Distinguished Contribution Award Address

Collision Theory

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http://bowers.chem.ucsb.edu
• A trip down memory lane
  • Selected highlights from past ASMS meetings

• Some science (sorry!)
  • ion-dipole theory
  • statistical phase space theory
  • combinations and applications

• Some current theoretical challenges
The Award

**Ionization Methods (5)**
(1) PD
(2) FAB
(3) ESI
(7) CI
(8) MALDI

**Instrumentation (5)**
(4) Triple Quad
(9) Simion
(10) FTICR
(11) Reflectron
(12) Ion Trap Mass Scan

**Chemistry/Analysis (4)**
(5) Negative Ion MS
(6) CID
(13) Peptide Fingerprinting
(14) Six-Member Ring Rearrangements

**Theory (1)**
(15) Collision Theory

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The Conference

Selected Highlights

1953 – 1969 Committee E14 of ASTM
1970 – Present ASMS

http://masspec.scripps.edu/information/history/
1969 · Dallas, TX

- My first meeting!!
- 177 papers, all oral
- 29 invited talks
- NO BIO TALKS!
First ASMS Conference; 18th ASTM/ASMS

Joe Franklin first President

Here Comes Bio!! 185 total talks → 11 Bio (6%)
- Catherine Fenselau

Some Important Statistics

- Members: 800
- Conference attendance: 619
- Male: 97%
- College degree: 97%
- PhD: 55%
- Average age: 39

Discipline:
- Phys/Inorg: 32.5%
- Organic: 31.8%
- Physics: 14.5%
- Biochem: 13.4%
- Geology: 7.8%
1971 • I meet Keith Jennings for the first time!

1972 • The first plenary lectures

*Are Charged Carbenes Intermediates in Mass Spectrometry Fragmentation Processes?*

Carl Djerassi

*Sequence Determination of Peptides by Mass Spectrometry*

Edgar Lederer

*The ADO precursor talk!!*

*Dipole Effects in Ion-Molecule Reactions*

M. T. Bowers and T. Su
• Frank Field is President

• Plenary lecture

*Carbocations in the Gas Phase and in Solution*

George Olah
• Plenary Lecture

*Studies in Reaction Dynamics*

Y. T. Lee

• Franklin Symposium

*MO Studies of the Energies and Structures of Polyatomic Cations*

J. L. Pople

• 311 papers, all oral → 54 Bio (17%)

*Applications of Phase Space Theory to Polyatomic Ion-Molecule Reactions*

W. J. Chesnavich and M. T. Bowers
• The first posters appear!
  Oral Talks: 244
  Posters: 88

• Polyatomic Phase Space Theory Applications to Bimolecular and Unimolecular Reactions
  W. J. Chesnavich and M. T. Bowers

• I chair my first symposium!
• Membership: 1270
Meeting: 985
Oral Talks: 279
Posters: 108

• Comments on the Entropy Change in Ion-Molecule Equilibria
  S. G. Lias and P. Ausloos

THE COLD FUSION of ASMS

• Ion Polar Molecule Collisions: The
  Average Dipole Orientation Theory with
  Conservation of Angular Momentum
  T. Su and M. T. Bowers
Seeds of internal energy effects in collisional activation planted.

**On the Question of Intermolecular Entropy Effects in Low Pressure Ion-Molecule Equilibria: An Analysis Based on the Langevin Model**

W. J. Chesnavich, H. Metiu, and M. T. Bowers

Conservation of energy and angular momentum and microscopic reversibility save the day!

