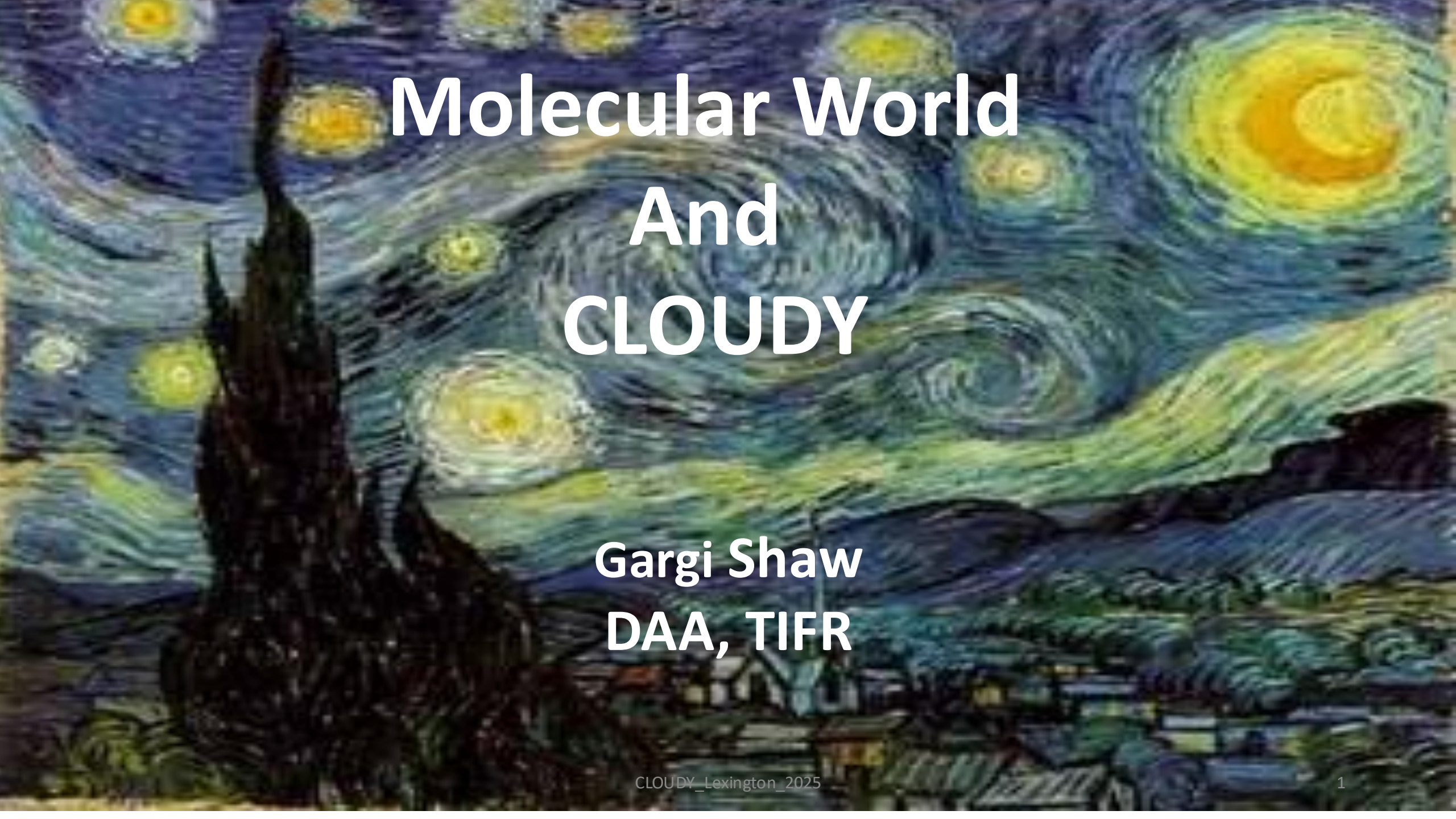


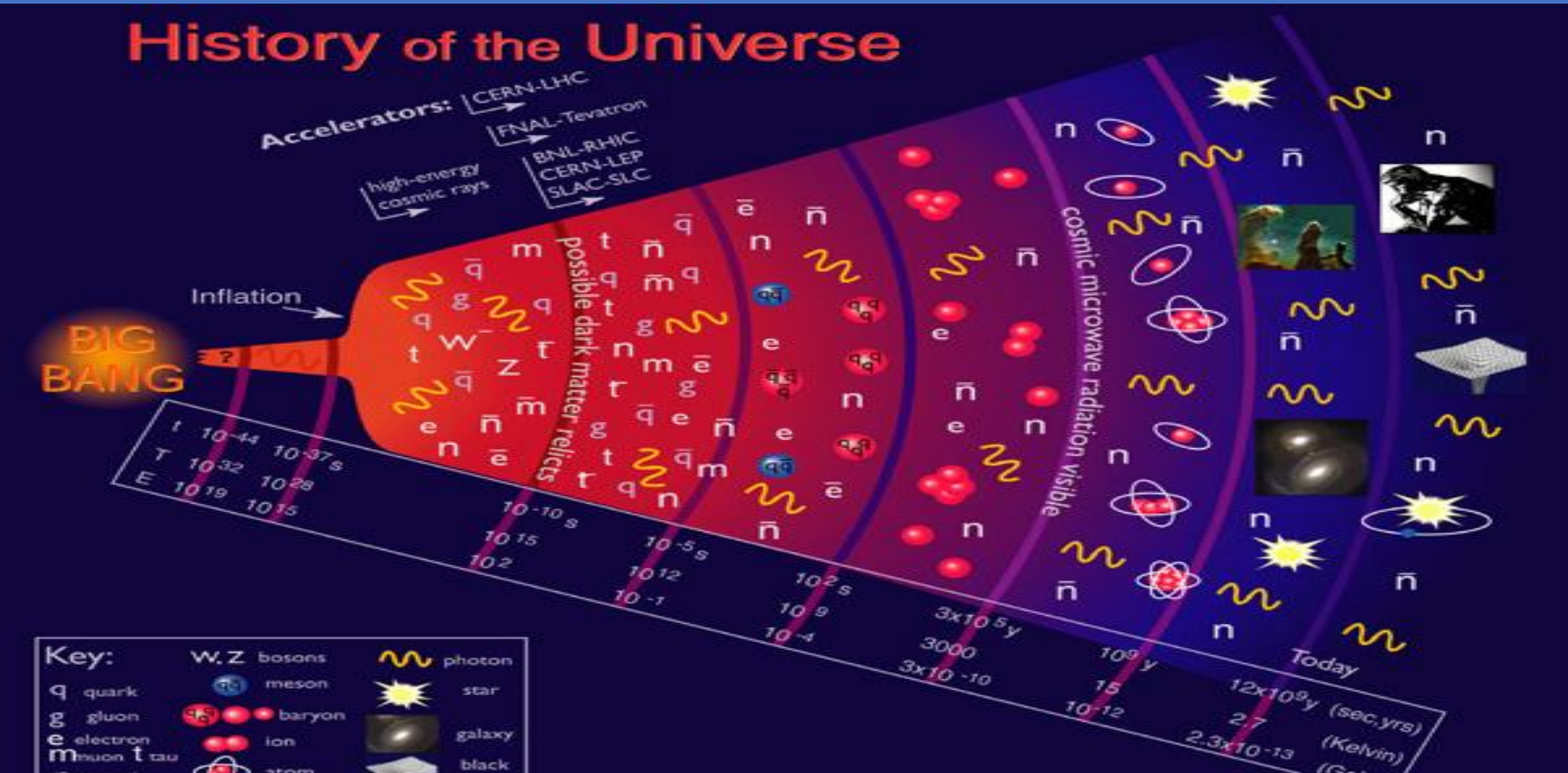
Molecular World And CLOUDY

Gargi Shaw
DAA, TIFR

Outline

- A brief introduction to molecules and its importance
- Molecular network of CLOUDY
- How to include new molecules in CLOUDY
- Molecular Hydrogen
- Test model

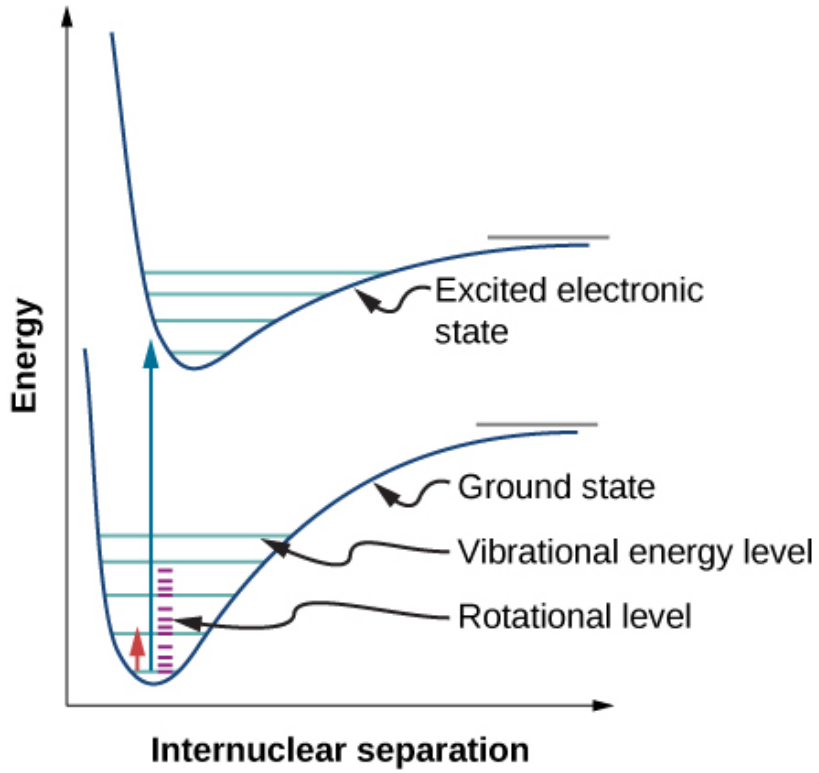
Molecules formed much later



Molecular Spectroscopy

E_molecule = E_electronic + E_vibrational + E_rotational

- Electronic transitions: UV-visible
- Vibrational transitions: IR
- Rotational transitions: Radio
- Molecular spectra is rich and complex

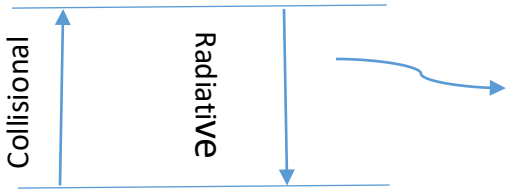


Why molecules are important?

❖Molecules are excellent coolants

Collisional excitation followed by radiative transition

- ➢ Radiation escapes from cloud => net kinetic energy lost
- ➢ cloud cools down => helps structure formation



❖Exotic chemistry: unique laboratory

Astrochemical evolution

❖ Molecules as diagnostics of physical parameters

temperature T_{kin}

density n_H

List of Molecules predicted by CLOUDY

Currently CLOUDY predicts 191 molecules and their column densities.

H_2, H_2^+, H_3^+

HeH^+, NeH^+, ArH^+

LiH, LiH^+

CH, CH^+, CH_2, CH_2^+, CH_3, CH_3^+, CH_4, CH_4^+, CH_5^+, C_2, C_2^+, C_2H, C_2H^+, C_2H_2, $C_2H_2^+$, $C_2H_3^+$, C_3, C_3^+, C_3H, C_3H^+

