# Laboratory Research for Planetary Atmospheres: A Review

(talk given at 1998 DPS Meeting in Madison)

**Glenn Orton, JPL**

- **Chemistry**
  - Chemical Kinetics
  - Photolysis
  - Surface Chemistry
  - Physical Chemistry
- **Spectroscopy of Gases**
  - Quantum
  - Band Model
  - Continuum
- **Spectroscopy of Condensates and Other Solids**
- **New Fields**
- **Laboratory Support for Specific Experiments**

# Laboratory support for atmospheric research needed for:

- **Accurate simulation of atmospheric processes, *e.g*.**
    - chemical reaction products and rates
    - cloud chemistry and physics
    - radiative equilibrium

- **Accurate remote sensing of planetary and cometary atmospheres, from ground-based, earth-orbiting, and interplanetary facilities.**
    - composition
    - atmospheric temperature
    - cloud structure and composition

# Models of Solar System Atmospheres Need Laboratory Measurements - 1

## Collisional Rate Constants

- Temperature dependence
- Pressure dependence
- 3-body recombination products
- Product species identification
- Heterogeneous processes

## Photocross-sections

- Wavelength dependence
- Temperature dependence
- Product yields

## Ion-electron recombination rate constants

- Temperature dependence
- Product yields

## Electron-neutral collisional rate constants

- Temperature dependence
- Product yields

## Vapor pressures

- Temperature dependence

## Models of Solar System Atmospheres Need Laboratory Measurements - 2

**Cloud physics**

- Coagulation

**Radiative transfer**

- Spectroscopic line parameters for all species of interest
  - -Temperature and pressure dependence
  - -Distant line wing behavior, temperature and pressure dependence
- Continuum absorption parameters
  - -Temperature and pressure dependence
- Tabulated absorption coefficients
  - -Temperature and pressure dependence
- Thorough inventory of relevant lines for each species
- Absorption of condensates and other solids
  - -Wavelength dependence
  - -Dependence on temperature of formation
  - -Dependence on irradiation history

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# "Executive Summary"

Virtually nothing known about **chemical kinetics** at low temperatures.

Virtually nothing known quantitatively about relevant **surface chemistry**

Ancient values for constants used routinely in models of **physical chemistry**.

Large number **of un- or understudied molecular and atomic transitions** (*e.g.* hydrocarbons or nitriles).

Difficult, **but good progress with major atmospheric constituents** (*e.g.* $CH_4$, $NH_3$ in the outer solar system).

Where necessary, increasingly **sophisticated band models** are being devised (e.g. temperature-dependent exponential sum coefficients).

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**Collision-induced spectroscopy** on firmer quantum mechanical basis but needs to be extended to shorter wavelengths.

Need for realistic models of **line wings** is just being recognized.

**Spectroscopy of solids or liquids** that are cometary or planetary atmospheric or constituents (or good candidates) needs to be performed (*e.g.* $NH_4SH$, to interpret Galileo probe data).

Innovative thinking may be required in order to **investigate new fields**, *e. g.* X-ray remote sensing.

**Deposition and dissemination of laboratory data** relevant to planetary atmospheres must be done through a peer-reviewed and regulated process.

**Specific mission experiments** often need *a posteriori* laboratory support unavailable through mission resources.

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Thanks go to all who gave me comments on my inquiries:

Joe Ajello
Sushil Atreya
Kevin Baines
Yves Benilan
Bruno Bezard
Linda Brown
Gordy Bjoraker
Barbara Carlson
Barney Conrath
Athena Coustenis
David Crisp
Pierre Drossart
Peter Gierasch
Martha Hanner
Janes Hoffman
Don Hunten
Roger Knacke
Patrick Irwin
Don Jennings
Keith Noll
Toby Owen
Boris Ragent
Francois Raulin
Dennis Reuter
Paul Romani
Al Seiff
Nick Smith
Paul Steffes
Darryl Stroebel
Prasad Varanasi
Robert West

# Chemical Kinetics

## Missing reaction rates

Hydrocarbons, nitriles, many of relevant kinetics

Many missing for polyyne species, $C_4H_2$ and higher

All molecules related to $C_6H_x$ and higher

Hydrocarbons such as $CH_3C_2H$ and $CH_2CCH_2$

Termolecular rates

## Reactions at low temperatures

- Current rates are extrapolated perilously to low temperatures

- Termolecular rate constants

- $CH_3$ recombination rate at low temperatures

  Good atmospheric tracer to derive useful value of eddy diffusion coefficient, detected by Bezard *et al*.

