



52nd ASMS Conference



Distinguished Contribution Award Address

Collision Theory

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Outline

- 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

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)

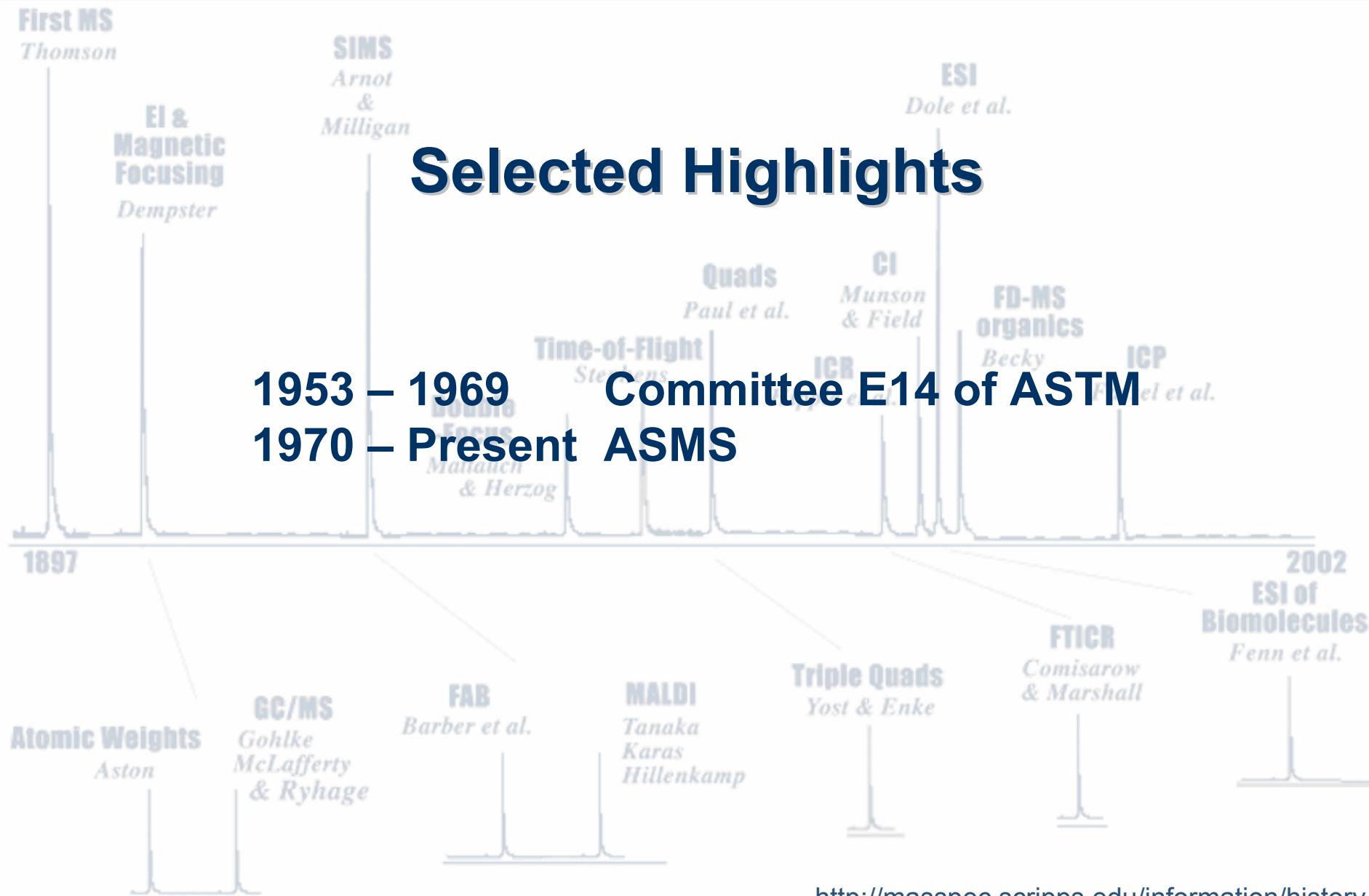
- (5) Negative Ion MS
- (6) CID
- (13) Peptide Fingerprinting
- (14) Six-Member Ring Rearrangements

Theory (1)