NH, NH^+, NH_2, NH_2^+, NH_3, NH_3^+, NH_4^+, CN, CN^+, HCN, HCN^+, HNC, $HCNH^+$, HC_3N, N_2, N_2^+, N_2H^+

OH, OH^+, H_2O, H_2O^+, H_3O^+, CO, CO^+, HCO^+, H_2CO, NO, NO^+, HNO, HNO^+, OCN, OCN^+, N_2O, O_2, O_2^+, NO_2, NO_2^+

HF, HF^+, H_2F^+, CF^+

SiH, SiH_2^+, SiN, SiN^+, SiO, SiO^+, $SiOH^+$, SiS

PH, PH^+, PH_2, PH_2^+, PH_3, PH_3^+, CP, CP^+, HCP, HCP^+, PN, PN^+, PO, PO^+

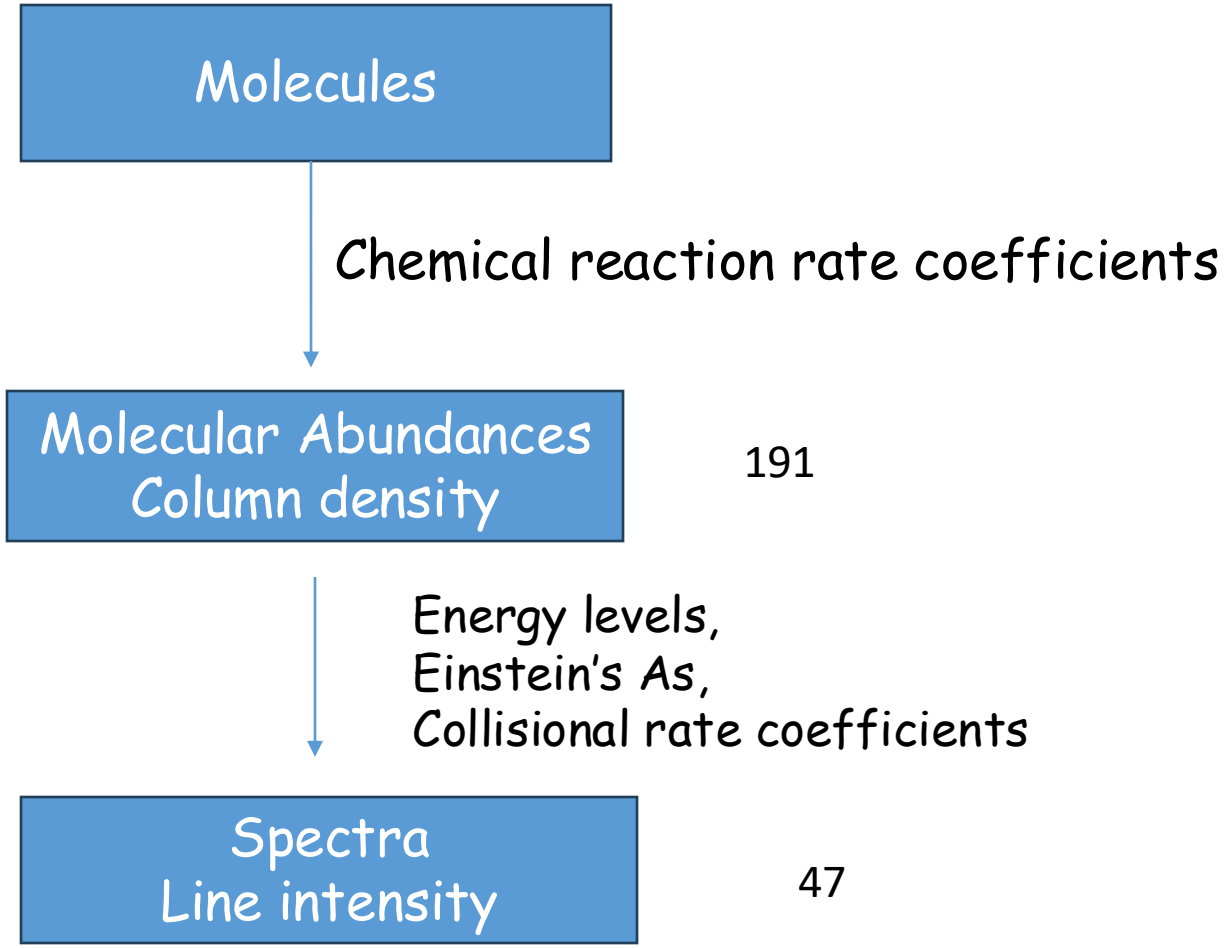
HS, HS^+, CS, CS^+, HCS^+, NS, NS^+, SO, SO^+, OCS, OCS^+, SO_2, SiS, S_2, S_2^+

HCl, HCl^+, H_2Cl^+, CCl, CCl^+, H_2CCl^+, ClO, ClO^+

TiH, TiH^+, TiH_2, TiH_2^+, TiC, TiC^+, HCTi, $HCTi^+$, TiC_2, TiC_2^+, TiN, TiN^+, HNTi, $HNTi^+$, TiNC, $TiNC^+$, TiO, TiO^+, $TiOH^+$, TiO_2, TiF^+, TiS, TiS^+, $HTiS^+$ .....

(Shaw et al. 2022,2023)

Molecular network of CLOUDY



Gas-phase reactions in the ISM

- ✓Ion-neutral ($A^+ + B \rightarrow C^+ + D$)
- ✓Neutral-neutral ($A + B \rightarrow C + D$)
- ✓Photodissociation ($AB + h\nu \rightarrow A + B$)
- ✓Charge transfer ($A^+ + B \rightarrow A + B^+$)
- ✓Radiative-association ($A + B \rightarrow AB + h\nu$)
- ✓Dissociative-recombination ($A^+ + e^- \rightarrow C + D$)
- ✓Associative detachment ($A^- + B \rightarrow AB + e^-$)

Reaction rate coefficients

For Two body reaction, the rate coefficient k($cm^3 s^{-1}$) is given by modified Arrhenius formula,

