Astrochemistry 2016

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http://www.sron.nl/~vdtak/astrochem.html
Importance of astrochemistry

- Understand evolution of interstellar medium
- Links to: star/planet formation, astrobiology
- Interesting basic chemistry at 'exotic' conditions
- Mix of astronomy, chemistry, and technology
Goals of the course

- describe types of chemical reactions in space
- know which reactions occur under which conditions
- tell the chemical composition of astrophysical objects
- use this composition to infer their physical properties
# Course Schedule

<table>
<thead>
<tr>
<th>Date</th>
<th>Topic</th>
<th>Literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>17-05-2016</td>
<td>I. Basic chemical processes</td>
<td>Tielens 2013, Rev. Mod. Phys.</td>
</tr>
<tr>
<td>19-05-2016</td>
<td>II. Gas-phase and grain surface reactions</td>
<td>Smith 2011, ARAA</td>
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<tr>
<td>24-05-2016</td>
<td>III. Early Universe chemistry</td>
<td>Galli &amp; Palla 2013, ARAA</td>
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<tr>
<td>26-05-2016</td>
<td>IV. Diffuse interstellar clouds</td>
<td>Snow &amp; McCall 2006, ARAA</td>
</tr>
<tr>
<td>02-06-2013</td>
<td>VI. Dense interstellar clouds</td>
<td>Bergin &amp; Tafalla 2007, ARAA</td>
</tr>
<tr>
<td>07-06-2016</td>
<td>VII. Star- and planet-forming regions</td>
<td>Herbst &amp; van Dishoeck 2009, ARAA</td>
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<tr>
<td>16-06-2016</td>
<td>Presentations</td>
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Literature

• Useful books about the ISM:
  • *Physics of the Interstellar and Intergalactic Medium*, B.T. Draine
  • *Physics and chemistry of the Interstellar Medium*, A.G.G.M. Tielens

• Books about astrochemistry:
  • *Astrochemistry: From astronomy to astrobiology*, A. Shaw (2006)

• For this course: use selected review papers mainly from ARAAA

• Homework: review slides *before* next lecture will be posted on-line
Prerequisites

- **Radiative Processes**
  - Planck function
  - Einstein coefficients
  - Concepts of flux, intensity, optical depth, opacity ...

- **Statistical physics**
  - Maxwell & Boltzmann distributions

- **Quantum physics**
  - Atomic structure (fine / hyperfine splittings)
  - Terms, configurations, selection rules
  - Molecular spectroscopy (electronic / vibrational / rotational)
Course Format

- Weeks 20 – 23  
  = May 17 – June 9

- Lectures Tuesday 09:00 & Thursday 15:00, ZG 161  
  move May 26 to morning?

- Check the website for changes  
  join e-mail list

- Exam = presentation of paper (June 16)  
  final grade = average of exercises & presentation
Today's lecture

Motivation
History
Observational techniques
Interstellar molecules
Current questions
Gas-phase processes
Introduction

- Molecules are found throughout the Universe
  - interstellar clouds
  - stellar & (exo)planetary atmospheres
  - ejecta of evolved stars
  - planet-forming disks
  - nuclei of galaxies (local & early universe)

- Typical conditions:
  - Diffuse clouds: $T \sim 100$ K, $n \sim 100$ cm$^{-3}$
  - Dense clouds: $T \sim 10$ K, $n \sim 10^4$ cm$^{-3}$
  - Star-forming regions: $T \sim 100$ K, $n \sim 10^6$ cm$^{-3}$
  - Protoplanetary disks: $T \sim 10$ K, $n \sim 10^8$ cm$^{-3}$

This lecture room: $T \sim 300$ K, $n \sim 3 \times 10^{19}$ cm$^{-3}$
... a highly exotic place!
Prehistory

- Bright/dark nebulae between stars: Messier, Herschel ~1800
- Interstellar Na absorption lines: Hartmann 1909
- First theory of ISM: Eddington 1926
- Predicted to be fully ionized (like IGM)
- First interstellar molecules: 1930-1940 (quite a shock!)

