavski, 1998)
 - acetic acid and acetyl cyanide - acetyl unimol. decomp is RRKM (Owrutsky and Baronavski, 1999)
 - RRKM unimol. decomp. correlates with prompt parent dissociation
 - ▶ Is MS unimolecular decomposition consistent with RRKM model?

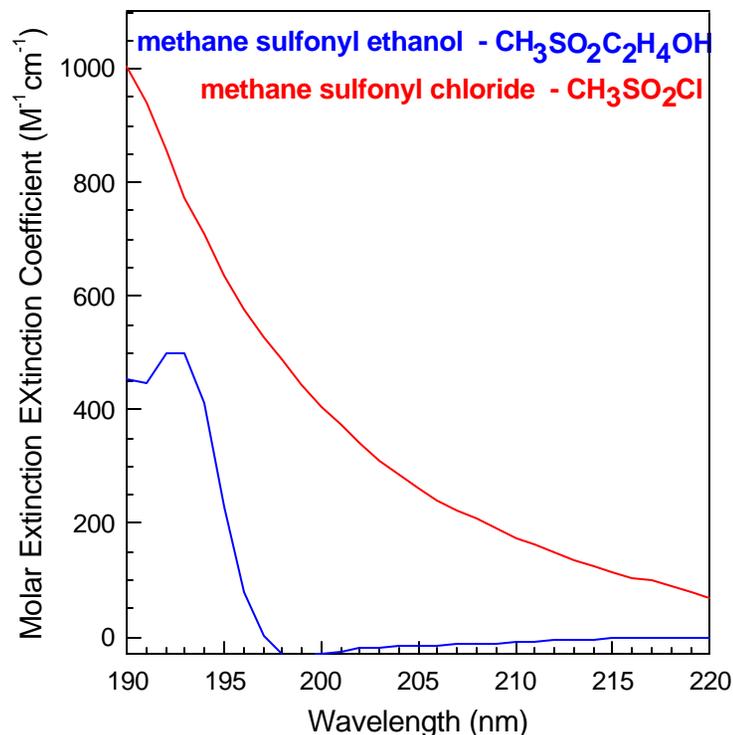


CH₃SO₂ Unimolecular Dynamics Study

- 1) Develop photolytic route to generate stable CH₃SO₂
- 2) Is CH₃SO₂ dissociation rate statistical/RRKM?

Deep UV fs photoionization study of dissociation dynamics

- Various precursors:
 - Methyl sulfonyl chloride (MSC)
 - Methyl sulfonyl ethanol (MSE)
- Measure dissociation rates: primary and secondary
- Fractional dissociation of MS (*i.e.*, stability) determined for each precursor