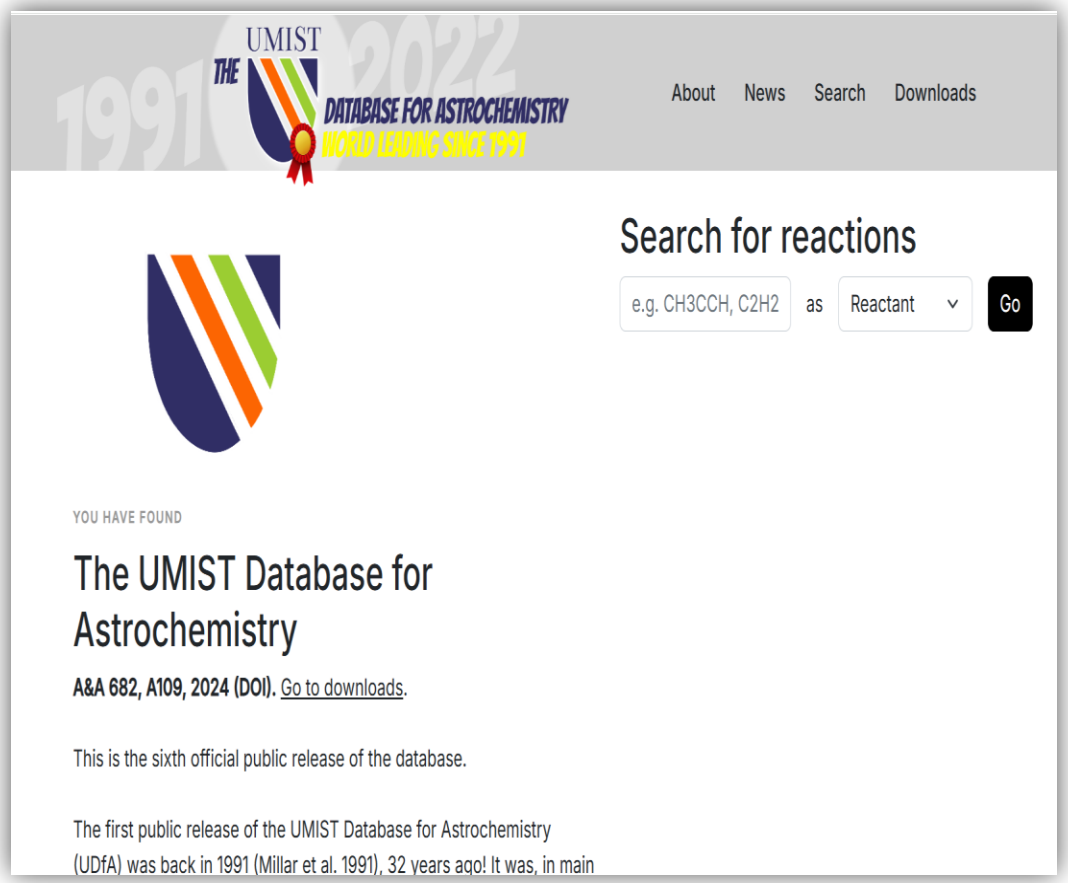
$$k = \alpha \left(\frac{T}{300} \right)^{\beta} \exp(-\gamma/T), \qquad (1)$$

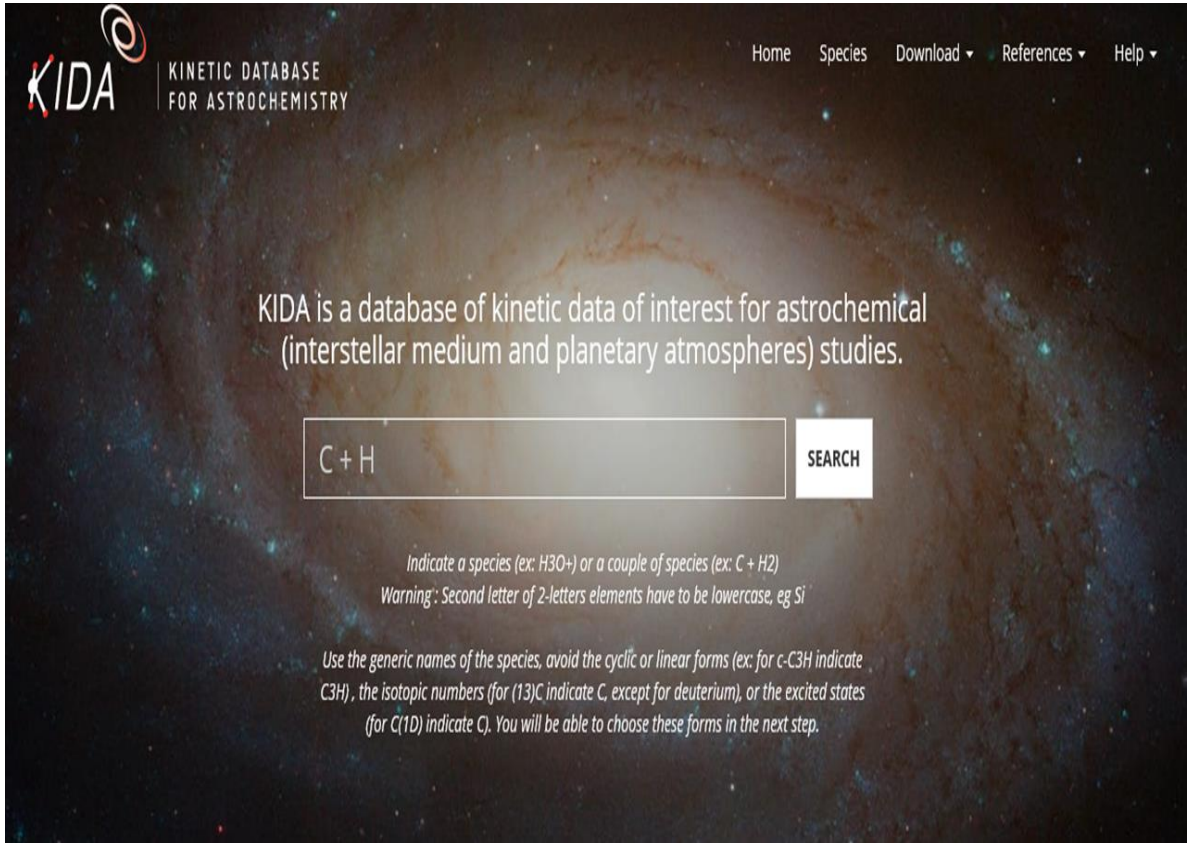
Photoreaction rate coefficient k(s^{-1}) is given by,

$$k = \alpha \exp(-\gamma A_V). \qquad (2)$$

The parameters α and γ used in the two-body reactions and photoreactions are not the same.

Reaction rate coefficients and databases





Chemical rate coefficients and Temperature

A wide range of temperatures occurs in nature.

A simple extrapolation of the rate coefficients can lead to unphysically large values. These result in unrealistic predictions.

$$k = \alpha \left(\frac{T}{300} \right)^{\beta} \exp(-\gamma/T), \qquad (1)$$

Rates for reactions with $\gamma < 0$ will become unphysically large at low temperatures.

- For $\gamma < 0$, $k(T < 10\ K) = k(T = 10\ K)$

Rate coefficients with a positive β can become large at high temperatures.