Today: dense interstellar clouds are essential part of formation process of stars and planets, and have a rich chemistry
Interstellar clouds: bright or dark
Lifecycle of gas in galaxies
Astrochemistry: a multi-field approach

- **Observations**
  - infrared
  - radio
  - visual / UV
  - X-rays

- **Models**
  - early universe
  - interstellar clouds
  - star-forming regions
  - planetary atmospheres

- **Laboratory / computation**
  - spectroscopy
  - collision rates
  - reaction rates
  - grain surface processes
Today's lecture

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Brief history of astrochemistry

- Diffuse interstellar bands: Heger 1922, Merrill 1934 remain unidentified today

- Sharp bands due to gas phase molecules: 1937 – 1940
  CH: Swings & Rosenfeld 1937
  CN: McKellar 1940
  CH+: Douglas & Herzberg 1941

- First astrochemical models: soon after
  Kramers & ter Haar 1946
  Bates & Spitzer 1951

High-resolution spectrum of ζ Oph: Adams 1941
The diffuse interstellar bands

- Over 300 bands known from UV to near-IR
  also in Magellanic Clouds
- Remain unidentified
  Noordwijk conference May 2013
- Must be exceptionally stable: survive harsh conditions
  probably medium-large hydrocarbons (Linnartz et al 2010, Oka et al 2013)
  2 features likely due to $C_{60}^+$ (Campbell et al 2015 Nature)
Brief history (2)

- **Development of radio astronomy**
  - [H I] 21 cm: Ewen & Purcell 1951, Oort & Muller 1951
  - OH 18 cm: Weinreb et al 1963 (emission!)
  - NH$_3$ 1.3 cm: Cheung, Townes et al 1968 (polyatomic!)
  - H$_2$O 1.3 cm: Cheung et al 1969
  - H$_2$CO 6 cm: Snyder et al 1969

- **Development of space-based UV astronomy**
  - H$_2$: Carruthers et al 1970 (Copernicus)

- **Development of mm-wave astronomy**
  - CO: Wilson et al 1970
1980s: The first mm-wave line surveys

Brief history (3): Infrared astronomy

- **1983: IRAS**
  - first full-sky survey at 12, 25, 60, 100 µm
  - cirrus clouds, dust properties
  - small dust particles (VSGs, 10 – 100 Å)
  - large molecules (PAHs)

- **1995-1998: ISO**
  - first complete 2.5 – 200 µm spectra
  - grain composition: silicates, ices, crystals
  - nature of PAHs
  - Far-IR cooling lines: H$_2$O, OH, [OI]
  - symmetric molecules: C$_2$H$_2$, CO$_2$, C$_6$H$_6$, CH$_3$, ...
  - Mid-IR lines of H$_2$ as tracers of shocks and PDRs

- **2003-2009: Spitzer**
  - high-sensitivity imaging, limited spectroscopy

- **Airborne**: KAO (1974-1995), SOFIA (since 2011)
- **Ground-based**: UKIRT, IRTF, ...
Polycyclic aromatic hydrocarbons

50-100 C atoms
neutral & cationic

Excited by UV radiation
tracer of star formation

Tielens, Allamandola et al
Interstellar buckminsterfullerene

Predicted: Kroto et al 1985, Nature

Detected: Cami et al 2010, Nature

Named after American architect Richard Buckminster Fuller
Ground-based infrared astronomy

Interstellar $\text{H}_3^+$: starting point of ion-molecule chemistry
predicted 1961, spectrum measured 1980, astronomical detection 1996
T. Oka, T. Geballe, B. McCall
Ice mantles due to condensation of volatile species onto dust grains visible as broad absorption features in mid-IR
### Solar abundances: Asplund et al 2009 ARAA