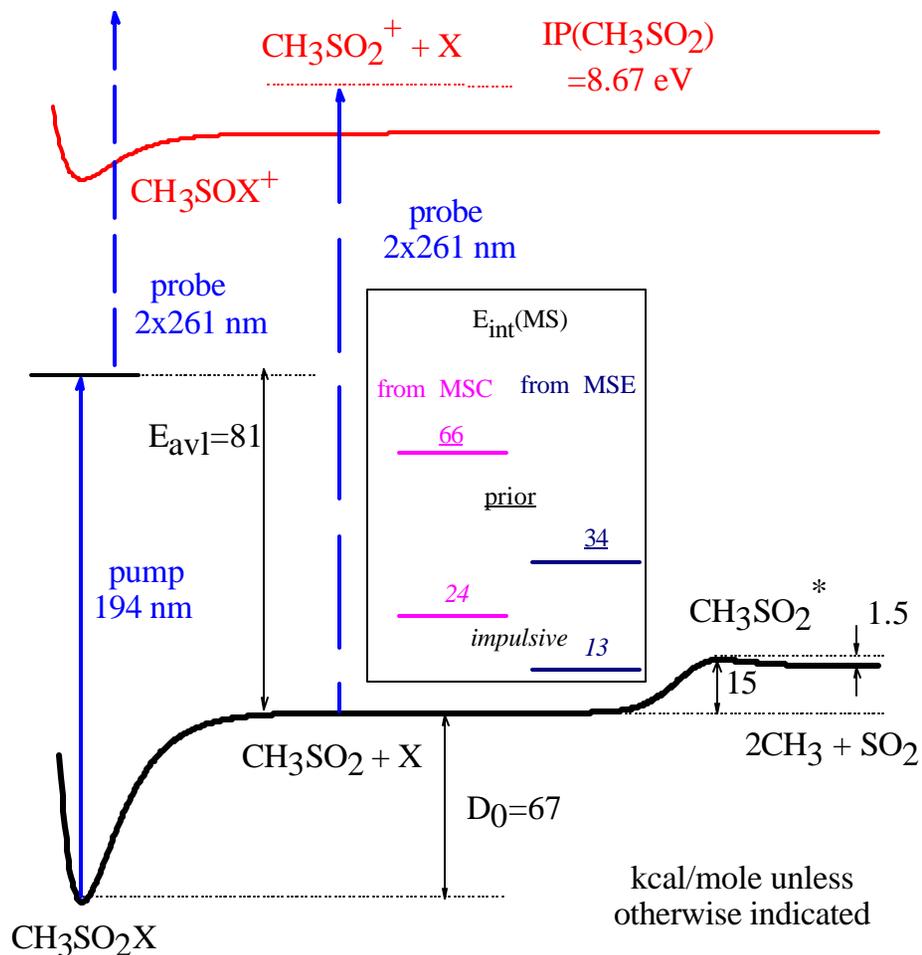




Methyl Sulfonyl Dissociation Dynamics

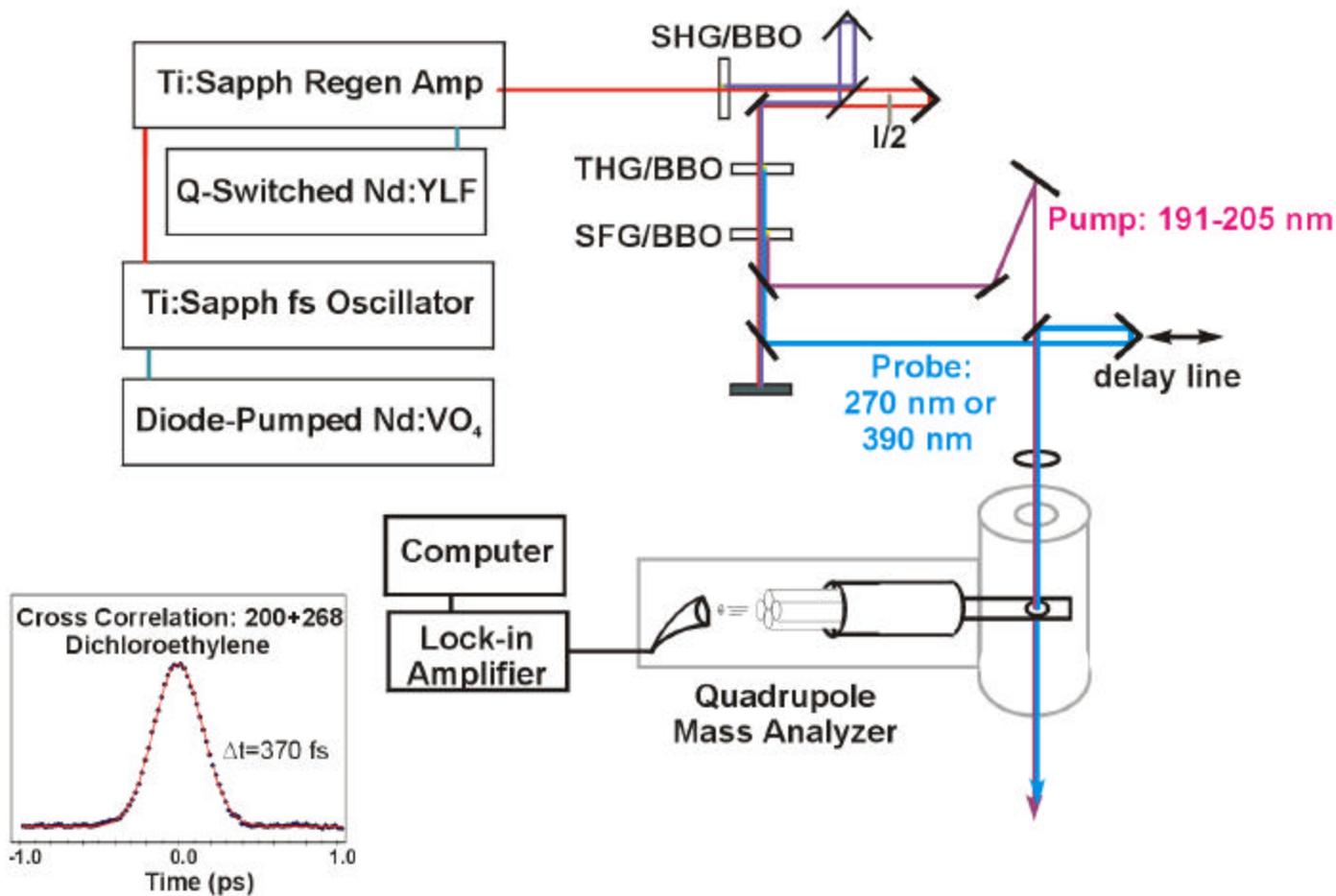
Compare measured and calculated rate

- NO PRODUCT STUDIES:
 - ▶ Almost anything goes!
 - ▶ *Assume* models for energy partitioning:
 - $\rho(E)$: impulsive or prior
- k_{uni} obs. vs. calc ($\langle k(E)\rho(E) \rangle$)
- fractional dissociation
- $k_{\text{RRKM}}(E)$:
 - ab initio* barrier and frequencies
 - ▶ Davis
 - ▶ Marshall
 - ▶ Franck and Turecek