- (15) Collision Theory

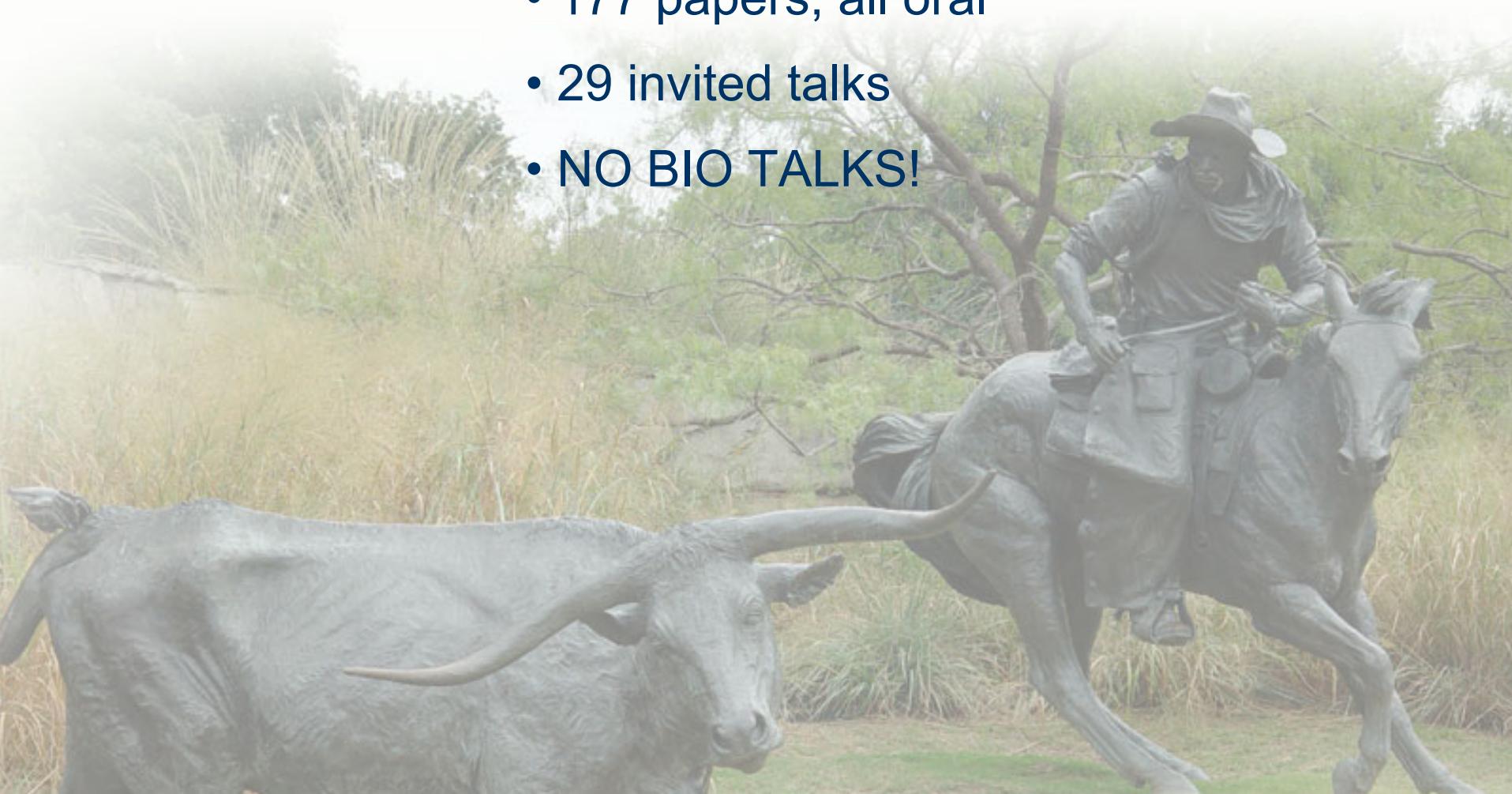


The Conference



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%

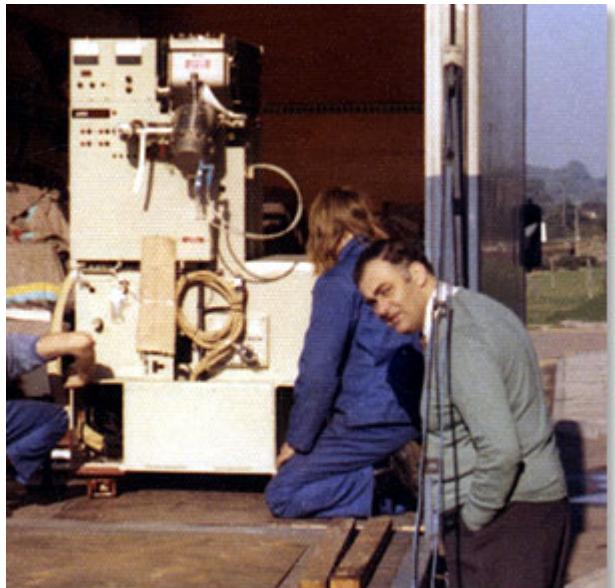
PhD: 55%

Average age: 39

| | | |
|-------------|------------|-------|
| Discipline: | Phys/Inorg | 32.5% |
| | Organic | 31.8 |
| | Physics | 14.5 |
| | Biochem | 13.4 |
| | Geology | 7.8 |



1971 • Atlanta, GA & 1972 • Dallas, TX



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





1975 • Houston, TX



- 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



1976 · San Diego, CA



- 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!



1977 • St. Louis, MO



- 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

- The Waldorf Astoria!

