Spectroscopy and chemistry of exoplanets

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Artist’s impression of HD189733b
C. Carreau, ESA
Transit hunters

Transits of objects down to Earth-size

**COROT** (CNES/ESA)
32 transiting planets found

**KEPLER** (NASA)
7 March 2009 – 13 Aug. 2013
954 confirmed planets so far + > 3600 candidates
3000+ planetary candidates discovered by Kepler

Exoplanets are common...
The Exoplanet Revolution

9 to ~2000 in 20 years!
Kepler Planets
As of February 27, 2012

Kepler-14b, 12.7 R_E
Kepler-17b, 14.7 R_E
Kepler-6b, 14.79 R_E
Kepler-8b, 15.86 R_E
Kepler-5b, 16.00 R_E
Kepler-7b, 16.52 R_E
Kepler-12b, 19.0 R_E

Kepler-27c, 4.9 R_E
Kepler-18c, 5.49 R_E
Kepler-18d, 6.98 R_E
Kepler-35b, 8.16 R_E
Kepler-16b, 8.45 R_E
Kepler-34b, 8.56 R_E
Kepler-9c, 9.2 R_E
Kepler-9b, 9.4 R_E
Kepler-30d, 10.7 R_E
Kepler-15b, 10.8 R_E
Jupiter, 11.2 R_E

Kepler-32c, 3.7 R_E
Kepler-33f, 3.83 R_E
Neptune, 3.88 R_E
Kepler-4b, 3.99 R_E
Kepler-27b, 4.1 R_E
Kepler-32b, 4.2 R_E
Kepler-31c, 4.3 R_E
Kepler-31b, 4.5 R_E
Kepler-25c, 4.52 R_E
Kepler-11e, 4.56 R_E
Kepler-33d, 4.56 R_E

Kepler-11c, 3.15 R_E
Kepler-23c, 3.2 R_E
Kepler-28c, 3.4 R_E
Kepler-11d, 3.43 R_E
Kepler-33e, 3.45 R_E
Kepler-26b, 3.6 R_E
Kepler-26c, 3.6 R_E
Kepler-28b, 3.6 R_E
Kepler-29b, 3.6 R_E
Kepler-11g, 3.66 R_E
Kepler-30b, 3.7 R_E

Kepler-19b, 2.21 R_E
Kepler-10c, 2.23 R_E
Kepler-22b, 2.38 R_E
Kepler-24b, 2.4 R_E
Kepler-25b, 2.61 R_E
Kepler-11f, 2.75 R_E
Kepler-33c, 2.75 R_E
Kepler-20d, 2.8 R_E
Kepler-24c, 2.9 R_E
Kepler-29c, 3.07 R_E
Kepler-20c, 3.07 R_E

Kepler-20e, 0.97 R_E
Kepler-20f, 1.03 R_E
Kepler-10b, 1.42 R_E
Kepler-33b, 1.5 R_E
Kepler-21b, 1.64 R_E
Kepler-9d, 1.64 R_E
Kepler-23b, 1.9 R_E
Kepler-20b, 1.91 R_E
Kepler-11b, 1.97 R_E
Kepler-18b, 2.0 R_E

Courtesy of Kepler’s team
HD 209458b

Period = 3.52 days

Mass = 0.69 ± 0.05 $M_{\text{Jupiter}}$

Radius = 1.35 ± 0.04 $R_{\text{Jupiter}}$

Density = 0.35 ± 0.05 g/cm$^3$
HD189733b: Primary transit with Spitzer

Water line list: BT2
Barber et al., 2006

Water, different T-P
Confirmation of Water, methane and hazes!

G. Tinetti (private communication, 2008)
So far discovered:
- Water \( \text{H}_2\text{O} \)
- Methane \( \text{CH}_4 \)
- Carbon dioxide \( \text{CO}_2 \)
- Carbon monoxide \( \text{CO} \)

**HCCH / HCN degeneracy**

On HD189733b
with more to come

HD189733b: \( T \sim 1300 \text{ K} \)
Too hot for life
Cool atmospheres: dominated by molecular absorption

The molecular opacity problem

Marley & Leggett (2008)
5 year project from May 2011
Provide data for all molecular transitions important for exoplanet atmospheres
Methodology: first principles quantum mechanical calculations, informed by experiment

Frontier Problems in Exoplanet Characterization

- Non-equilibrium processes in exoplanet atmospheres
  \( \text{CH}_4, \text{CO}, \text{NH}_3 \)  
  (Stevenson et al. 2010; Madhusudhan & Seager 2011; Moses et al. 2013)