- For $\beta > 0$, $k(T > 5000\ K) = k(T = 5000\ K)$
- For $\beta < 0$, $k(T < 10\ K) = k(T = 10\ K)$

Internal structure of molecules and databases

LAMDA

Leiden Atomic and Molecular Database

Data format | RADEX

Atoms and ions

C C^+ O O^{2+}

N^+ Si S

Diatomic molecules

ArH^+ CF^+ CH

CH^+ CN CO

CS HCl HD

HF NH NO

NO^+ NS^+ OH

OH^+ O_2 PN

PO SiO SiS

SO

Triatomic molecules

C_2H C_2S CH_2

D_2H^+ HCN HCO^+

The aim of this project is to provide users of radiative transfer codes with the basic atomic and molecular data needed for the excitation calculation. Line data of a number of astrophysically interesting species are summarized, including energy levels, statistical weights, Einstein A-coefficients and collisional rate coefficients. Available collisional data from quantum chemical calculations and experiments are in some cases extrapolated to higher energies.

Currently the database contains data for 7 atomic / ionic and 50 molecular species. In addition, several isotopomers and deuterated versions are available, usually via the page for the main species. Work is permanently underway to add more datafiles. We encourage comments from the users in order to improve and extend the database.

This database should form an important tool in analyzing observations from current and future infrared and (sub)millimetre telescopes. Databases such as these rely heavily on the efforts by the chemical physics community to provide the relevant atomic and molecular data. We strongly encourage further efforts in this direction, so that data for more species become available and the current extrapolations of collisional rate coefficients can be replaced by actual calculations in future releases.

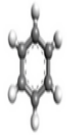
RADEX, a computer program for performing statistical equilibrium calculations is made publically available as part of the data base. The program comes in 2 versions: an on-line calculator for quick checks, and a stand-alone version for extensive calculations. **For publication-quality results, always use the stand-alone version.**

For new or changed datafiles, see the update history or follow us on Twitter.

If you use the data files in your work please refer to the publication by **Schöier, F.L., van der Tak, F.F.S., van Dishoeck E.F., Black, J.H. 2005, A&A 432, 369-379** introducing this data base. Please mention the date when you accessed the database, in case questions arise about different versions of datafiles. When individual molecules are considered, we strongly suggest that you also refer to the original papers providing the spectroscopic and collisional data.

The Cologne Database for Molecular Spectroscopy

CDMS



CLASSIC portal

VAMDC consortium

VAMDC portal (beta)

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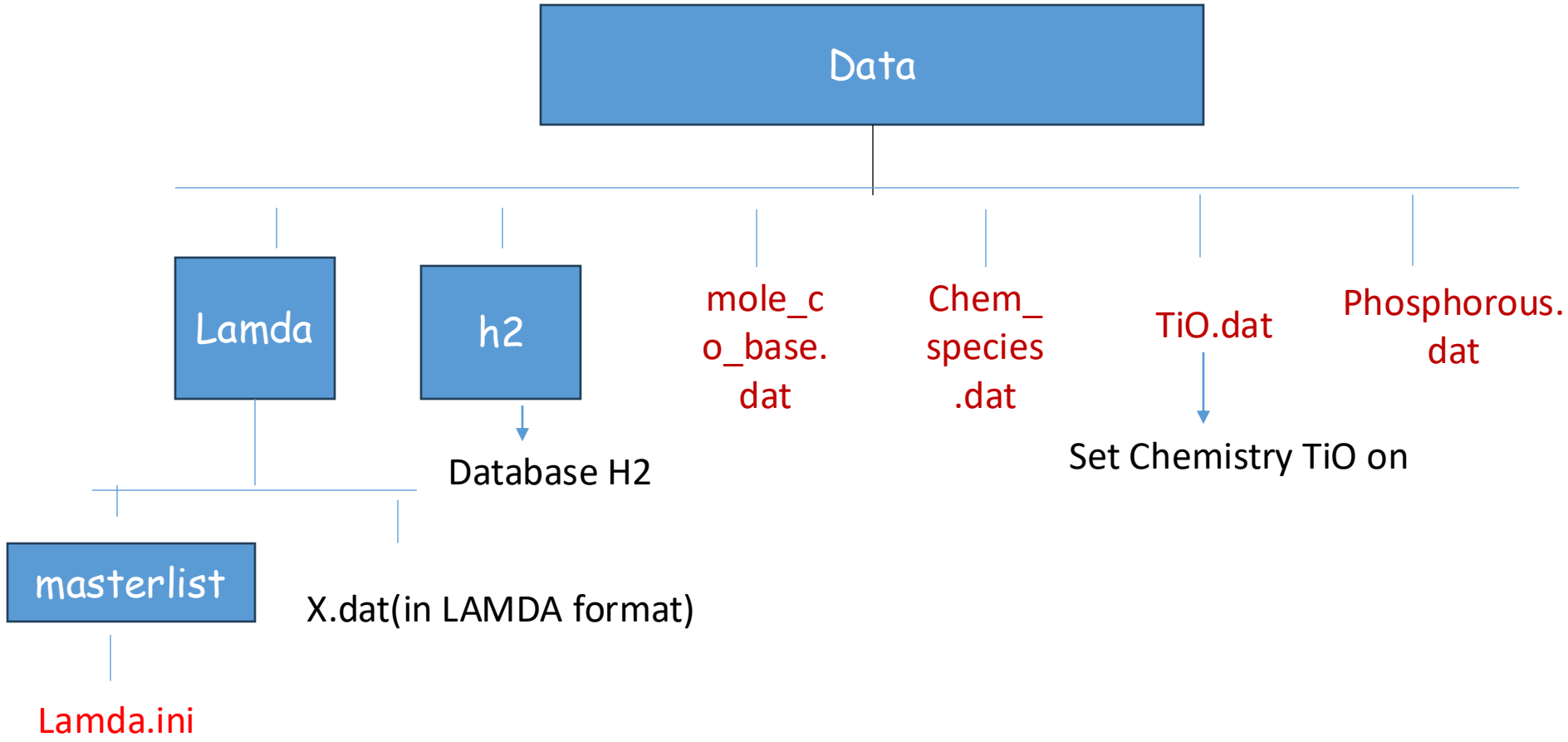
Adding new molecules



Adding new molecule in LAMDA format

- Data dir => mole_co_base.dat

  add reaction rates

  CH3,CN=>HCN,CH2:hmrate:9.21e-12:0.7:1500 # UMIST

- Data dir => Chem_species.dat

  add Species label and formation enthalpy at 0K in KJ/mol

  CN 436.8

- Data dir => lamda dir -> CN.dat

  molecule.dat stores internal structure in LAMDA format

- Data dir => lamda dir ->masterlist ->Lamda.ini

  modify Lamda.ini

  CN cn.dat

Run tsuite models and check asserts

Hydrogen Molecule

- About 90% of the current Baryonic matter is in the form of Hydrogen.