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



1983 • Boston, MA



- 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

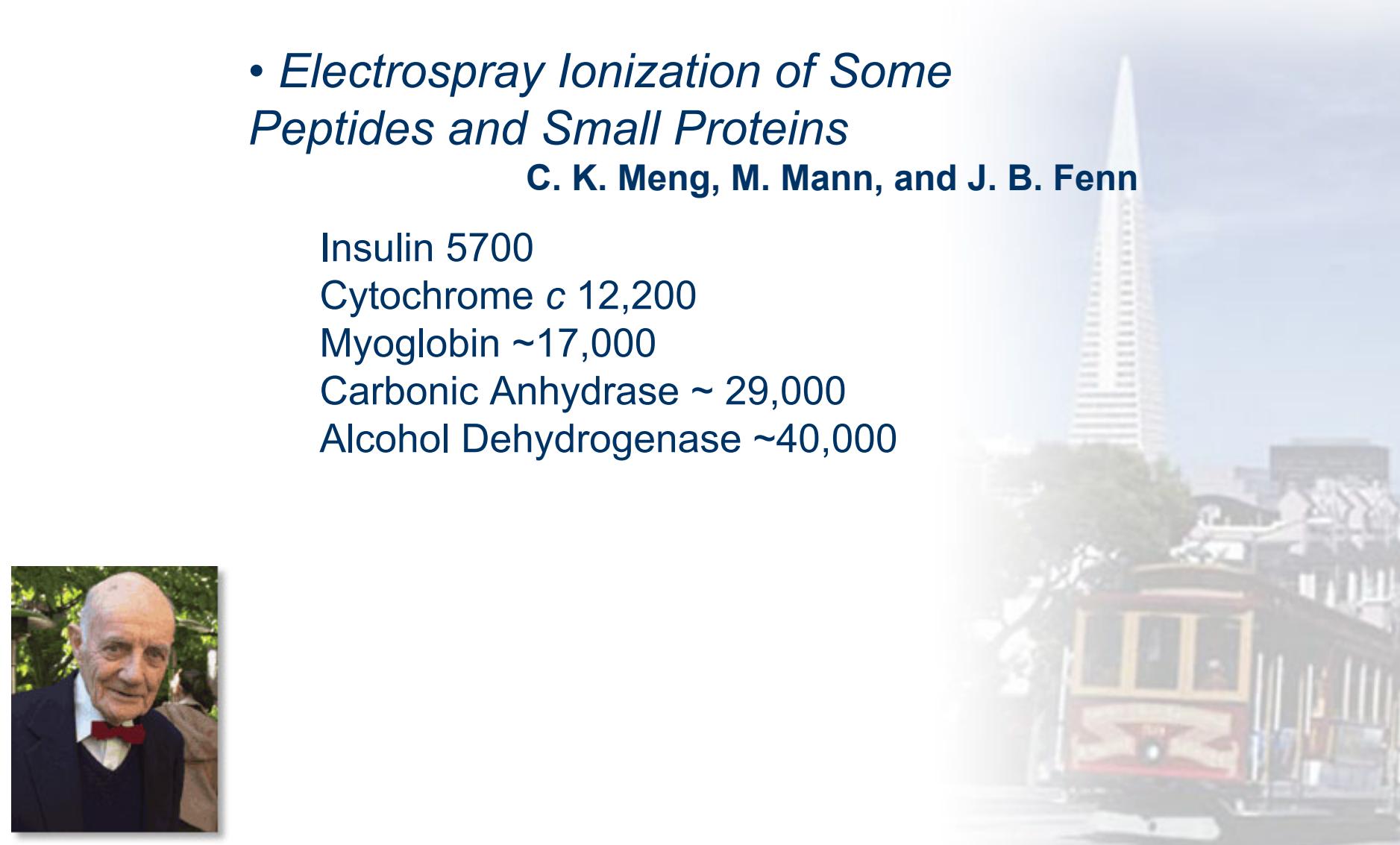
Insulin 5700

Cytochrome c 12,200

Myoglobin ~17,000

Carbonic Anhydrase ~ 29,000

Alcohol Dehydrogenase ~40,000





1989 • Miami Beach, FL



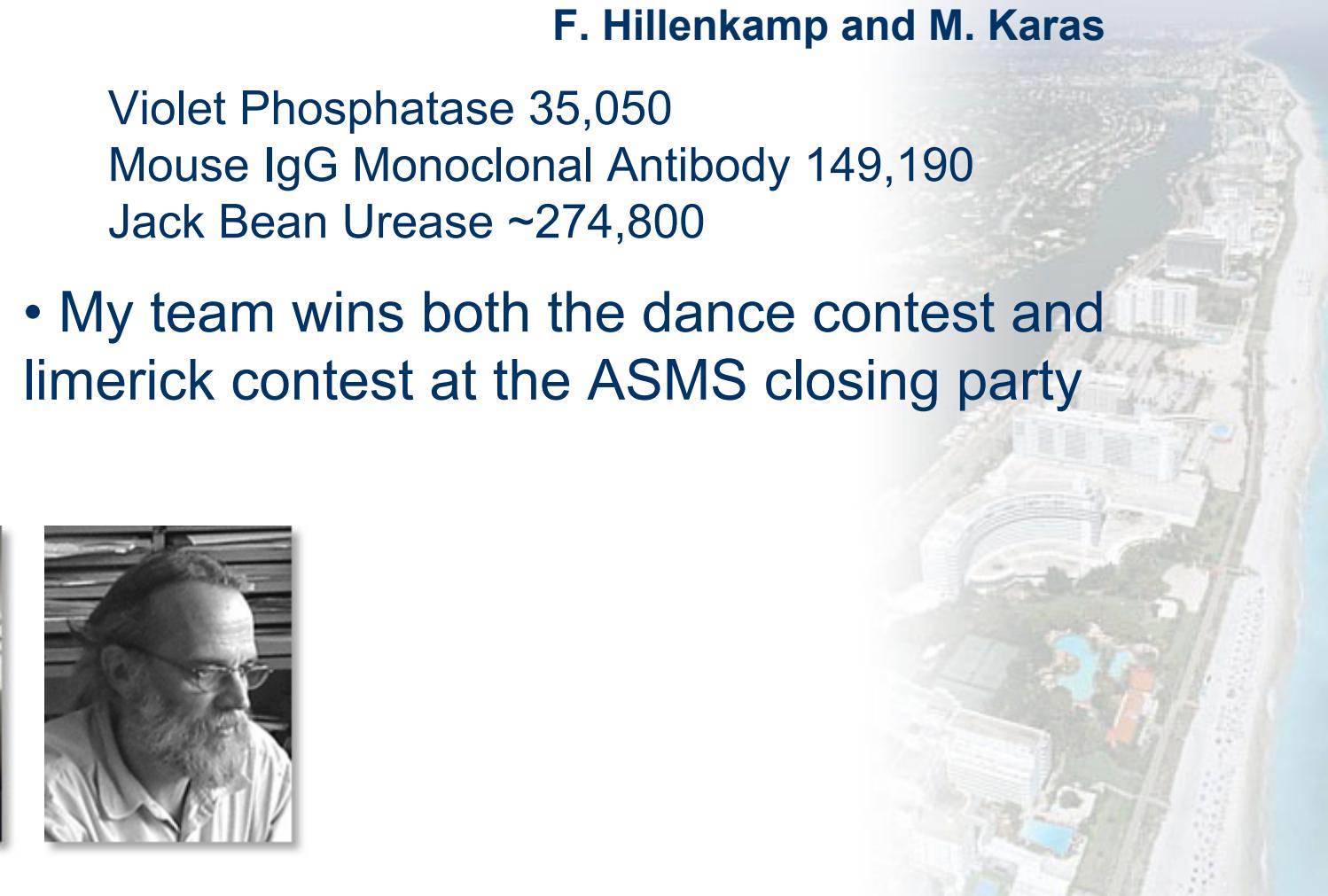
- *Ultraviolet Laser Desorption/Ionization of Biomolecules in the High Mass Range*
F. Hillenkamp and M. Karas

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



- 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



- 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



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

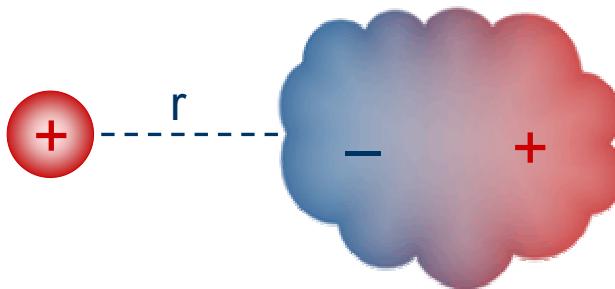
- Tim Su
- Walt Chesnavich
- Lew Bass

Applications continue to the present day

1. Pure Polarization (no dipole)
2. Locked Dipole
3. Average Dipole Orientation (ADO)
4. Conservation of Angular Momentum (AAD)
5. Variational Transition State Theory
6. Trajectory Calculations

Assumptions:

- Point charge
- Point polarizable neutral



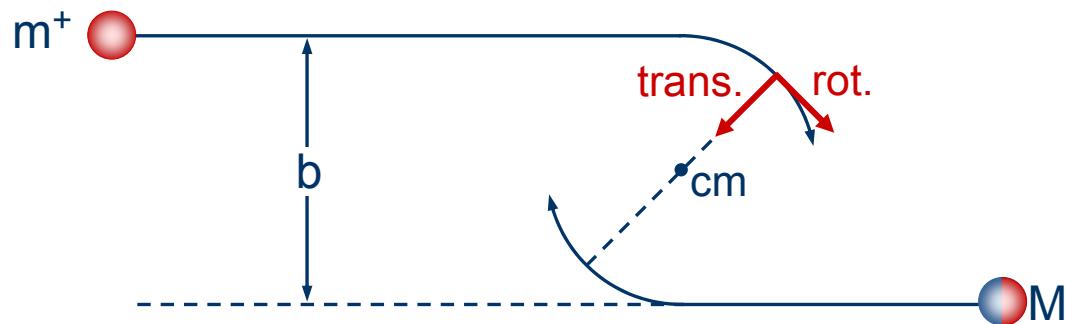
$$V(r) = -\frac{\alpha q^2}{2r^4}$$



- P. M. Langevin, *Ann. Chem. Phys.* **5**, 245 (1905)
- G. Gioumousis and D. P. Stevenson, *J. Chem. Phys.* **29**, 294 (1958)



Idea: Calculate maximum impact parameter for ion-neutral capture



capture : $r_{m^+M} \rightarrow 0$

orbiting collision : dividing surface between capture and scattering

$$E_{\text{trans}} = 0$$

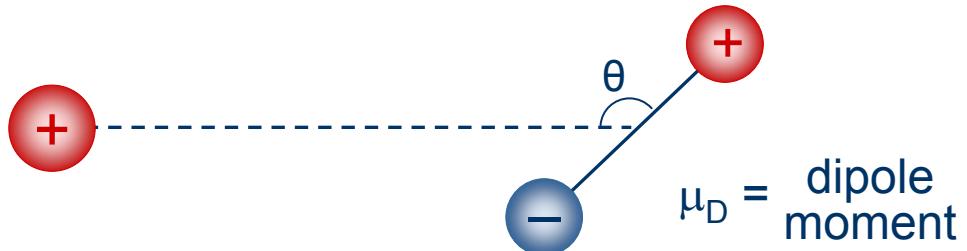
$$E_{\text{tot}} = E_{\text{rot}} + V(r) = V_{\text{eff}}(r) = \frac{L}{2\mu r^2} - \frac{\alpha q^2}{2r^4}$$

$$k_P = 2\pi q \left(\frac{\alpha}{\mu}\right)^{1/2}$$

Ion Dipole Theory

Assumptions:

- Point charge
- Point dipole



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

Maximum Effect:

$\cos\theta = 1 \rightarrow$ Locked Dipole

T. F. Moran and W. H. Hamill,
J. Chem. Phys. **39**, 1413 (1963)

$$V_{\text{eff}}(r) = \frac{1}{r^2} \left(\frac{L^2}{2\mu} - q\mu_D \right) - \frac{1}{r^4} \left(\frac{\alpha q^2}{2} \right)$$

$$k_{LD} = k_P + q\mu_D \left(\frac{8\pi}{kT} \right)^{1/2}$$



Ion Dipole Theory vs. Experiment

Exothermic Proton Transfer Reactions: $\text{AH}^+ + \text{B} \rightarrow \text{BH}^+ + \text{A}$

- R. S. Helmsworth et al., *Chem. Phys. Lett.* **26**, 417 (1974)
- G. I. Mackay et al., *J. Phys. Chem.* **80**, 2919 (1976)

| # Expts. | % Deviation | |
|----------|-------------|----------|
| | k_P | k_{LD} |
| 63 | -43 | +170 |

Better Treatments of the Dipole Term

Average Dipole Orientation Theory (ADO)



- T. Su and M. T. Bowers, *J. Chem. Phys.* **58**, 3027 (1973)
- L. Bass, T. Su, W. Chesnavich, and M. T. Bowers, *Chem. Phys. Lett.* **34**, 119 (1975)

Idea:

- Calculate an average value of θ or $\cos\theta$ as a function of r
- Dipole rotation does not couple to system rotation



Average Dipole Orientation Theory (ADO)

For $\overline{\theta(r_C)}$, obtain (similar results for $\overline{\cos\theta(r_C)}$):

$$\sigma(v) = \underbrace{\pi r_C^2 + \frac{\mu q^2 \alpha}{r_C^2 \mu v^2}}_{\text{Polarization}} + \underbrace{\frac{2\pi q \mu_D}{r_C \mu} \cos \overline{\theta(r_C)}}_{\text{ADO}}$$

Polarization

ADO

$$k_{\text{ADO}} = \int_0^\infty v \sigma(v) P(v) dv$$

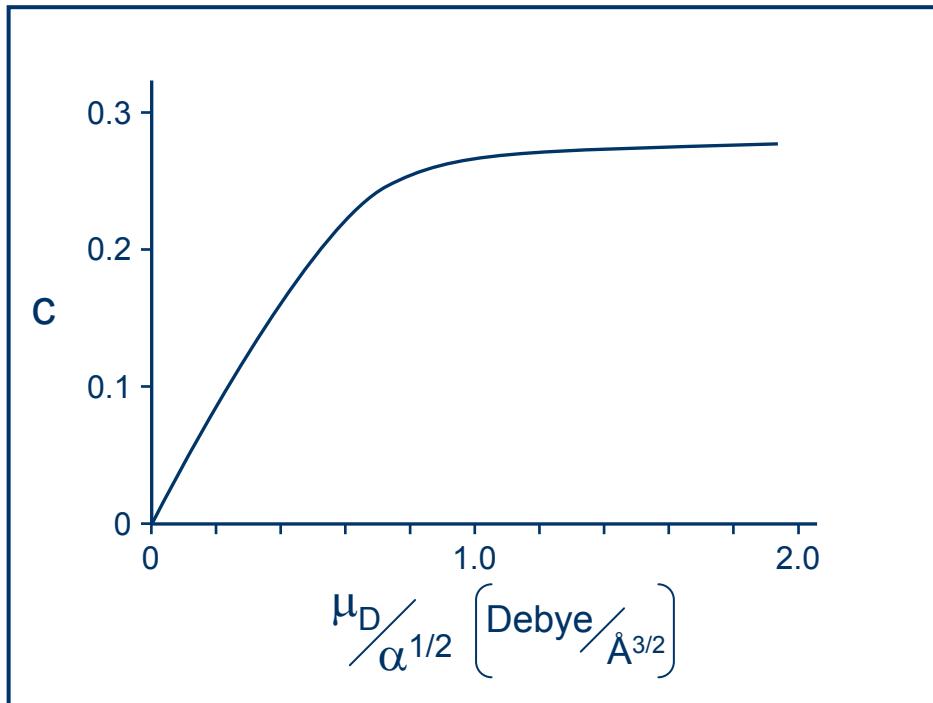
Must integrate numerically for each system

Average Dipole Orientation Theory (ADO)

T. Su and M. T. Bowers, *Int. J. Mass Spectrom. Ion Phys.* **12**, 347 (1973)

$$k_{\text{ADO}} = k_c + cq\mu_D \left(\frac{8\pi}{kT} \right)^{1/2}$$

c = dipole locking constant



Comparison:

| # Expts. | % Deviation | | |
|----------|-------------|------------------|-----------------|
| | k_p | k_{ADO} | k_{LD} |
| 63 | -43 | -5.2 | +170 |



The Question of Angular Momentum

AADO Theory

T. Su, E. C. F. Su, and M. T. Bowers, *J. Chem. Phys.* **69**, 2243 (1978)

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

Assumption:

\vec{L} and \vec{J} are collinear

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

$A = \text{angular momentum constant}$
 $= f(I, \text{other system constants})$

AADO vs. ADO



Reaction

Type

| | $k_{\text{expt}}/k_{\text{ADO}}$ | $k_{\text{expt}}/k_{\text{AADO}}$ |
|-------------------|----------------------------------|-----------------------------------|
| I (11 reactions) | 1.12 (± 0.1) | 0.99 (± 0.04) |
| II (10 reactions) | 1.21 (± 0.2) | 0.99 (± 0.15) |