  Poorly constrained, owing to lack of accurate recombination rate.

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- Uncertain kinetic reaction rates - progress

| | |
|---|---|
| $C_2H + H + CH_4$ | Opansky *et al.* |
| CH | Rowe *et al.* |

- Problem is not so much measuring reaction rates at low temperatures (they can be estimated), as much as it is determining products.

- Example: Romani *et al*. re-examined $C_2H_3 + H_2$ and $C_2H_3 + H$ reaction to explain chronic mismatch between theory and observation in Jupiter's $C_2H_2$ and $C_2H_2$ ratios.

  While their re-examination of these rates put the theory and observations into better agreement, other examinations of the chemical product channels (Monks *et al*.) tended to make the theory disagree again.

  "What the laboratory chemist taketh away, doth he not also restore?"

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## Re-examine Photolysis Data

- For temperature dependence, *e.g*. $C_4H_2$ absorption as a function of temperature.
- For influence of contaminants, *e.g*. influence of 1% acetone in $C_2H_2$ spectrum
- For dependence of quantum yield on photolysis wavelength
- For quantum yields of formation
- For quantum yields of photodegradation, particularly high molecular weight products of cometary interest
- For dependence on the "bath" gas, particularly in 3-body reactions

**Another example (Stroebel): Chemistry of CNN in Triton's atmosphere**

- How are energy sources partitioned between solar EUV and magnetospheric electrons?

- Answer depends critically on $C_2^+ + C \rightarrow C^+ + N$, for which there are no laboratory measurements available.

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### Physical Chemistry

- Galileo probe results for “middle cloud” attributed to $NH_4SH$, consistent with decades-old equilibrium chemistry-based paradigm.

- Relevant thermodynamical data are ancient, however:

Walker and Lumsden (1897) J. Chem. Soc. London **71**, 428.

Isambert (1879) Comptes Rendus **89**, 96.

Isambert (1871) Comptes Rendus **92**, 919.

- General work on binary, ternary and higher systems on gas-liquid and gas-solid equilibrium in general, $C_2H_2$ - $C_2H_2$ - $N_2$ in particular for Titan

## Surface Chemistry

- Paradigm from terrestrial chemistry: $O_3$ chemistry cannot be understood with gas phase chemistry alone - heterogeneous reactions occur on polar stratospheric cloud particles (essential ingredient in $O_3$ chemistry)

- Giant planets, Titan and Triton have significant level of haze particles, but measurements of chemistry have all so far been for gas phase

- Conversion between ortho- and para-$H_2$

  Important as tracer of circulation

  Important as possible source of latent heat, particularly in the atmospheres of Uranus and Neptune where it is comparable to diabatic heating

  Need laboratory studies to address equilibration times in presence of photon-activated paramagnetic sites on surfaces of $NH_3$ or $CH_4$ ice crystals

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## Non-LTE effects in stratospheres

- Vibrational relaxation rates at low temperature

  $CH_4$

  $C_2H_2$

  $C_2H_2$

  $C_2H_6$

- VT rates relatively secure
- VV rates uncertain

- Relevant to radiative cooling in upper stratospheres of Giant planets and Titan

- Relevant to remote sensing of stratospheric hydrocarbons with ISO and Cassini CIRS.

# Spectra of Gases

- Very important for radiative equilibrium, but most of user-originated motivation for remote sensing

- Composition: planets, comets

- Clouds, hazes

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## Discrete Spectroscopy

- Subject of intense work
- We inherit some of terrestrial gas parameters
- But need to determine lines parameters for higher temperature regimes: Venus, brown dwarfs
- Need to understand long-path, low-pressure line shapes for Mars' atmosphere

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Examples given for outer planet atmospheres.