- Molecular hydrogen plays an important role in astrophysics.

  - It is the first and the most abundant neutral molecule to be formed in the Universe.

  - As a highly efficient coolant, it increases the rate of formation of galaxies in primordial gas

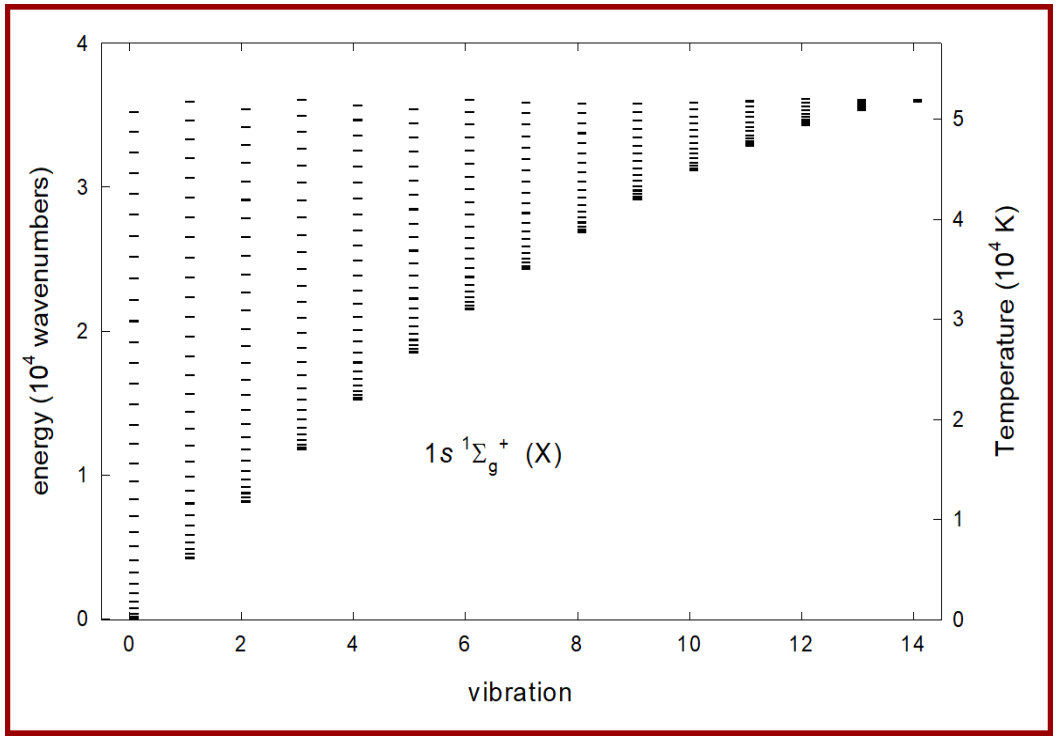
  - In the interstellar gas, the formation of molecular hydrogen controls
    * Ionization
    * Thermal balance
    * Mechanism of star formation.

  - Molecular hydrogen is a major constituent of giant molecular clouds.

Hydrogen Molecule

- Hydrogen molecule (H_2) is the simplest neutral molecule consisting of two protons and two electrons.
- H_2 has several electronic energy states and each electronic state consists of several vibrational and rotational levels.
- It is a symmetric molecule and does not have a permanent electric dipole moment.

Energy levels within the ground electronic state



Shaw et al. 2005

Hydrogen Molecule

Fermi statistics

- Total (nuclear × electronic) wave function must be anti-symmetric under the exchange of nuclei

- Ortho states : Total spin I =1, Degeneracy : 3 × (2J+1)
  Nuclear spin wave function : symmetric
  Spatial wave function : anti-symmetric

- Para states : Total spin I=0, Degeneracy : 2J+1
  Nuclear spin wave function : anti-symmetric
  Spatial wave function : symmetric

Ground state

Even J : Para state Odd J : Ortho state

In ground state rovibrational transitions can occur only via quadrupole transitions with ΔJ=0, ±2.

Micro-physics of H_2

Formation of H_2	Destruction of H_2
• Catalysis on the grain surface $H + H + grain \rightarrow H_2 + grain$ • Radiative association processes *i.* $H^- + H \rightarrow H_2 + e^-$ *ii.* $H_2^+ + H \rightarrow H_2 + H^+$	• Solomon process • Direct photo-dissociation • Collisional dissociation