**Multiple Transition States in Ion Molecule Reactions: A Unified Statistical Theory Approach**

W. J. Chesnavich, L. Bass, and M. T. Bowers
• The Hilton Hawaiian Village!
• Judith Watson née Sjoberg establishes an ASMS “office”
• Keith Jennings wears Bermuda Shorts

• Inaugural Feature Lecture
  *All You Always Wanted to Know About Collision Theory but Were Afraid to Ask*
  
  M. T. Bowers

• Workshop
  *Internal Energy Effects in Collisional Activation: Part 1*
  
  Keith Jennings Presiding
  Mike and Fred Colliding
  Everyone Present Energized
• Workshop

*Internal Energy Effects in Collisional Activation: Part 2*

Keith Jennings Refereeing
Standing Room Only
Fred Turns 60
Mike & Fred Mud Wrestling Postponed

• Five Feature Lectures (Tutorials)

• Boston Pops concert
• Electrospray Ionization of Some Peptides and Small Proteins
  
  C. K. Meng, M. Mann, and J. B. Fenn

  Insulin 5700
  Cytochrome c 12,200
  Myoglobin ~17,000
  Carbonic Anhydrase ~ 29,000
  Alcohol Dehydrogenase ~40,000
• *Ultraviolet Laser Desorption/Ionization of Biomolecules in the High Mass Range*
  F. Hillenkamp and M. Karas

Violet Phosphatase 35,050
Mouse IgG Monoclonal Antibody 149,190
Jack Bean Urease ~274,800

• My team wins both the dance contest and limerick contest at the ASMS closing party
1995 · Atlanta, GA

- Chris Enke President
- Ronnie Bierbaum VP Program
  Hank Bierbaum runs the posters
- I GIVE MY FIRST BIO TALK!
  Structures of Biopolymers: A Combined MALDI Ion Chromatography Approach
  T. Wyttenbach, G. von Helden, S. Lee, and M. T. Bowers
- Keith Jennings selected for Distinguished Contribution Award
1998 · Orlando, FL

- The last “book”: 1538 pages
- Ronnie Bierbaum is President
- Hank Bierbaum still runs the posters
- Bob Squires wins the Biemann Medal
- Papers presented: 1501
  Oral Talks: 252 → 114 Bio (45%)
  Posters: 1249 → 738 Bio (59%)
- I win low gross at the Golf Outing
Warning

Now a little theory
(I’ll wake you when it’s over)
Keith & Chris Jennings
The Golden Decade for Theory at UCSB

Published 38 primary theory papers
  • most with some experiment
  • many cited here

Major players
  • Tim Su
  • Walt Chesnavich
  • Lew Bass

Applications continue to the present day
1. Pure Polarization (no dipole)
2. Locked Dipole
3. Average Dipole Orientation (ADO)
4. Conservation of Angular Momentum (AADO)
5. Variational Transition State Theory
6. Trajectory Calculations
Pure Polarization Theory

Assumptions:
- Point charge
- Point polarizable neutral

\[ V(r) = -\frac{\alpha q^2}{2r^4} \]

**Pure Polarization Theory**

**Idea:** Calculate maximum impact parameter for ion-neutral capture

Capture: \( r_{m^+ - M} \to 0 \)

Orbiting collision: dividing surface between capture and scattering

\[
E_{\text{trans}} = 0
\]
\[
E_{\text{tot}} = E_{\text{rot}} + V(r) = V_{\text{eff}}(r) = \frac{L}{2\mu r^2} - \frac{\alpha q^2}{2r^4}
\]

\[
k_P = 2\pi q \left( \frac{\alpha}{\mu} \right)^{1/2}
\]
**Ion Dipole Theory**

**Assumptions:**
- Point charge
- Point dipole

Where:
- $\theta$ is the angle between the dipole moment and the line connecting the center of the charge and the point of interest.
- $\mu_D$ is the dipole moment.