Some More Exact Treatments

1. Variational Transition State Theory

W. Chesnavich, T. Su, and M. T. Bowers, *J. Chem. Phys.* **72**, 2641 (1980)

Idea: Calculate minimum flux through dividing surface using Variational Methods

$$\text{Flux(variational)} \geq \text{Flux(true)}$$

and $k_{\text{VAR}} \geq k_{\text{TRUE}}$

Note: $k_{\text{VAR}} = k_{\text{TRUE}}$ if no surface recrossing occurs

Solution: $k_{\text{VAR}} = f(\mu_D, \alpha, T)$



Some More Exact Treatments

2. Trajectory Calculations

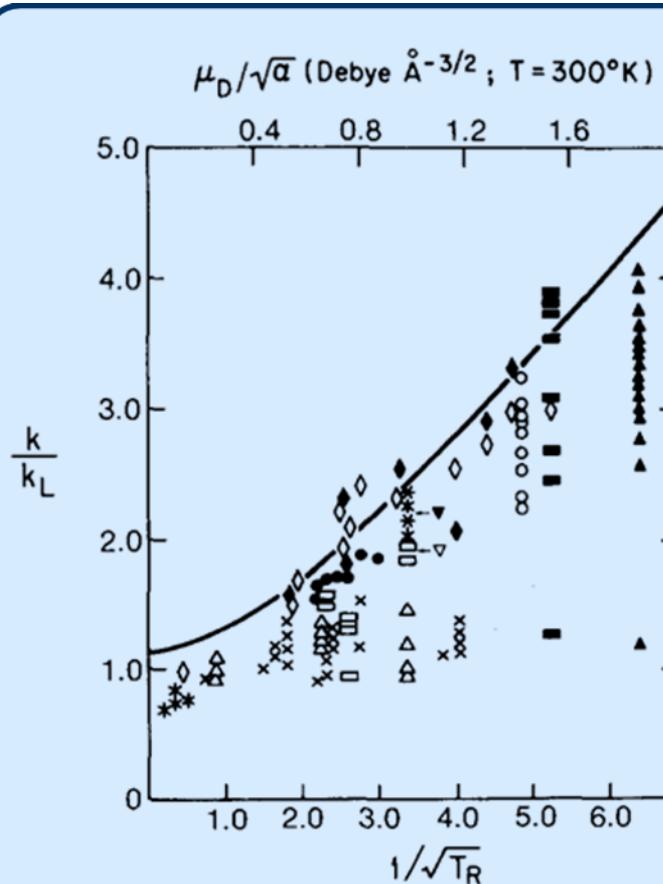
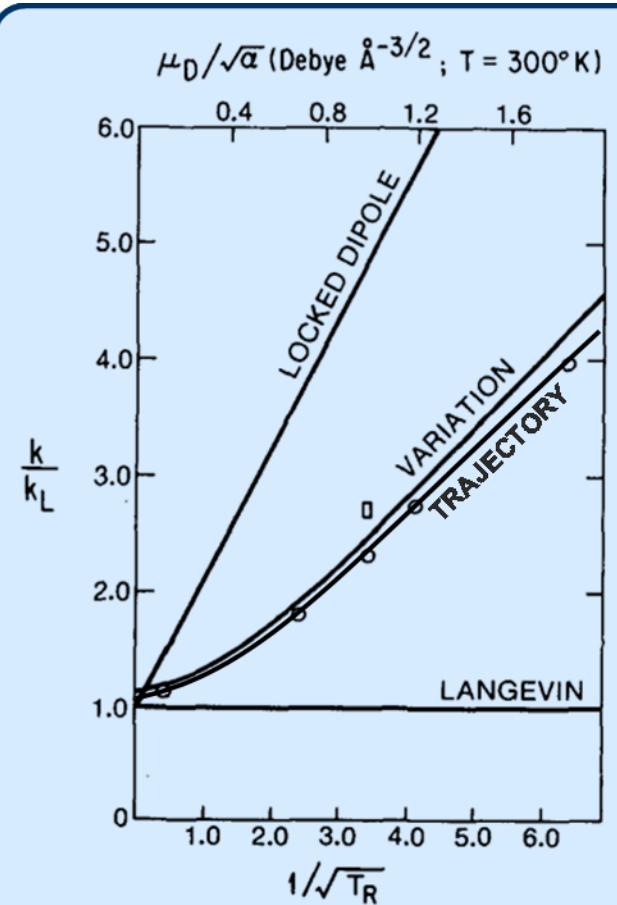
W. Chesnavich, T. Su, and M. T. Bowers, *J. Chem. Phys.* **72**, 2641 (1980)