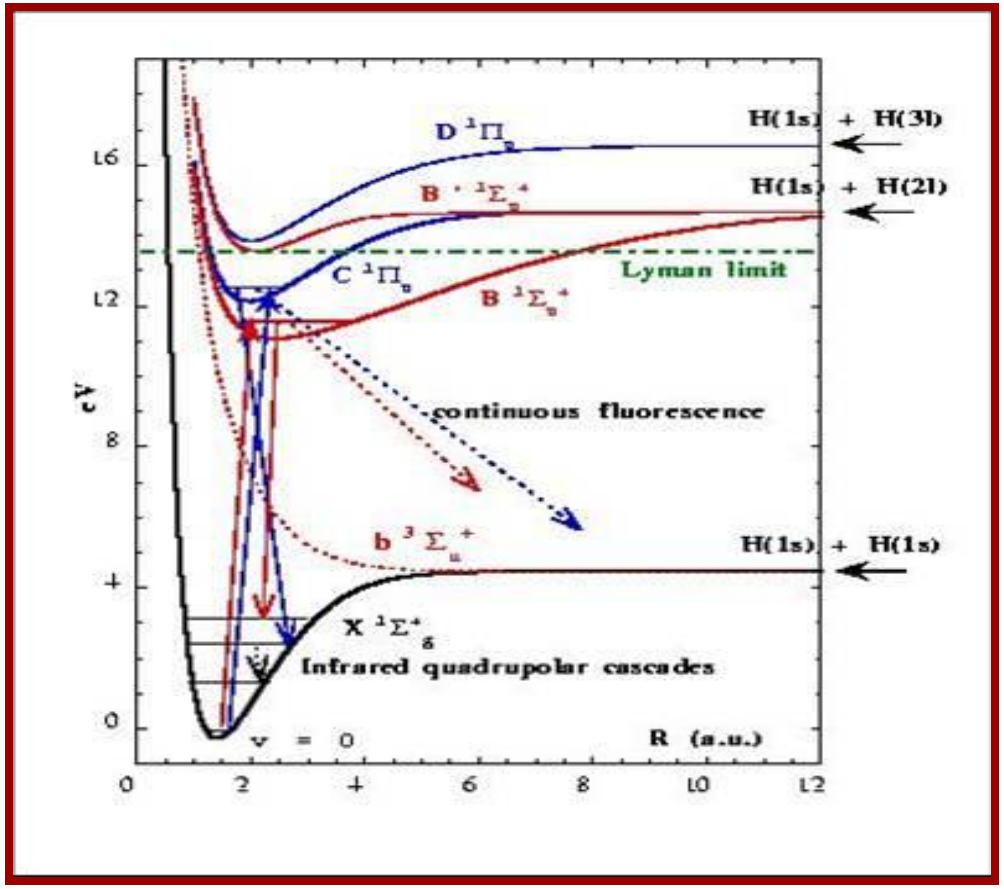
Shaw et al. 2005

DESTRUCTION OF H_2

Solomon process

- Molecular hydrogen is excited to $B^1\Sigma_u^+$ or $C^1\Pi_u^{\pm}$ states by absorbing Lyman & Werner band photons.

- About 85% of the electronically excited state decay to the bound ground state and 15% decay to the continuum of the ground state.



Roueff 2000

DESTRUCTION OF H_2

- Collisional dissociation

  Collisional dissociation by H, He, H_2 and e^- are also possible from higher vib-rotational state

- Pumping via X-ray electrons

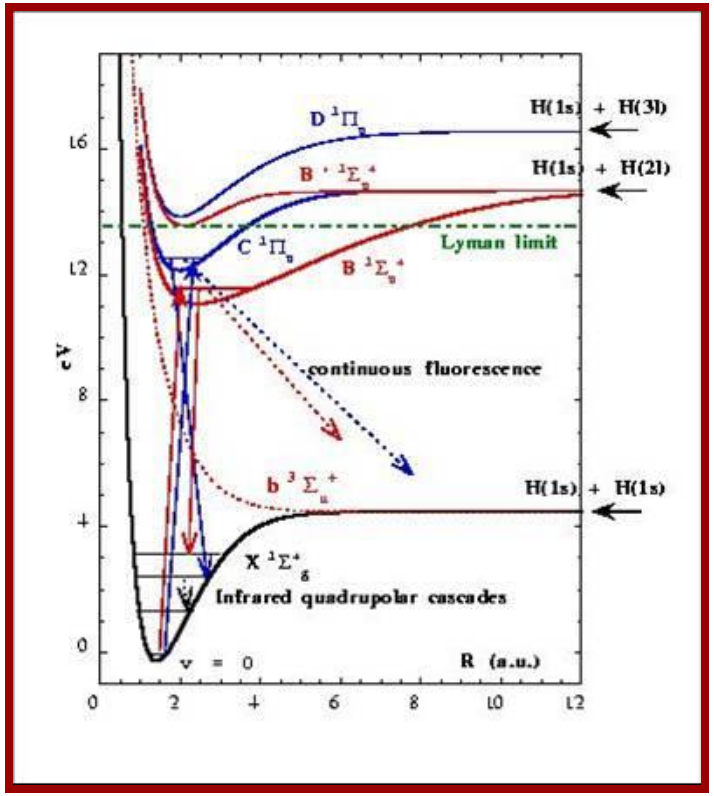
  Molecular hydrogen is excited to $B^1\Sigma u^+$ or $C^1\Pi_u^{\pm}$ state by secondary electrons.

- Excitation to the triplet b state

  Molecular hydrogen is excited to triplet b state by energetic secondary electrons and is dissociated