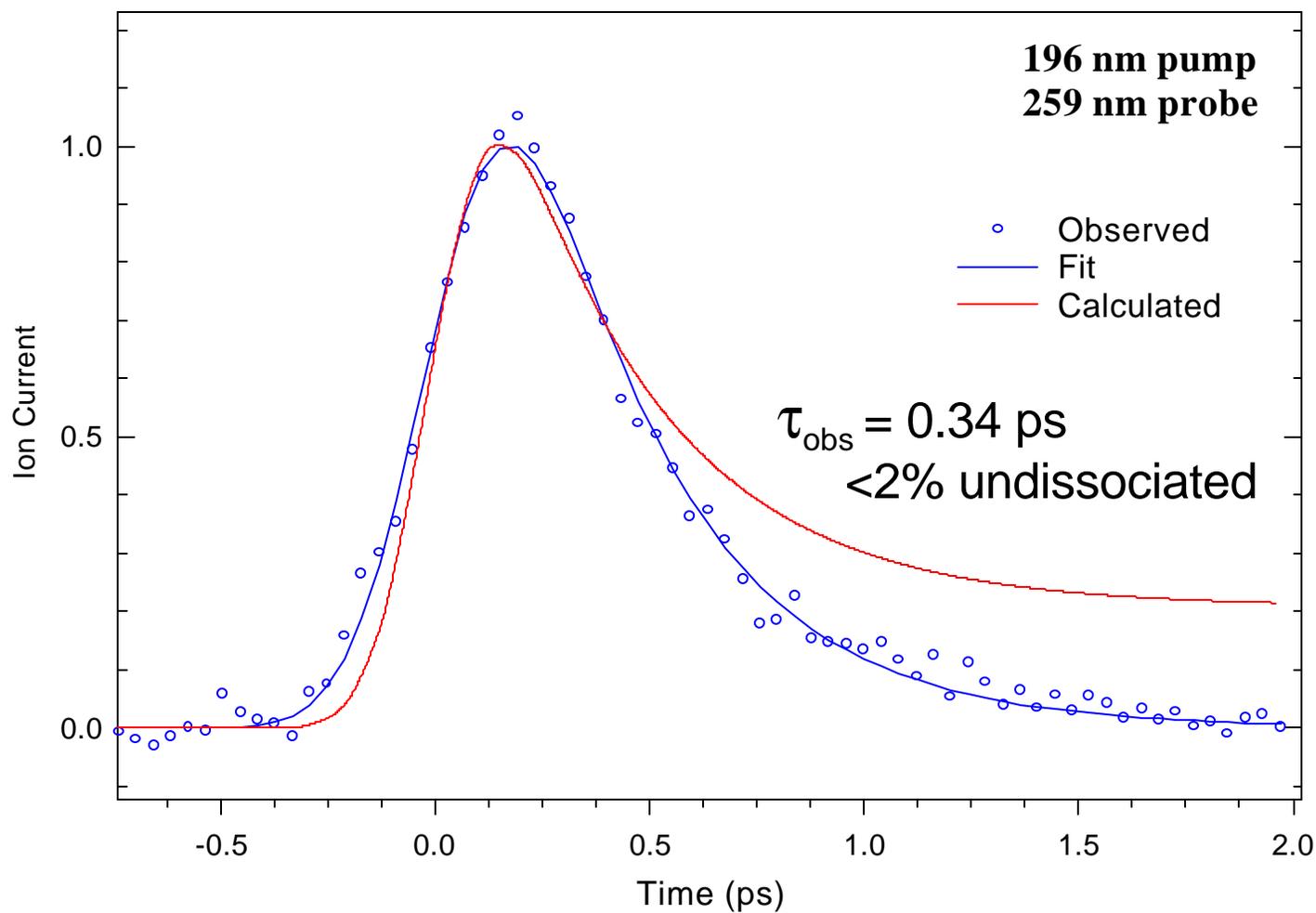


Mass-Resolved Deep UV Femtosecond Photoionization Spectroscopy



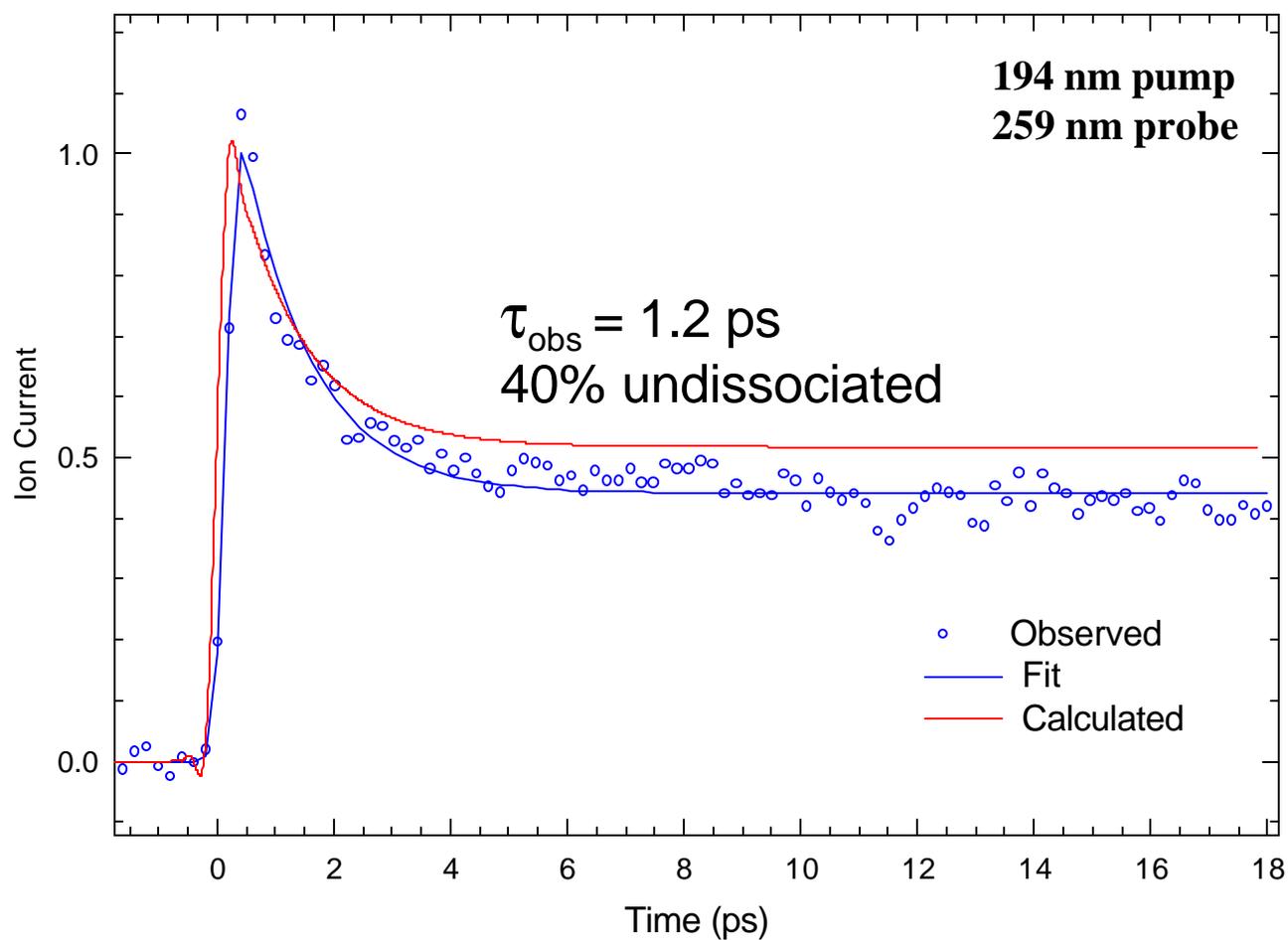


Ultrafast Photoionization: CH₃SO₂ from MS-Chloride





Ultrafast Photoionization: CH_3SO_2 from MS-EtOH





Measured and Calculated Dissociation Rates

Measured:

- Primary dissociation: prompt for both precursors
- CH_3SO_2 unimolecular dissociation: rates and degree of dissociation