The effective potential energy $V_{\text{eff}}(r)$ is given by:

$$V_{\text{eff}}(r) = \frac{L}{2\mu r^2} - \frac{\alpha q^2}{2r^4} - \frac{q\mu_D}{r^2} \cos \theta$$

**Maximum Effect:**

$$\cos \theta = 1 \rightarrow \text{Locked Dipole}$$


**Kagamihara's Model:**

$$k_{LD} = k_P + q\mu_D \left(\frac{8\pi}{kT}\right)^{1/2}$$
Exothermic Proton Transfer Reactions: $\text{AH}^+ + \text{B} \rightarrow \text{BH}^+ + \text{A}$


<table>
<thead>
<tr>
<th># Expts.</th>
<th>$k_P$</th>
<th>$k_{LD}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>63</td>
<td>-43</td>
<td>+170</td>
</tr>
</tbody>
</table>
Better Treatments of the Dipole Term

Average Dipole Orientation Theory (ADO)


Idea:
• Calculate an average value of $\theta$ or $\cos \theta$ as a function of $r$
• Dipole rotation does not couple to system rotation
For $\overline{\theta(r_C)}$, obtain (similar results for $\overline{\cos\theta(r_C)}$):

$$\sigma(v) = \pi r_C^2 + \frac{\mu q^2 \alpha}{r_C^2 \mu v^2} + \frac{2\pi q\mu_D}{r_C \mu} \cos\theta(r_C)$$

- Polarization
- ADO

$$k_{ADO} = \int_{0}^{\infty} v \sigma(v) P(v) \, dv$$

Must integrate numerically for each system
Average Dipole Orientation Theory (ADO)


\[
k_{ADO} = k_C + cq\mu_D \left(\frac{8\pi}{kT}\right)^{1/2}
\]

\(c = \text{dipole locking constant}\)

**Comparison:**

<table>
<thead>
<tr>
<th># Expts.</th>
<th>(k_P)</th>
<th>(k_{ADO})</th>
<th>(k_{LD})</th>
</tr>
</thead>
<tbody>
<tr>
<td>63</td>
<td>-43</td>
<td>-5.2</td>
<td>+170</td>
</tr>
</tbody>
</table>
The Question of Angular Momentum

AADO Theory


**Idea:** Couple rotational angular momentum of the dipole (J) to orbital angular momentum of the system (L)

**Assumption:**
\[ \hat{L} \text{ and } \hat{J} \text{ are collinear} \]

**Result:**
\[
k_{\text{AADO}} = k_{\text{ADO}} + A \frac{2q\mu_D}{(\mu\alpha)^{1/2}}
\]

A = angular momentum constant

= \( f(I, \text{other system constants}) \)
### AADO vs. ADO

<table>
<thead>
<tr>
<th>Type</th>
<th>Reaction</th>
<th>Helmsley et al.</th>
<th>Mackay et al.</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>$XH^+ + NH_3 \rightarrow NH_4^+ + X$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>$XH^+ + HCN \rightarrow H_2CN^+ + X$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$X^- + HCN \rightarrow HCN^- + X$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Reaction Type</th>
<th>$k_{\text{expt}}/k_{\text{ADO}}$</th>
<th>$k_{\text{expt}}/k_{\text{AADO}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I (11 reactions)</td>
<td>1.12 (±0.1)</td>
<td>0.99 (±0.04)</td>
</tr>
<tr>
<td>II (10 reactions)</td>
<td>1.21 (±0.2)</td>
<td>0.99 (±0.15)</td>
</tr>
</tbody>
</table>
1. Variational Transition State Theory


**Idea:** Calculate minimum flux through dividing surface using Variational Methods

\[
\text{Flux(variational)} \geq \text{Flux(true)} \quad \text{and} \quad k_{\text{VAR}} \geq k_{\text{TRUE}}
\]

**Note:** \( k_{\text{VAR}} = k_{\text{TRUE}} \) if no surface recrossing occurs

**Solution:** \( k_{\text{VAR}} = f(\mu_D, \alpha, T) \)
2. Trajectory Calculations


**Idea:** Solve Newton’s equations rigorously for

\[
V(r) = -\frac{\alpha q^2}{2r^4} - q\mu_D\cos\theta
\]

**Solution:** general for all \(\mu_D, \alpha, T\)
Comparisons

\( \frac{\mu_D}{\sqrt{\alpha}} \) (Debye \( \AA^{-3/2} \); \( T = 300^\circ K \))