Idea: Solve Newton's equations rigorously for

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

Solution: general for all μ_D , α , T

Comparisons



Other Effects

1. Kinetic Energy Dependence

M. T. Bowers, T. Su, and V. Anicich, *J. Chem. Phys.* **58**, 5175 (1973)

2. Ion Size

T. Su and M. T. Bowers, *Int. J. Mass Spectrom. Ion Phys.* **12**, 347, (1973)

3. Molecular Size

T. Su and M. T. Bowers, *J. Am. Chem. Soc.* **95**, 7609 (1973)

4. Average Quadrupole Orientation

T. Su and M. T. Bowers, *Int. J. Mass Spectrom. Ion Phys.* **17**, 309 (1975)

5. Temperature Dependence

T. Su and M. T. Bowers, *Int. J. Mass Spectrom. Ion Phys.* **17**, 211 (1975)

6. Induced Dipole – Induced Dipole Potential

T. Su, E. C. F. Su and M. T. Bowers, *Int. J. Mass Spectrom. Ion Phys.* **28**, 285 (1978)

7. Anisotropy in the Polarizability

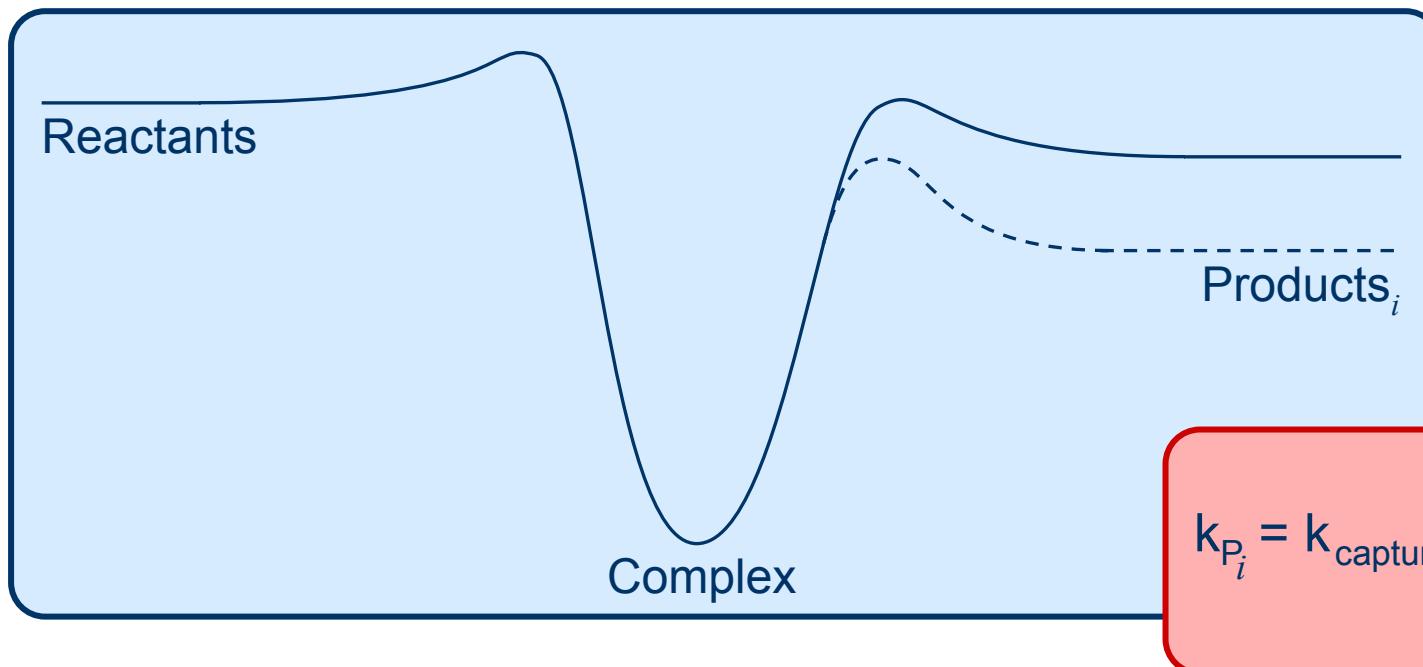
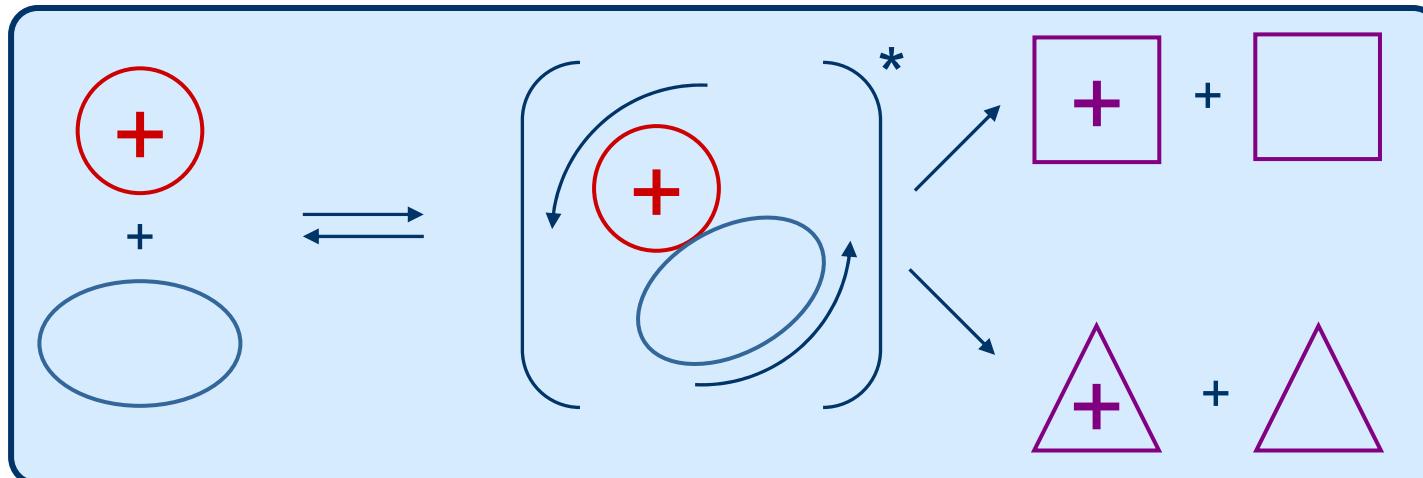
L. Bass, T. Su, and M. T. Bowers, *Int. J. Mass Spectrom. Ion Phys.* **28**, 389 (1978)

Summary to Date

1. Ion-molecule capture: a solved problem
2. Capture collisions create “chemically activated” complexes with known E, J distributions
3. What happens next?

Product Formation

Question: What governs the product distribution once a complex is formed?



$$k_{P_i} = k_{\text{capture}} \left(\frac{\omega_{P_i}}{\sum_j \omega_{P_j}} \right)$$



Statistical Phase Space Theory

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)

W. J. Chesnavich and M. T. Bowers, *J. Chem. Phys.* **66**, 2306 (1977)

Bimolecular Reactions

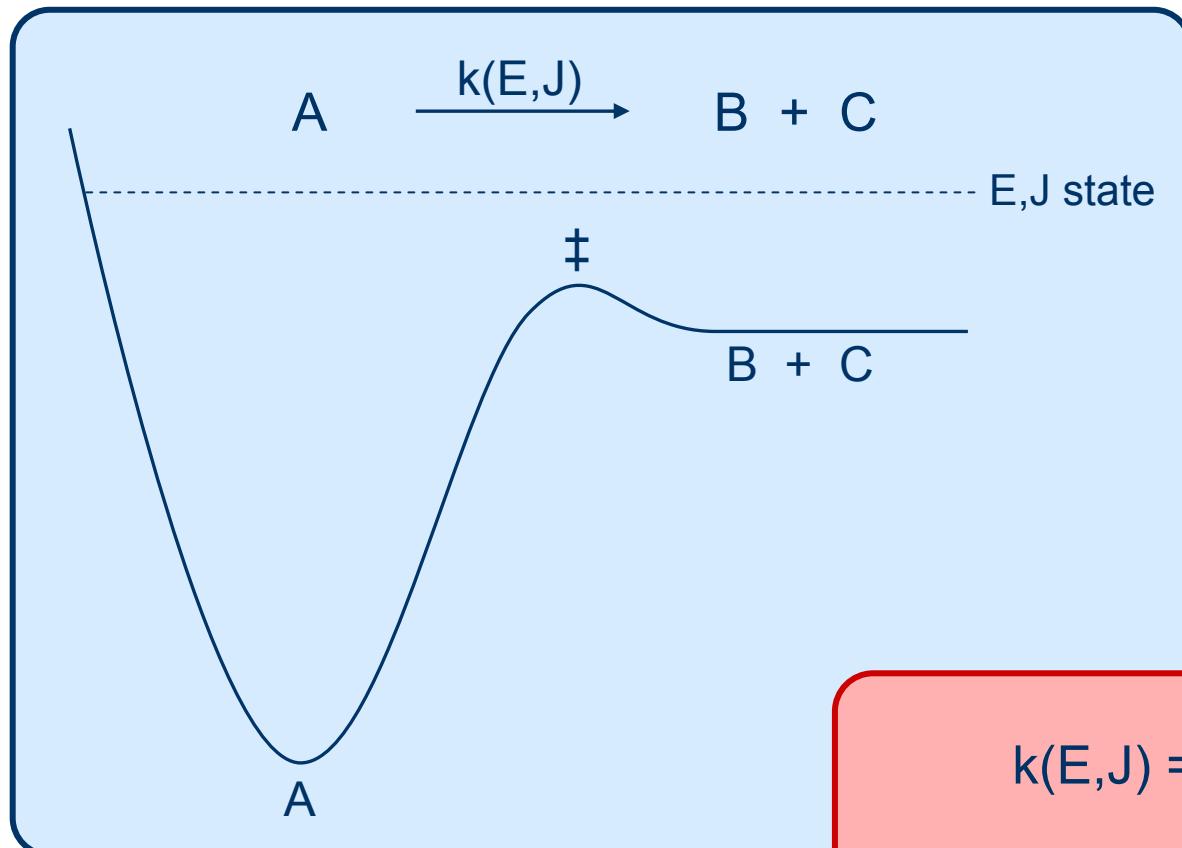
W. J. Chesnavich and M. T. Bowers, *J. Am. Chem. Soc.* **98**, 8301 (1976)

Unimolecular Reactions

W. J. Chesnavich and M. T. Bowers, *J. Am. Chem. Soc.* **99**, 1705 (1977)

We'll take the unimolecular perspective.