- Constraints on thermal inversions in hot Jupiters
  \( \text{TiO}, \text{VO}, \text{H}_2\text{S} \)  
  (Fortney et al. 2008; Spiegel et al. 2009)

- C/O ratios and Carbon-rich atmospheres
  \( \text{H}_2\text{O}, \text{CO}, \text{HCN}, \text{CH}_4, \text{C}_2\text{H}_2, \text{TiH}, \text{FeH} \)  
  (Fortney et al. 2008; Spiegel et al. 2009)

- Constraints on exoplanet formation conditions
  \( \text{H}_2\text{O}, \text{CO}, \text{CH}_4 \)  
  (Madhusudhan et al. 2011; Oberg et al. 2011)

- Atmospheres and interiors of super-Earths
  \( \text{H}_2\text{O}, \text{CO}_2 \)  
  (Bean et al. 2011; Desert et al. 2011; Miller-Ricci Kempton et al. 2011)

Slide courtesy of N Madhusudhan (Cambridge)
### Molecular line lists for exoplanet & other atmospheres

<table>
<thead>
<tr>
<th></th>
<th>Primordial (Metal-poor)</th>
<th>Terrestrial Planets (Oxidising)</th>
<th>Giant-Planets &amp; Cool Stars (Reducing atmospheres)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Already available</strong></td>
<td>H₂, LiH, HeH⁺, H₃⁺, H₂D⁺</td>
<td>OH, CO₂, O₃, NO, H₂O, HDO, NH₃</td>
<td>H₂, CN, CH, CO, CO₂, TiO, HCN/HNC, H₂O, NH₃,</td>
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<tr>
<td><strong>ExoMol</strong></td>
<td>O₂, CH₄, SO₂, SO₃, HOOH, H₂CO, HNO₃</td>
<td>CH₄, PH₃, C₂, C₃, HCCH, H₂S, C₂H₆, C₃H₈, VO, O₂, AlO, MgO,</td>
<td></td>
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<tr>
<td>Available from elsewhere</td>
<td>CH₄, PH₃, C₂, C₃, HCCH, H₂S, C₂H₆, C₃H₈, VO, O₂, AlO, MgO,</td>
<td>CrH, MgH, FeH, CaH, AlH, SiH, TiH, NiH, BeH, YO</td>
<td></td>
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<tr>
<td><strong>Already calculated at UCL</strong></td>
<td>CH₄, PH₃, C₂, C₃, HCCH, H₂S, C₂H₆, C₃H₈, VO, O₂, AlO, MgO,</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Will be calculated during the ExoMol project</td>
<td>CH₄, PH₃, C₂, C₃, HCCH, H₂S, C₂H₆, C₃H₈, VO, O₂, AlO, MgO,</td>
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Full details:


[www.exomol.com](http://www.exomol.com)
Why theory, not experiment?
Absorption ($T=300K$) spectrum of NH$_3$: Accuracy

[Graph showing absorption spectrum with experimental and theoretical data]

- **Experiment**
- **Theory**
Absorption \((T=300K)\) spectrum of \(\text{NH}_3\): Accuracy
Absorption ($T=300K$) spectrum of NH$_3$: Accuracy
Absorption ($T=300K$) spectrum of NH$_3$: Accuracy
Completeness: Absorption of ammonia (T=300 K)

Less than 30,000 NH₃ lines known experimentally:
BYTe contains 1.1 billion lines, about 40,000 times as many!

Absorption spectra of $^{14}$NH$_3$: Temperature effect

$$I(f \leftarrow i) = S(f \leftarrow i) \frac{e^{-E_i/kT}}{Q(T)} \left[1 - e^{-h \nu_{if}/kT}\right] \frac{8\pi^3 N_A \tilde{V}_{if}}{(4\pi \varepsilon_0)3hc}$$
Method: Spectrum from the “first-principles”

Ab initio calculations

- DMS
- PES

Variational calculations

- Rovibrational wavefunctions
- Rovibrational energies

Intensities (Einstein $A_{if}$)

Refinement

Line list
Ab initio: solve for motion of electrons

Potential energy curve

Solve for the motion of the nuclei

Line list: MgH

Dipole moment curve

MOLPRO

REFINED

LEVEL 8.0
R. Le Roy,
Waterloo, Canada

Line list (in progress): $C_2$

Potential energy

Dipole moment

Solve for the motion of the nuclei

New program *duo*
Sergei Yurchenko

T. W. Schmidt et al 2011

Istvan Szabo
**Dipole moment**

LEVEL 8.0  
DVR3D  

**Potential energy**

Ab initio: solve for motion of electrons

Ab initio  
18 electrons  
Ground electronic state

C3

CASSCF  
P. Jensen, C. McMichael Rohlfing, and J. Almlöf, 1992,  

**Line list:**

Intensity (cm/mol)  
Wavelength (\(\mu\)m)

Solve for the motion of the nuclei

**LEVEL 8.0**  
**DVR3D**
300 K line list, Clara Sousa-Silva

**Potential energy**

Ab initio PES

[CCSD(T)/aug-cc-pV(Q+d)Z]

R. I. Ovsyannikov et al.


Refined using lab spectra

**Dipole moment**

Ab initio:

CCSD(T)/aug-cc-pVTZ

S.N. Yurchenko et al.