\( \frac{k}{k_L} \) vs. \( \frac{1}{\sqrt{T_R}} \)

Locked Dipole

Variation Trajectory

Langevin

\( \frac{\mu_D}{\sqrt{\alpha}} \) (Debye \( \AA^{-3/2} \); \( T = 300^\circ K \))

\( \frac{k}{k_L} \) vs. \( \frac{1}{\sqrt{T_R}} \)
1. **Kinetic Energy Dependence**

2. **Ion Size**

3. **Molecular Size**

4. **Average Quadrupole Orientation**

5. **Temperature Dependence**

6. **Induced Dipole – Induced Dipole Potential**

7. **Anisotropy in the Polarizability**
1. Ion-molecule capture: a solved problem

2. Capture collisions create “chemically activated” complexes with known $E$, $J$ distributions

3. What happens next?
Question: What governs the product distribution once a complex is formed?

\[ k_{P_i} = k_{\text{capture}} \left( \frac{\omega_{P_i}}{\sum_j \omega_{P_j}} \right) \]
**Idea:** Reaction probabilities are proportional to the fluxes through the transition states for the various reaction channels.

How do we calculate fluxes for complex ion-neutral systems?

**Statistical Phase Space Theory (Fluxes)**


**Bimolecular Reactions**


**Unimolecular Reactions**


We’ll take the unimolecular perspective.
1) Simple Example:

\[ k(E,J) = \frac{F^\dagger(E,J)}{\rho_A(E,J)} \]

\[ k(T) = \int_E \int_J P_T(E,J) k(E,J) dJ dE \]
2) Life is more complicated!

Multiple transition states and transition state switching


\[
A \xrightarrow{k(E,J)} B + C
\]

\[
k(E,J) = \frac{F^+(E,J)}{\rho_A(E,J)} \omega(E,J)
\]

\[
\omega(E,J): \text{probability}
\]

\[
A \rightarrow B + C \text{ once it passes the first transition state}
\]

\[
\omega(E,J) = \frac{F^\text{orb}}{F^+ + F^\text{orb} - \frac{F^+ F^\text{orb}}{F^\text{max}}}
\]
Statistical Phase Space Theory

Limiting cases:

ω(E,J) = \frac{F^{\text{orb}}}{F^+ + F^{\text{orb}} - \frac{F^+ F^{\text{orb}}}{F^{\text{max}}}}

1) Energy Barrier

F^+ \ll F^{\text{orb}}
F^{\text{max}} \approx F^{\text{orb}}
ω \rightarrow 1

k = \frac{F^+}{\rho_A}

Same as our simple example.
Statistical Phase Space Theory

Limiting cases:

\[ \omega(E, J) = \frac{F_{\text{orb}}}{F^+ + F_{\text{orb}} - \frac{F^+ F_{\text{orb}}}{F_{\text{max}}}} \]

2) Near Threshold, NO Barrier

\[ E \approx E_0 \]
\[ F_{\text{orb}} \ll F^+ \approx F_{\text{max}} \]
\[ \omega \rightarrow \frac{F_{\text{orb}}}{F^+} \]
\[ k = \frac{F_{\text{orb}}}{\rho_A} \]
Statistical Phase Space Theory

Limiting cases:

ω(E,J) = \frac{F_{\text{orb}}}{F^{\dagger} + F_{\text{orb}} - \frac{F^{\dagger} F_{\text{orb}}}{F^{\text{max}}}}

3) Well Above Threshold, \text{NO Barrier}

E \gg E_0 \implies F^{\dagger} \ll F_{\text{orb}} \approx F^{\text{max}}

\omega \to 1

k = \frac{F^{\dagger}}{\rho_A}
Limiting cases:

\[ \omega(E,J) = \frac{F_{\text{orb}}}{F^\dagger + F_{\text{orb}} - \frac{F^\dagger F_{\text{orb}}}{F_{\text{max}}}} \]

4) At intermediate energies, full expression for \( \omega(E,J) \) used.
Double Deep Well Potentials