1) Simple Example:



$$k(E,J) = \frac{F^\ddagger(E,J)}{\rho_A(E,J)}$$

$$k(T) = \int_E \int_J P_T(E,J) k(E,J) dJ dE$$

2) Life is more complicated!

Multiple transition states and transition state switching

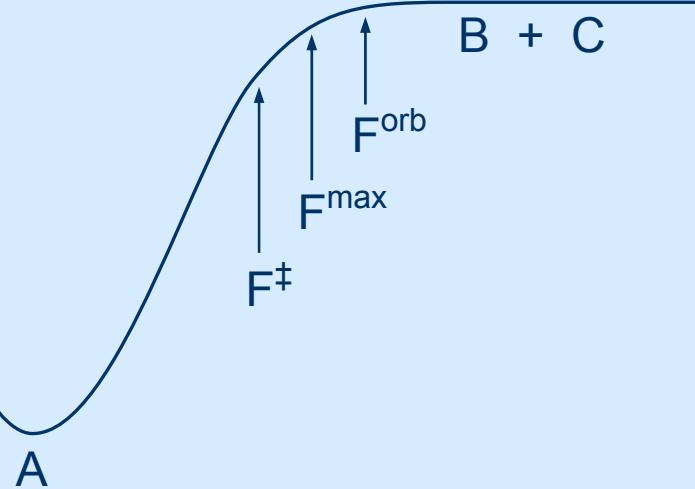
W. J. Chesnavich, L. Bass, T. Su, and M. T. Bowers, *J. Chem. Phys.* **74**, 228 (1981)



$$k(E,J) = \frac{F^\ddagger(E,J)}{\rho_A(E,J)} \omega(E,J)$$

$\omega(E,J)$: probability
 $A \rightarrow B + C$ once it
passes the first
transition state

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



Limiting cases:

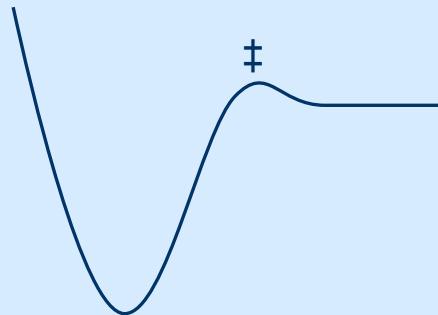
$$\omega(E, J) = \frac{F^{\text{orb}}}{F^\ddagger + F^{\text{orb}} - \frac{F^\ddagger F^{\text{orb}}}{F^{\text{max}}}}$$

1) Energy Barrier

$$F^\ddagger \ll F^{\text{orb}}$$

$$F^{\text{max}} \approx F^{\text{orb}}$$

$$\omega \rightarrow 1$$



$$k = \frac{F^\ddagger}{\rho_A}$$

Same as our simple example.

Limiting cases:

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

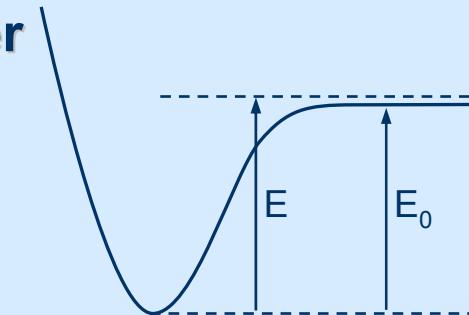
2) Near Threshold, NO Barrier

$$E \approx E_0$$

$$F^{\text{orb}} \ll F^\ddagger \approx F^{\text{max}}$$

$$\omega \rightarrow \frac{F^{\text{orb}}}{F^\ddagger}$$

$$k = \frac{F^{\text{orb}}}{\rho_A}$$



Limiting cases:

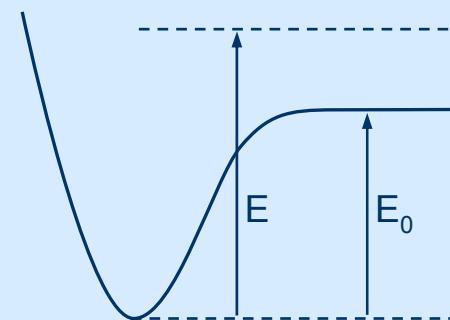
$$\omega(E, J) = \frac{F^{\text{orb}}}{F^\ddagger + F^{\text{orb}} - \frac{F^\ddagger F^{\text{orb}}}{F^{\text{max}}}}$$

3) Well Above Threshold, NO Barrier

$$E \gg E_0 \Rightarrow F^\ddagger \ll F^{\text{orb}} \approx F^{\text{max}}$$

$$\omega \rightarrow 1$$

$$k = \frac{F^\ddagger}{\rho_A}$$





Statistical Phase Space Theory

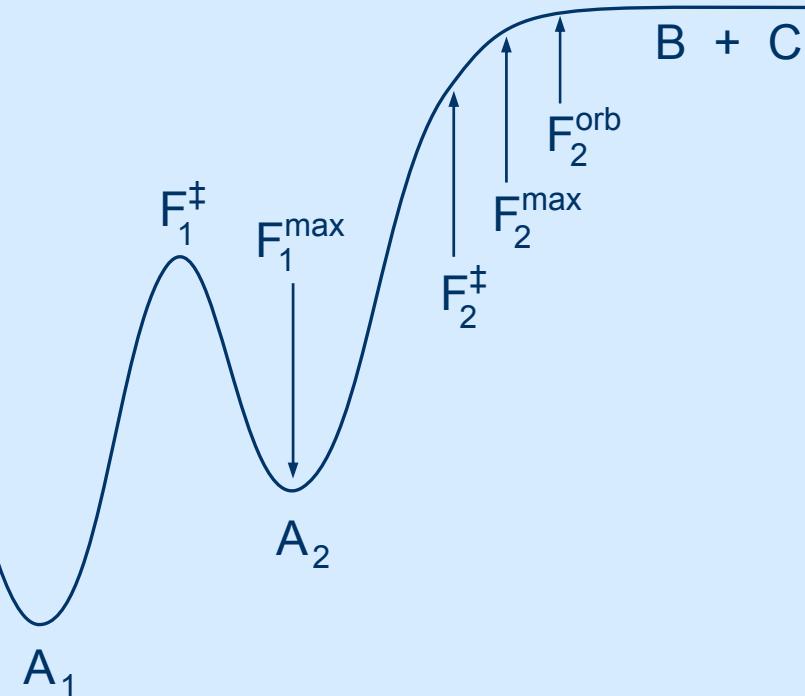
Limiting cases:

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

- 4) At intermediate energies, full expression for $\omega(E, J)$ used.