First principles

Predictions of tunnelling being investigated

**Solve for the motion of the nuclei**

**TROVE: Yurchenko, Thiel, Jensen**

T=300 K  ~ 14 M transitions

Hot (T < 1500 K) 16 billion
Ab initio: solve for motion of electrons

Potential energy

9D surface
130,000 geometries
MOLPRO
CCSD(T)-f12/QZ

Dipole moment

Three 9D surfaces
130,000 geometries
MOLPRO
CCSD(T)-f12/QZ

Solve for the motion of the nuclei

TROVE
Yurchenko, Thiel, Jensen

10 to 10

Line list:


9.8 Billion transitions
\[ I(f \leftarrow i) = S(f \leftarrow i) \frac{e^{-E_i/kT}}{Q(T)} \left[ 1 - e^{-hc\tilde{v}_{if}/kT} \right] \frac{8\pi^3 N_A \tilde{v}_{if}}{(4\pi \varepsilon_0)^3hc} \]

CH₄ diagonalization: Size of the problem

Acknowledgment: Andrey Kaliazin  Dirac/COSMOS
CH$_4$ diagonalization: Size of the problem

Number of eigenvalues $N$

Matrix dimension (F symmetry)

16 nodes = 1 DARWIN socket

2.5 hours

15 hours

6 hours
CH$_4$ diagonalization: Size of the problem

Matrix dimension (F symmetry)

Number of eigenvalues

- **COMSOS II**: 4 hours, 64 cores
- **DARWIN**: 6 hours, 96 cores
- 9 hours, 144 cores
- 11 hours, 160 cores
NH$_3$ diagonalization: Size of the problem

- Dimension of the matrix
- Non-zero part
- Number of eigenvalues below 18000 cm$^{-1}$

LAPACK: DSYEV
PARPACK

Graph showing the growth of dimension, non-zero part, and number of eigenvalues below 18000 cm$^{-1}$ with respect to $J$.
Absorption spectra of CH$_4$: from experimental line list

- HITRAN12: ~350000 lines
- ExoMol: ~$10^{10}$ lines
The image shows a graph with the x-axis labeled as 'wavenumber 1/cm' and the y-axis labeled as 'intensity, cm/molecule'. The graph is labeled 'HITRAN12' and contains data points depicted in blue and red. The graph also includes a label '10to10' at the top.
Temperature-dependent colours of methane
Model of a T4.5 Brown Dwarf: a “methane dwarf”

SN Yurchenko, J Tennyson, J Bailey, MDJ Hollis, G Tinetti, PNAS, 111, 9379 (2014)
In progress: HNO₃ and C₂H₄

Calculated spectra for Nitric Acid

Calculated spectra for Ethylene

The region of 0 - 1800 cm⁻¹

The region of 700 - 3250 cm⁻¹

Anatoly Pavlyuchko
• 50,000 processor hours.

• Wavefunctions > 0.8 terabites

• 221,100 energy levels (all to J=50, E = 30,000 cm\(^{-1}\))
  14,889 experimentally known

• 506 Million transitions (PS list has 308M)
  >100,000 experimentally known with intensities

∀ → Partition function 99.9915% of Vidler & Tennyson’s value at 3,000K

BT2 linelist
http://www.tampa.phys.ucl.ac.uk/ftp/astrodata/water/BT2/
Brown and M-dwarfs

Atmosphere of Venus

Exoplanets (4 so far!)

BT2 linelist used to detect/model water

Nova-like V838 Mon

Cometary coma
As well as.....

Water concentrations in explosions

Imaging gas turbine engines

Atmospheric models

Remote detection of forest fires

Design of high-T gas sensors

Temperature profile in flames
### ExoMol: List of molecules

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<td><strong>ExoMol In progress</strong></td>
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<td><strong>Released</strong></td>
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**Full details:**
MSc students: SiO, CS, NaCl, KCl
Citizen scientist: AlH
About the first edition
“The best book for anyone who is embarking on research in astronomical spectroscopy”
Contemporary Physics (2006)

Published 2011