Line lists for hot hydride molecules

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Physics and Astronomy
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Calculated molecular line lists for the opacity of exoplanets, cool stars and other hot atmospheres

Hydride Toolbox
Paris
December 2016

Image credit: Shutterstock
“Molecular physics challenge for exoplanet studies”

Line lists for hot hydride molecules and their friends

Jonathan Tennyson
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ExoMol

Calculated molecular line lists for the opacity of exoplanets, cool stars and other hot atmospheres

Hydride Toolbox
Paris
December 2016
The Exoplanet Revolution

9 to > 3000 in 20 years!
HD 209458b

Period = 3.52 days

Mass = 0.69 ± 0.05 M_{Jupiter}

Radius = 1.35 ± 0.04 R_{Jupiter}

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

Beaulieu et al., 2007

Knutson et al., 2007
Water line list: BT2
Barber et al., 2006

Water, different T-P

Confirmation of Water, methane and hazes!

G. Tinetti (private communication, 2008)
Cool atmospheres: dominated by molecular absorption

The molecular opacity problem

M Dwarf
Brown Dwarfs
Planet

Exoplanets?

Marley & Leggett (2008)
• 5 year project: 2011-16
• Provide data for all molecular transitions important for exoplanet atmospheres
• Methodology: first principles quantum mechanical calculations, informed by experiment

Line list = line positions + line intensities

This is our 2016-line list for water
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>Primordial (Metal-poor)</th>
<th>Terrestrial Planets (Oxidising)</th>
<th>Giant-Planets &amp; Cool Stars (Reducing atmospheres)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Already available</td>
<td>O$_2$, CH$_4$, SO$_2$, SO$_3$</td>
<td>H$_2$, CN, CH, CO, CO$_2$, TiO</td>
</tr>
<tr>
<td>H$_2$, LiH</td>
<td>OH, CO$_2$, O$_3$, NO</td>
<td>H$_2$O, HDO, NH$_3$,</td>
</tr>
<tr>
<td>HeH$^+$, H$_3^+$</td>
<td>H$_2$O, HDO, NH$_3$</td>
<td>HCN/HNC, H$_2$O, NH$_3$,</td>
</tr>
<tr>
<td>H$_2$D$^+$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**ExoMol**

| Available from elsewhere | O$_2$, CH$_4$, SO$_2$, SO$_3$   | CH$_4$, PH$_3$, C$_2$, C$_3$, HCCCH, H$_2$S, |
|                          | HOOH, H$_2$CO, HNO$_3$         | C$_2$H$_6$, C$_3$H$_8$, VO, O$_2$, AlO, MgO, |
|                          |                                 | CrH, MgH, FeH, CaH, AlH, SiH, TiH, NiH, BeH, YO |

**Full details:**


www.exomol.com
Why theory, not experiment?
Exoplanets

Brown Dwarfs
Dwarf Stars

Lab Flames
Spectra

Earth 300 1000 1500
Sunspots 3000 4000
The Sun 6000

T / K 8000

hitran hitemp
diatom ic molecules
polyatomic molecules

H^+
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!

Method: Spectrum from the “first-principles”

Ab initio calculations

DMS

PES

Variational calculations

Rovibrational wavefunctions

Intensities (Einstein $A_{if}$)

Rovibrational energies

Refinement

Line list
**Ab initio:** solve for motion of electrons

**Potential energy curve**

![Potential energy curve](Shayesteh et al 2007)

**Dipole moment curve**

![Dipole moment curve](MOLPRO)

**Line list:** 6690 lines, $N_{\text{max}}=60$

**Solve for the motion of the nuclei**

**LEVEL 8.0**

R. Le Roy, Waterloo, Canada

New general diatomic code

Duo

Freely available from CCPforge
ccpforge.cse.rl.ac.uk
Line list: CaO

Khalil et al (2011)

Potential energy curves, cm$^{-1}$

- $A^1 +$
- $b^3 +$
- $a^3$

Spin-orbit, cm$^{-1}$

- $SO_4$
- $SO_3$
- $SO_2$
- $SO_5$

Large: $\sim 50-100$ cm$^{-1}$

Duo

Solve for the motion of the nuclei


Dipole moment

Transition dipole moment curves, Debye

- X-A
- X-A'
- A-A'
- a-b

Line list: 22 M lines

Absorption, cm$^2$/molecule

- X-X
- A'-X
- A-X

$T=1500$ K
$T = 2000$ K

Bernath

CrH

Maire N. Gorman, PhD UCL (2016)
Ab initio PES
[CCSD(T)/aug-cc-pV(Q+d)Z]
R. I. Ovsyannikov et al.
Refined using lab spectra

Solve for the motion
of the nuclei

Ab initio:
CCSD(T)/aug-cc-pVTZ
S.N. Yurchenko et al.