- Unified Statistical Theory
- Transition State Branching Analysis

M. T. Bowers, M. F. Jarrold, W. Wagner-Redeker, P. R. Kemper, L. M. Bass, *Faraday Discuss. Chem. Soc.* **75**, 57 (1983)



General solution: $A_1 \rightleftharpoons A_2 \rightarrow B + C$

$$k(E,J) = \frac{F_1^\ddagger F_1^{\min}}{F_1^\ddagger(\rho_{A_1} + \rho_{A_2}) + \rho_{A_2} F_1^{\min}}$$

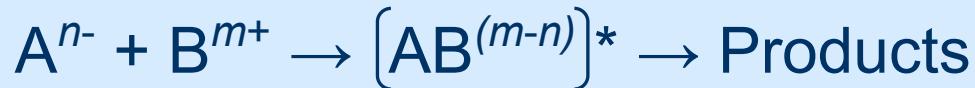
$$F^{\min} = \text{lesser}(F_2^\ddagger, F_2^{\text{orb}})$$

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

Well, you get the idea

Some Current Theoretical Challenges

1. Ion-Ion Recombination Reactions



- Rates
- Product distributions
- Energy partitioning
- PES

Scott McLucky
Tim Su
Others?

2. Fragmentation of Multiply-Charged Ions



- Which products?
- What charges?
- Energy partitioning
- PES

Some Current Theoretical Challenges

3. Dissociation of Large Clusters/Assemblies



- Asymmetric charge distribution Carol Robinson
- Transition state structures Evan Williams
- Microscopic reversibility? John Klassen
- Energy issues Albert Heck
 - kinetic shift Joe Loo
 - product energy distributions Others?

Some Current Theoretical Challenges

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



2004 • Mike and ASMS



Tues. AM

Metals in Biology

Determination of the Structure of the Zn²⁺ 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

2004 • Mike and ASMS





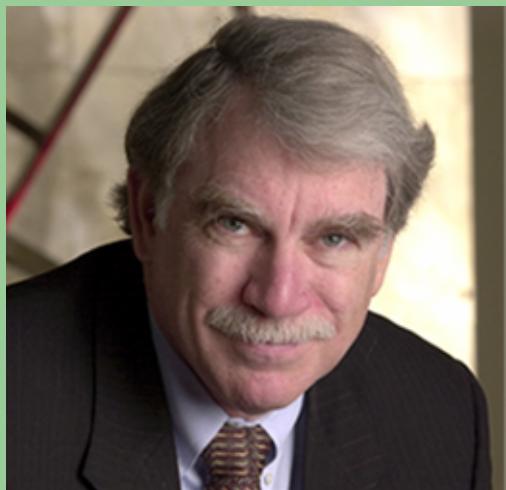
Coming Attractions



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 | |

1975 • Houston, TX

Fourier Transform Ion Cyclotron Resonance Spectroscopy M. Comisarow and A. G. Marshall

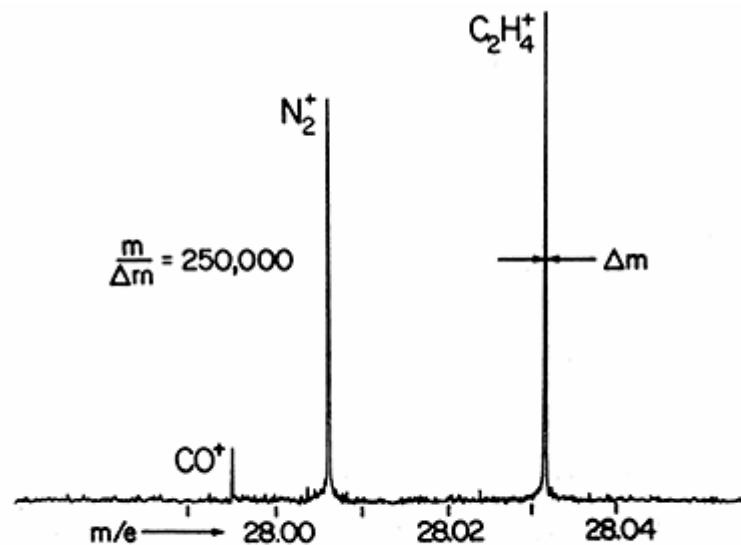
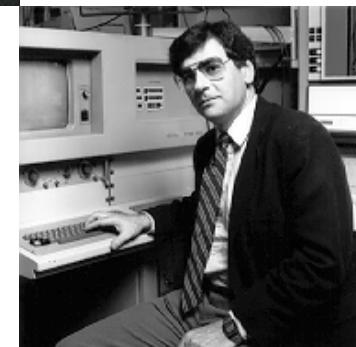
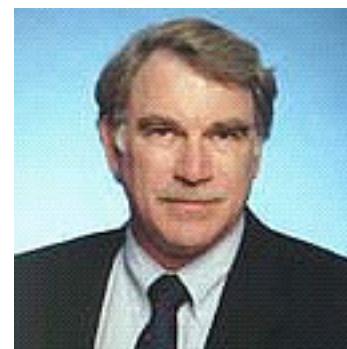
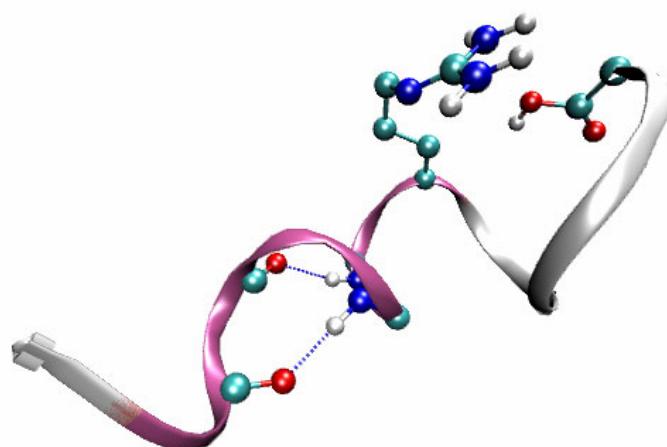


Figure 2. Ultra-high resolution FT-ICR mass spectrum of a ternary mixture of CO , N_2 , and ethylene near $m/e = 28$.



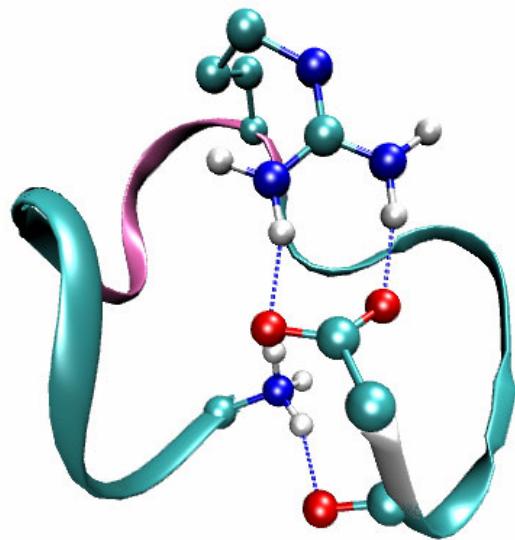
ALANMARSHALL¹⁺

Charge Solvation



300\AA^2

Salt Bridge



283\AA^2