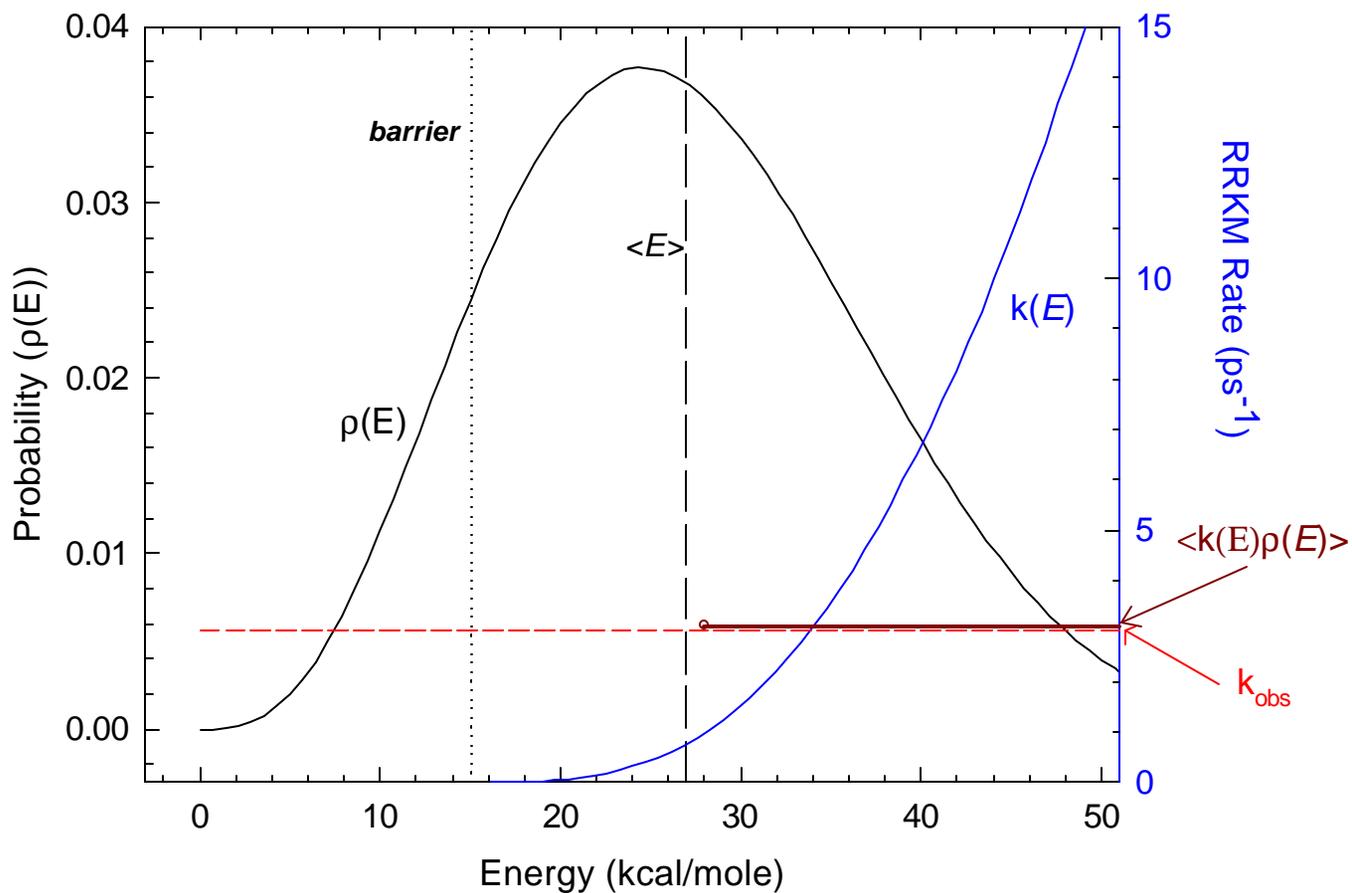
Calculate rates assuming impulsive energy partitioning:

- k_{uni} (RRKM):
 - ▶ impulsive partitioning: E_{T} and $E_{\text{int}}(X)$, $X = \text{Cl}$ or EtOH
 - ▶ use binomial distribution for $\rho(E)$:
$$\rho(E) = [E_{\text{avl}} - E_{\text{T}} - E_{\text{int}}] (E/E_{\text{avl}})^a (1-E/E_{\text{avl}})^b$$
 - ▶ $k(E)$ from E_{barr} and ν_{vib}
 - ▶ $\langle \rho(E), k(E) \rangle_{\rho}$ agrees better than $k(\langle E \rangle_{\rho})$
- % dissociation = $I \rho(E > E_{\text{barr}}) / I \rho(E)$, $E_{\text{barr}} = 14.3$ kcal/mole



Calculated Internal Energy Distribution and Dissociation Rate

For MS from MSC:





Methyl Sulfonyl Dissociation Results

Dissociation rates and fractional dissociation of MS:

Impulsive partitioning/RRKM - Very close to observations

Prior - overpredicts fractional dissociation for MSE and both rates

Precursor	Calculated time (ps)	Observed time (ps)	Calc'd fraction undiss.	Obs. fraction undiss.
MSchl	0.34	0.34	0.11	<0.02
MSEtOH	1.2	1.2	0.46	0.40

Calculated fractional absorption higher than observed:
calculated energy distribution too broad or too low?

Long lived (>20 ps) MS? From MSE not MSC



Summary and Conclusions

- **Unimolecular Dynamics of MS**

- ▶ Very good agreement between observed and calculated rates and fractional dissociation using impulsive partitioning and RRKM
- ▶ Calculations are **NOT** unique: fortuitous?
 - unrestricted by experimental product energy distributions
- ▶ RRKM unimolecular dissociation with prompt parent dissociation - similar to acetyl from acetic acid and acetyl cyanide

- **Precursor for MS with photolysis at 193 nm:**

MSE better than MSC - suitable precursor for kinetic studies