Potential energy

Tunneling motion neglected

Dipole moment

TROVE: Yurchenko, Thiel, Jensen

16.8 billion transitions for T up to 1500 K

TROVE

JPL

HITRAN

It has a nice strong feature at 4.5 μm

No detection yet of phosphine on exoplanets
First principles Predictions of tunnelling

Ab initio: solve for motion of electrons

Potential energy

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

Dipole moment

10 to 10

Solve for the motion of the nuclei

TROVE
Yurchenko, Thiel, Jensen

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

Ab initio
10 electrons
Ground electronic state

Line list:

HITRAN

9.8 Billion transitions

Intensity (cm/molecule)

CH$_4$ diagonalization: Size of the problem

Acknowledgment: Andrey Kaliazin Dirac/COSMOS

SGI: Jan Wilson, Simon Appleby Cheng Liao

Matrix dimension (F symmetry)

Number of eigenvalues

Diagonalization: Size of the problem

LAPACK (DSYEV)
DARWIN

SCALAPACK (PDSYEV)
COSMOS III/DARWIN

J

N

0 5 10 15 20 25 30 35 40 45 50

0 20000 40000 60000 80000 100000 120000 140000 160000 180000 200000 220000

Size of the problem

Number of eigenvalues

Matrix dimension (F symmetry)
CH$_4$ diagonalization: Size of the problem

Matrix dimension (F symmetry)

Number of eigenvalues

16 nodes = 1 DARWIN socket

2.5 hours

6 hours

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

Number of eigenvalues $N$ and matrix dimension (F symmetry) for different computation times and core counts:

- **COMSOS II**
  - 4 hours, 64 cores
  - 9 hours, 144 cores
  - 11 hours, 160 cores

- **DARWIN**
  - 6 hours, 96 cores

Number of eigenvalues $N$ increases with the matrix dimension $J$. The graph shows the trade-off between computation time and core count for solving the problem.
Absorption spectra of CH$_4$: from experimental line list
Temperature-dependent coLOURS of methane
VSTAR spectra of the T4.5 brown dwarf: a “methane dwarf”

T 4.5 Observed (SpeX@IRTF)
VSTAR STDS CH\textsubscript{4} (empirical)
VSTAR ExoMol CH\textsubscript{4} (10to10)

2MASS 0559-14

SN Yurchenko, J Tennyson, J Bailey, MDJ Hollis, G Tinetti, PNAS, 111, 9379 (2014)

Cushing, Rayner, Vacca (2005)
Published in MNRAS
I. BeH, MgH, CaH
II. SiO
III. HCN/HNC
IV. CH$_4$
V. NaCl, KCl
VI. PN
VII. PH$_3$
VIII. H$_2$CO
IX. AlO
X. NaH
XI. HNO$_3$
XII. CS
XIII. CaO
XIV. SO$_2$
XV. HOOH
XVI. H$_2$S
XVII. SO$_3$
XVIII. VO

(Virtually) Complete
XIX. H$_2^{18}$O, H$_2^{17}$O
XX. H$_3^+$
XXI. H$_2^{16}$O
XXII. NO
XXIII. TiO
• NS
• CrH

In progress
• C$_3$
• PH, PO, PS
• TiH
• MnH
• NaO
• SH
• AlH
• C$_2$H$_4$
• SiH
• HCCH
• SrH
• CH$_3$Cl
• SiH$_4$

Planned
• NH$_3$
• MgO
• NiH
• FeH
• Larger hydrocarbons


Updated data structure
New functionality
Other features:

1. Lifetimes (Tennyson et al, J Phys B, 49, 044002 (2016))
2. Lande g-factors (Semenov et al, J Molec Spectrosc (2016))
3. Pressure broadening (Barton et al, JQSRT (2017) + submitted)
   H₂ and He
   J and T dependence (only)
4. Dipoles for molecular control/orientation effects
   (A Yachmenev, RichMol project)
First detection of super-Earth atmosphere
Exoplanet 55 Cancri e has a dry atmosphere without any indications of water vapor.

HCN (weakly) detected!
“Hydrogen cyanide, or prussic acid, is highly poisonous, so it is perhaps not a planet I would like to live on!”
J. Tennyson, UCL press release

H$_2$CO, HOOH, CO$_2$, O$_3$, ScH, TiH, CrH, NaCl, KCl, SO$_3$, HNO$_3$, SO$_2$, C$_3$, NH$_3$, NH$_3$, HCCH, VO, TiO, C$_2$H$_4$, CH$_4$, PH$_3$
About the first edition
“The best book for anyone who is embarking on research in astronomical spectroscopy”
Contemporary Physics (2006)

Published 2011
Anatoly Pavlyuchko (1956-2015)


Vibrational Hamiltonian matrix:
A dense near the diagonal,
B sparse elsewhere
Vibrational Hamiltonian matrix:
Diagonalise region 1 only
Include effects of region 2 using perturbation theory

Rotation-Vibration Hamiltonian:
Treat vib state by vib state
Include Coriolis coupling via perturbation theory

$T = 298$ K spectrum of nitric acid (HNO$_3$)

Nitric acid as a bio-signature?

Absorption ($T=300\text{K}$) spectrum of $\text{NH}_3$: Accuracy

[Graph showing absorption spectrum with labeled axes: Intensity [cm/mol] on the y-axis and Wavenumber [cm$^{-1}$] on the x-axis. The graph compares experimental and theoretical data.]
Absorption ($T=300K$) spectrum of NH$_3$: Accuracy
Absorption ($T=300\,\text{K}$) spectrum of $\text{NH}_3$: Accuracy