- $CH_4$
- $NH_3$
- Both exemplify the need for very faint lines and very high frequencies (short wavelengths) that are needed
- Some lines known very well
- Some lines known empirically, but no quantum identification is possible
- Some absorptions have band estimates only

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## Incomplete litany of spectroscopic line parameter needs

- Need $CO_2$, $CH_4$ for "warm" planets, brown dwarfs

- Need $PH_3$ near 3 µm.

  (Successes near 5 µm allowed identifications of trace gases, such as $GeH_4$.)

- $AsH_3$ - although lots of work on this in last 3-4 years, have these parameters been entered in any data base?

- Hydrocarbons and nitriles

  $C_2N_2$ hot band

  $HC_3O$ at 670, 719 cm-1

  $C_3H_4$ at 710, 1241 cm-1

  $C_2H_2$ at 1304 $cm^{-1}$

## Non-LTE Lines: FUV and EUV Electron Impact

- Required for auroral-related processes
- For earth, involves ions of N (also Titan) and O
- For outer planets, involves H (Lyman series) and $H_2$ (Rydberg series)
- Recent line theory (Abgrall *et al.*) works well in FUV
- Difficulty, particularly in EUV, is the abundance of highly overlapping and mutually perturbing transitions
- Requires high-resolution measurements resolving individual lines

- $GeH_4$ - only 1 of 5 isotopes measured
- Complete parameter lists for $C_4H_2$, allene, methyl acetylene
- $SiH_4$
- Rotational $CH_4$

Some successes at GSFC

- $CO_2$, $CO_2$+$N_2$
- C3H4 (allene)
- C2H4 - complete $\nu_2$, $\nu_7$, $\nu_{10}$ and $\nu_{12}$
- $C_2H_6$ - torsional splitting.

# Band Models

- Because there are no quantum identifications or even empirical measurements of individual lines
  - For example, work of Karkoschka et al. using planetary atmospheres as "natural laboratories"
  - Laboratory work of O'Brien et al.

- Because it's convenient
  - Quickly computable transmission values, usually in form of

$$\sum_{I} \exp(-k_i \tau)$$

  to simulate various contributions from a finite set of monochromatic components (amenable to multiple scattering).

  - Predominant use is in near infrared:
    Baines *et al.,*
    Strong,
    Irwin *et al* (NIMS data analysis).

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# *Ab initio* characterization of collision-induced phenomena relevant to the atmospheres of the outer planets, Titan and Venus

- **Paradigm of communication between theorists and spectroscopic user community.**

J. Borysow, L. Frommhold and G. Birnbaum. 1987. Collision-induced rototranslational absorption spectra of $H_2$-He pairs at temperatures from 40 to 3000 K. ***Astrophys. J.*** **326**, 509-515.

**A.** Borysow and L. Frommhold. 1986. Theoretical collision-induced rototranslational absorption spectra for modeling Titan's atmosphere: $H_2$-$N_2$ pairs. ***Astrophys. J.*** **303**, 495-510.

**A.** Borysow and L. Frommhold. 1986b. Theoretical collision-induced rototranslational absorption spectra for the outer planets: $H_2$-$CH_4$ pairs. ***Astrophys. J.*** **304**, 849-865.

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A. Borysow and L. Frommhold 1986c. Collision-induced rototranslational absorption spectra of **$N_2$-$N_2$** pairs at temperatures from 50 to 300 K. ***Astrophys. J***. **318**, 940-943.

G. Marcia and A. Borysow. 1997. Rototranslational collision induced absorption of **$CO_2$** for the atmosphere of Venus at frequencies from 0 to 250 $cm^{-1}$, at temperatures from 200 to 8800 K.. ***Icarus*** **129**, 172-177.