<table>
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<tr>
<th>Element</th>
<th>Abundance</th>
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<tr>
<td>H</td>
<td>1.00</td>
</tr>
<tr>
<td>He</td>
<td>0.085</td>
</tr>
<tr>
<td>C</td>
<td>2.69 x 10^{-4}</td>
</tr>
<tr>
<td>N</td>
<td>6.76 x 10^{-5}</td>
</tr>
<tr>
<td>O</td>
<td>4.90 x 10^{-4}</td>
</tr>
<tr>
<td>Ne</td>
<td>8.51 x 10^{-5}</td>
</tr>
<tr>
<td>Na</td>
<td>1.73 x 10^{-6}</td>
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<tr>
<td>Mg</td>
<td>3.98 x 10^{-5}</td>
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<tr>
<td>Al</td>
<td>2.82 x 10^{-6}</td>
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<tr>
<td>Si</td>
<td>3.24 x 10^{-5}</td>
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<tr>
<td>S</td>
<td>1.32 x 10^{-5}</td>
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<tr>
<td>Ar</td>
<td>2.51 x 10^{-6}</td>
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<tr>
<td>Ca</td>
<td>2.19 x 10^{-6}</td>
</tr>
<tr>
<td>Fe</td>
<td>3.16 x 10^{-5}</td>
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ISM is enriched by AGB winds and (super)novae

Depends on SF history: Galactic gradients, metallicity effects

Some atoms locked up in dust grains, cannot do gas-phase chemistry
He \sim 0.1; C, N, O \sim 10^{-4}; Mg, Fe, Si, S \sim 10^{-5}
Interstellar dust

- Solid particles
  silicate ("sand") + carbonaceous ("soot") material
  in cold dense clouds: ice mantle

- Average size 0.1 µm
  range from 0.01 to 0.5 µm
  larger in protoplanetary disks

- Abundance 1% by mass, $10^{-12}$ by number
  silicate core contains most Si, Fe, Mg
  carbonaceous part ~60% of C, 30% of O

- Observed by optical extinction & reddening
  and infrared emission
Today's lecture

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Observational techniques: Diffuse clouds

- Diffuse clouds: $A_V < 1$ mag (i.e., extinction = factor 2.5 at 5500 Å) UV-optical starlight penetrates photochemistry important

- For $A_V < 0.3$ mag, most H is atomic else mostly molecular

- Conversion factor: $N_H / A_V = 1.8 \times 10^{21}$ cm$^{-2}$
  with $N_H = N$(H) + 2$N$(H$_2$)
  UV: Bohlin et al 1978
  X-ray: Güver & Özel 2009

- Observed by absorption lines toward background stars
  optical since 1930s, UV since 1970s
  broad stellar / sharp interstellar lines
  classic example: cloud toward ζ Oph
Molecular spectroscopy

Energy = electronic + vibrational + rotational
far apart: coupling usually negligible

Electronic transitions in ultraviolet
usually in absorption against stars

Vibrational transitions in mid-infrared
usually in absorption against dust

Rotational transitions in submillimeter
usually in emission

Smaller splittings in radio
  e.g., NH$_3$ inversion, OH Λ-doublet
Submillimeter telescopes

JCMT
CSO
APEX
IRAM 30m
IRAM PdBI
Herschel
Since 2011: The ALMA interferometer
Dense interstellar clouds

- **Opaque in optical-UV**
  shielded from dissociating radiation

- **Millimeter-wave emission: rotational transitions**
  +: emission: map spatial distribution
  +: access to low abundances, kinematics
  -: need permanent dipole moment, cannot see H₂, CH₄, ...

- **Mid-infrared absorption: vibrational transitions**
  +: access to symmetric species & solid state features
  +: obtain `full’ view of excitation
  -: need background source, only LOS info

- **Earth atmosphere prevents observation of key species**
  H₂O, O₂, CO₂, ...
Infrared absorption of gas and solid phases

- Hot dust: 300–1000 K, $10^7$ cm$^{-3}$
- Gas-phase molecules: 20–200 K
- Cold dust (ice mantles): 10–100 K, $10^4$ cm$^{-3}$

Flux

- Continuum due to hot dust
- Absorption by cold dust

Wavelength
Today's lecture

Motivation
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Identified interstellar molecules