- **Unified Statistical Theory**
- **Transition State Branching Analysis**


General solution: \( A_1 \rightleftharpoons A_2 \rightarrow B + C \)

\[
k(E,J) = \frac{F_1^+ F_{\min}}{F_1^+(\rho_{A_1} + \rho_{A_2}) + \rho_{A_2} F_{\min}}
\]

\( F_{\min} = \text{lesser}(F_1^+, F_{2\text{orb}}) \)

- add multiple reaction channels
- add \( P(E,J) \)…

Well, you get the idea
Some Current Theoretical Challenges

1. Ion-Ion Recombination Reactions

\[ A^{n-} + B^{m+} \rightarrow [AB^{(m-n)}]^* \rightarrow \text{Products} \]

- Rates
- Product distributions
- Energy partitioning
- PES

Scott McLucky
Tim Su
Others?

2. Fragmentation of Multiply-Charged Ions

\[ (AB)^{x+} \rightarrow A^{y+} + B^{(x-y)+} \]

- Which products?
- What charges?
- Energy partitioning
- PES
3. Dissociation of Large Clusters/Assemblies

\[(A)_n^{x+} \rightarrow (A)_{n-1}^{y+} + A^{(x-y)+}\]

- Asymmetric charge distribution
- Transition state structures
- Microscopic reversibility?
- Energy issues
  - kinetic shift
  - product energy distributions

Carol Robinson
Evan Williams
John Klassen
Albert Heck
Joe Loo
Others?
4. Structures of Peptides & Oligonucleotides

- The protein folding problem!!
- Solvation effects
- New MM/MD protocols

The Bowers Group
- Martin Jarrold
- David Clemmer
- David Russell
- Many Others

5. Electron Capture Dissociation

- Mechanism
- Ergodic vs. nonergodic
- Product distributions
- PES

Fred McLafferty
- Roman Zubarev
- Frantisek Turecek
- Einer Uggerud
- Alan Marshall
- Many Others
Tues. AM  
Metals in Biology  
*Determination of the Structure of the Zn^{2+} Oxytocin Complex: Implications for Oxytocin-Receptor Binding*  
A. B. Seuthe, D. Liu, O. T. Ehrler, X. Zhang,  
T. Wyttenbach, and M. T. Bowers

Tues. PM  
Solvation vs. Gas-Phase Biomolecule Structure  
*Solution-Phase Structures Can Be Sprayed into the Gas Phase and Survive: Some Examples and Some Reasons Why*  
M. T. Bowers, T. Wyttenbach, S. L. Bernstein,  
A. Ferzoco, and E. Shammel Baker

Wed. PM  
Fundamentals of Oligonucleotide Reactions  
*Onset of Helix Formation and Other Structural Aspects in DNA Duplexes*  
A. Ferzoco, E. Shammel Baker,  
J. Gidden, and M. T. Bowers
Please Remain in Your Seats!

A special (short) presentation will follow the Distinguished Contribution Award Presentation
Alan G. Marshall

Professor of Chemistry
Florida State University

Director of National High Magnetic Field Laboratory ICR Program

AGM Turns 60
## Some Fast Facts

### Academics
- **1970**: PhD, age: 26
- **1969**: Lecturer, 25
- **1980**: Professor, 36
- **1993**: Professor, 49
- **2004**: VP Program, 60

### Awards
- **1995**: Field & Franklin, ACS
- **1999**: Distinguished Contribution, ASMS
- **2000**: Thomson Gold Medal, IMSS
- **2004**: Special Honor Issue, IJMS

### Publications
- ~380: At this moment
- >10,000: Citations
Fourier Transform Ion Cyclotron Resonance Spectroscopy
M. Comisarow and A. G. Marshall

Figure 2. Ultra-high resolution FT-ICR mass spectrum of a ternary mixture of CO, N₂, and ethylene near m/e = 28.
ALANMARSHALL$^{1+}$

Charge Solvation

Salt Bridge

300 Å$^2$

283 Å$^2$