G. Birnbaum, A. Borysow, and G. S. Orton. 1996. Collision-induced absorption spectra of **$H_2$-$H_2$** and **$H_2$-He** in the rotational and fundamental band for planetary applications ***Icarus*** **123**, 4-22.

$H_2$ collision-induced absorption to overtones in visible region:

- New observations by Brodbeck *et al*.
- Extension of ab initio theory by Borysow and students in progress

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## “Continuum” Spectroscopy

### Collision-induced phenomena

- Series of studies by Frommhold, Borysow and students with direct input on studies of outer planets and Titan

### Microwave “Continuum”

- **$NH_3$**- combination of Spilker and Joiner & Steffes models has opacity modeled well up to $\lambda = 2$ mm, but not shorter

- **$SO_2$**- well characterized by Suleiman and Steffes

- **$PH_3$**- (this meeting) 10x opacity than implied by predictions of Poynter-Pickett-Cohen catalogue

  possible solution to unexpected “large” opacity required in Jupiter to model $NH_3$ mixing ratio derived by Galileo probe relay signal attenuation experiment (Folkner *et al*.)

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# Spectroscopy of Solids

**Cometary needs**

- Infrared spectra of silicates of various types
  (much work already being done outside U.S.)

- Ices of low-temperature formation

- Laboratory work needed on structure and composition of chondritic aggregate interstellar dust particles of cometary origin

- Recent successes in interpreting Titan's spectrum to analyze better various candidate condensates

- Continued work on "tholins" to characterize compositional difference to expand the venerable work of Khare *et al.* Some recent work has begun by Coll *et al.*

## General

- Space weathering is a big concern, both for the surfaces of icy satellites, as well as for atmospheric particulates

  Some work, *e.g.* Moore et al., addresses this need.

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# New Topics?

- X-ray emission has been detected from Jupiter and comets

  New studies required in:

  charge transfer

  electron stripping

  cross sections of energetic oxygen and sulfur ions interacting with atomic and molecular hydrogen

- Surface-atmospheric chemical and physical interactions

  For Mars, chemical kinetics of water govern its stability in the atmosphere, not simple phase boundaries.

  Kinetics controlled by local heating rate, solute composition and abundance, surface tension, etc. as much as local pressure and temperature.

  Problem is sufficiently complex that a laboratory experiment should be designed to study these processes for Mars-like conditions

## Practical Experiments

- Devise some means to do *in situ* "wet chemistry" with small direct sampling experiments.

- Devise other compositional experiments besides mass spectroscopy and gas chromatography that are simple, precise and unambiguous (*e.g.* spectroscopic)

- Provide better simulations of atmospheric probe descent conditions, *e.g.* Galileo probe parachute drag coefficient

# CONCLUSIONS

- Clearly communications between users and laboratory researchers are improving, more can be done
- We should establish a "road map" for laboratory studies, based on user-developed requirements
- We should establish a clearinghouse of user needs and laboratory capabilities
    - Develop quantitative requirements by users for laboratory measurements
    - Deposit laboratory data
    - Data to be reviewed and disseminated by others

      (e.g. HITRAN and other terrestrial atmospheric analogs)

**This is a vast topic; with luck this was better than a half-vast review!**

# Other "Miscellaneous" Topics

## •CNN radicals in Triton's atmosphere

Determination of sources and sinks for Triton's upper atmospheric chemistry (solar EUV *vs* solar EUV plus magnetospheric electrons) depends critically on key reaction rate for

$$C_2^+ + C \rightarrow C^+ + N,$$

for which no appropriate laboratory measurements are available.

## •Photoionization lifetime of cometary Na

Cometary observers and quantum-mechanical calculations imply that it is 3x longer than last measured laboratory value which clearly should be repeated.

## •UV spectrum of $N_2$

Voyager UVS occultation results for Titan and Triton require supporting laboratory measurements in 700 - 1000 Angstrom range. The absence of a detailed laboratory $N_2$ band structure in laboratory measurements prevents the detailed analysis of these atmospheres. For Triton, the UVS occultation is the only measurement of the $N_2$ density profile from 0 - 400 km.