- Currently about 190 molecules known in space
  a few new ones every year since 30 years
  about 60 seen in other galaxies
  See www.cdms.de for up-to-date list
- Many di/tri-atomic radicals and cations
  carbon chains
  some anions
- Some species known on Earth
  $\text{H}_2\text{O}$, $\text{NH}_3$, $\text{H}_2\text{CO}$, $\text{C}_2\text{H}_5\text{OH}$
- Others 'exotic'
  $\text{N}_2\text{H}^+$, $\text{HC}_{11}\text{N}$
- Some first seen in space
  X-ogen = HCO$^+$ (Buhl & Snyder 1970; Krämer & Diercksen 1976)
Millimeter-wave spectrum of G327-0.6 hot core

About 50% of lines unidentified

Gibb et al 2000
Some disputed detections, e.g. glycine = simplest amino acid
Interstellar $\text{H}_2\text{D}^+$ & $\text{D}_2\text{H}^+$

- Interstellar D/H $\sim 10^{-5}$
  D formed in early universe, destroyed in stars
- Small difference in zero point vibration
  $x\text{D}/x\text{H} \gg \text{D}/\text{H}$
  "fractionation" by orders of magnitude

Herschel 2010 detection of $\text{H}_2\text{O}^+$ & $\text{H}_2\text{Cl}^+$

- $\text{H}_2\text{O}^+$ widespread also extragalactic
- $\text{H}_2\text{Cl}^+$ confirms simple Cl network
  - HCl:Cl$^+$::H$_2$Cl$^+$ ratio as predicted
  - absolute abundance 10x higher than in models

A&A special issue HIFI
Interstellar benzene

Cernicharo et al 2001 (ISO)
Interstellar amino-aceto-nitrile

- Precursor of glycine
- Challenge: close to confusion limit
- Multi-telescope approach
detect ~100 lines in broad-band spectrum
image ~10 of these with interferometer

Belloche et al 2008
Detection of extragalactic $\text{H}_3\text{O}^+$

- Precursor of water and tracer of ionization rate
- Starburst galaxy M82 photo-ionization by young stars
- Luminous merger Arp220 X-rays from central black hole
- 10-100x Galactic rate

Van der Tak et al 2008
Molecules at high redshift

- Lines of CO, $^{13}$CO, [CI], H$_2$O, and H$_2$O$^+$ at $z = 2.0 - 5.7$
- Vieira et al 2013, Nature
Interstellar \( \text{ArH}^+ \): The first noble gas molecule

- Rapidly destroyed by \( \text{H}_2 \): Traces purely atomic gas
- \( \text{Ar} \) isotopic ratios: from \(^{40}\text{K}\) decay on Earth / SN fusion in ISM
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The astrophysical use of molecules

- ’Exotic’ conditions in space: unique laboratory
  low density, high/low temperature, radiation field, ...
- Chemical composition: estimate object properties
  age, ionization rate, ...
- Use line ratios to estimate physical conditions
  $T$ from NH$_3$, $n$ from CS, $V$ from CO, $N$ from CO isotopes ...
- Contributions to cooling of interstellar clouds
  collisional excitation
  radiative decay
  photon escape

- Excitation often not in thermodynamic equilibrium
  collisions and radiation compete
- Critical density proportional to $\mu^2 \nu^3$
  higher frequencies probe higher densities (and temperatures)
Chemical gradients in dark clouds & hot cores

TMC-1: 0.5 pc offset between ammonia and cyanopolyyne peaks (1 pc = \(3 \times 10^{18}\) cm)

NGC 6334: source I much richer in molecules than I(N)

Olano et al 1988; Thorwirth et al 2003
Today's lecture

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Gas-phase processes
Basic molecular processes: gas phase

- Low temperatures and densities
  - interstellar chemistry not in thermodynamic equilibrium
- limited by kinetics; only two-body reactions
  - 3-body interactions enter at $n > 10^{12} \text{ cm}^{-3}$ as on Earth
- therefore time dependence is important
  - other parameters: $T$, $n$, $Z$, radiation, ...
- Modern models contain thousands of reactions
  - but of only a few different types
- Reaction rate: $k n(X) n(Y) [\text{cm}^{-3} \text{s}^{-1}]$
  - with $k =$ rate coefficient [cm$^3$ s$^{-1}$]
Types of chemical reactions

Formation of bonds:
- radiative association
  \[ X + Y^+ \rightarrow XY^+ + h\nu \]
- associative detachment
  \[ X^- + Y \rightarrow XY + e \]
- grain surface
  \[ X + Y:g \rightarrow XY + g \]

Destruction of bonds:
- photodissociation
  \[ XY + h\nu \rightarrow X + Y \]
- dissociative recombination
  \[ XY^+ + e \rightarrow X + Y \]
- collisional dissociation
  \[ XY + M \rightarrow X + Y + M \]

Rearrangement of bonds:
- ion-molecule reaction
  \[ X^+ + YZ \rightarrow XY^+ + Z \]
- charge transfer reaction
  \[ X^+ + YZ \rightarrow X + YZ^+ \]
- neutral-neutral reaction
  \[ X + YZ \rightarrow XY + Z \]
Radiative association

Proceeds through excited state:

\[ X + Y^+ \rightarrow XY^* \rightarrow XY^+ + h\nu \]

Energy conservation requires photon emission, which is rate-limiting step

- step 1: collision time \( \sim 10^{-13} \) s (both directions)
- step 2: vibrational decay rate \( \sim 10^{-3} \) s

Thus molecule formation occurs once in \( 10^{10} \) collisions

More efficient if electronic state available

- step 2: electronic decay rate \( \sim 10^{-8} \) s
  - efficiency increased to \( 1:10^5 \)
Radiative association (2)

Other way to increase efficiency: slow down
\[ X + Y^+ \leftrightarrow XY^* \]

- option 1: entrance channel has barrier
- option 2: large molecule (long collision time)

Most data based on theory; accurate to order of magnitude

hard to measure in laboratory: 3-body reactions dominate

solution: measure rates as function of pressure

Well-known R.A. rate: \( \text{C}^+ + \text{H}_2 \rightarrow \text{CH}_2^+ + \text{hv} \)

rate \( k \sim 10^{-15} \text{ cm}^3 \text{ s}^{-1} \) within factor of 2-3

starter of gas-phase carbon chemistry
Associative detachment

Important if fractional ionization is high (early Universe!)

step 1: form anion (slow) \( X + e \rightarrow X^- + h\nu \)
step 2: form molecule \( X^- + Y \rightarrow XY + e \)

Examples:
formation of H\(_2\) in early Universe \((X = Y = H)\)
gas-phase formation of OCS \((X = S, Y = CO)\)
Photodissociation

Basic process: $X + h\nu \rightarrow X + Y$

route 1: direct p.d. ($H_2O, O_3$)
route 2: predissociation (CO)
route 3: spontaneous radiative dissociation ($H_2$)

Routes 2+3: small cross-section
self-shielding for $H_2$ and CO

For $H_2$, only 10% of Lyman-Werner photons lead to dissociation
Photodissociation rates

Experiments exist only for stable species

Small radicals / ions: calculation possible
  step 1: potential surface of excited state
  step 2: transition dipole moment
  step 3: dynamics → cross sections

Interstellar radiation field:
  OB-type stars dominate UV range
  inside cloud: apply shielding

CR-induced UV field:
  effective $A_V$ ceiling of 5 mag
Dissociative recombination

Radiative recombination (atoms): \( X^+ + e \rightarrow X + hv \)
slow: must emit photon

Dissociative process (molecules): \( XY^+ + e \rightarrow X + Y \)
fast – if potential curves of \( XY^+ \) and \( X + Y \) cross

Rates well known from theory / experiment
but products uncertain (branching ratios)

Example: \( H_3O^+ + e \) has 4 outcomes
\( H_2O + H / OH + H_2 / OH + H + H / O + H_2 + H \)
recent experiments: small products favoured

CRYRING, Stockholm
Exercise: Telescopes

- Of the telescopes in this lecture, compare the:
  - wavelength coverage
  - angular resolution
  - spectral resolution

- Plot these properties against each other
  *feel free to add other telescopes*