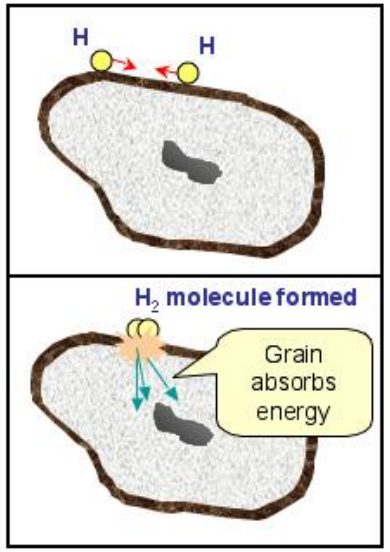
- Cosmic ray ionization

  $H_2 + CR \rightarrow H_2^+ + e^-$



FORMATION OF H_2

Catalysis on grain surfaces



$H + H + grain \rightarrow H_2 + grain$

Other processes

i. $H^- + H \rightarrow H_2 + e^-$

ii. $H_2^+ + H \rightarrow H_2 + H^+$

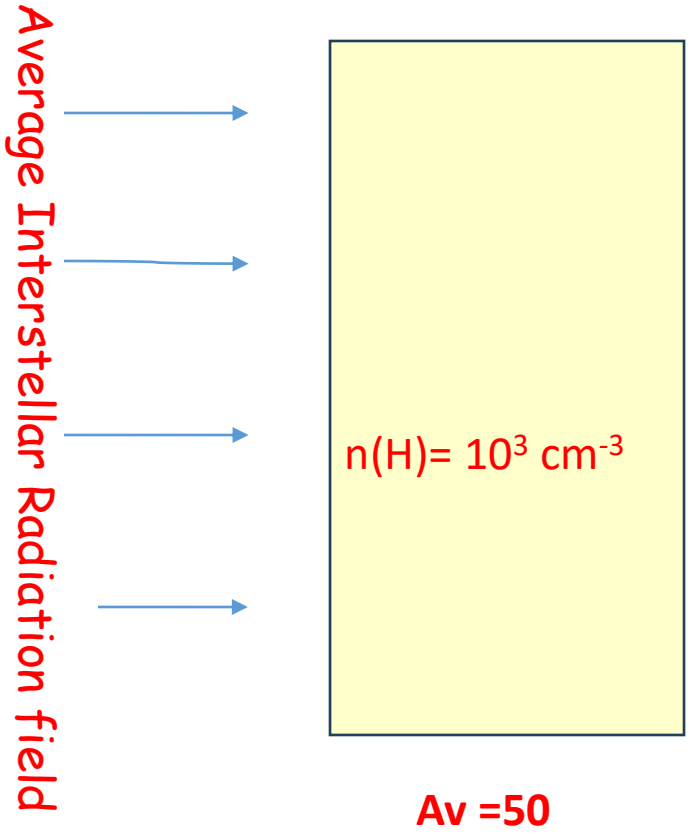
Ortho-Para conversion

- No Radiative decay
- Exchange collisions between H_2 and H, H^+ and H_3^+
  - $H_2(v, J) + H \rightarrow H_2(v', J') + H$ (Sun & Dalgarno 1994)
  - $H_2(v, J) + H^+ \rightarrow H_2(v', J') + H^+$ (Gerlich 1990)
  - $H_2(v, J) + H_3^+ \rightarrow H_2(v', J') + H_3^+$ (Same as H^+)
- On grain surfaces (below critical temperature)

Source Dir => h2.cpp, mole_h2.cpp, mole_h2_io.cpp, mole_h2_coll.cpp, mole_h2_create.cpp
Data Dir => H2 dir

Test model (input script)

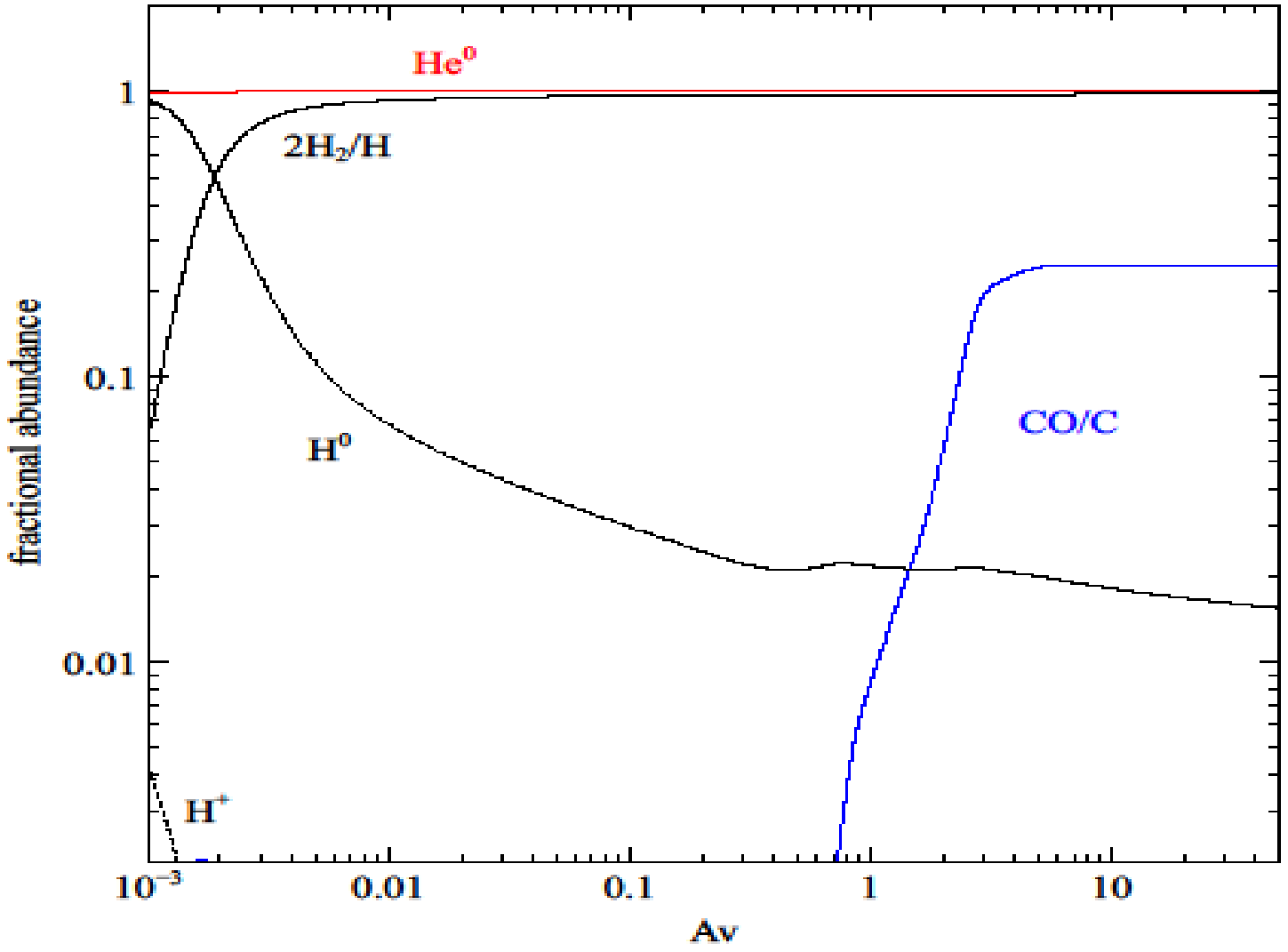
```
title test_Lexington_2025
set save prefix "test_lexington"
# commands controlling continuum =========
Table ISM
# commands for density & abundances =========
# hydrogen density
hden 3.
abundances gass10 no grains
#
# commands controlling H2  =========
database h2
# commands conrolling dust grains ======
grains ism
# command controlling cosmic rays
COSMIC RAYS BACKGROUND
CMB
# commands controlling Ti-Chemistry ====
set chemistry TiO on
# commands controlling stopping criteria ===
stop temperature 3 linear
stop Av 50
# commands controlling output    =========
print line faint -7
print lines column
print lines sort wavelength
save overview ".ovr"
save continuum ".con"
save grain dust temperature ".grn"
save chemistry rates destruction ".H2d" "H2"
save chemistry rates creation ".H2c" "H2"
save H2 lines ".h2lin"
save H2 column density ".h2.col"
# test_lexington.in
```



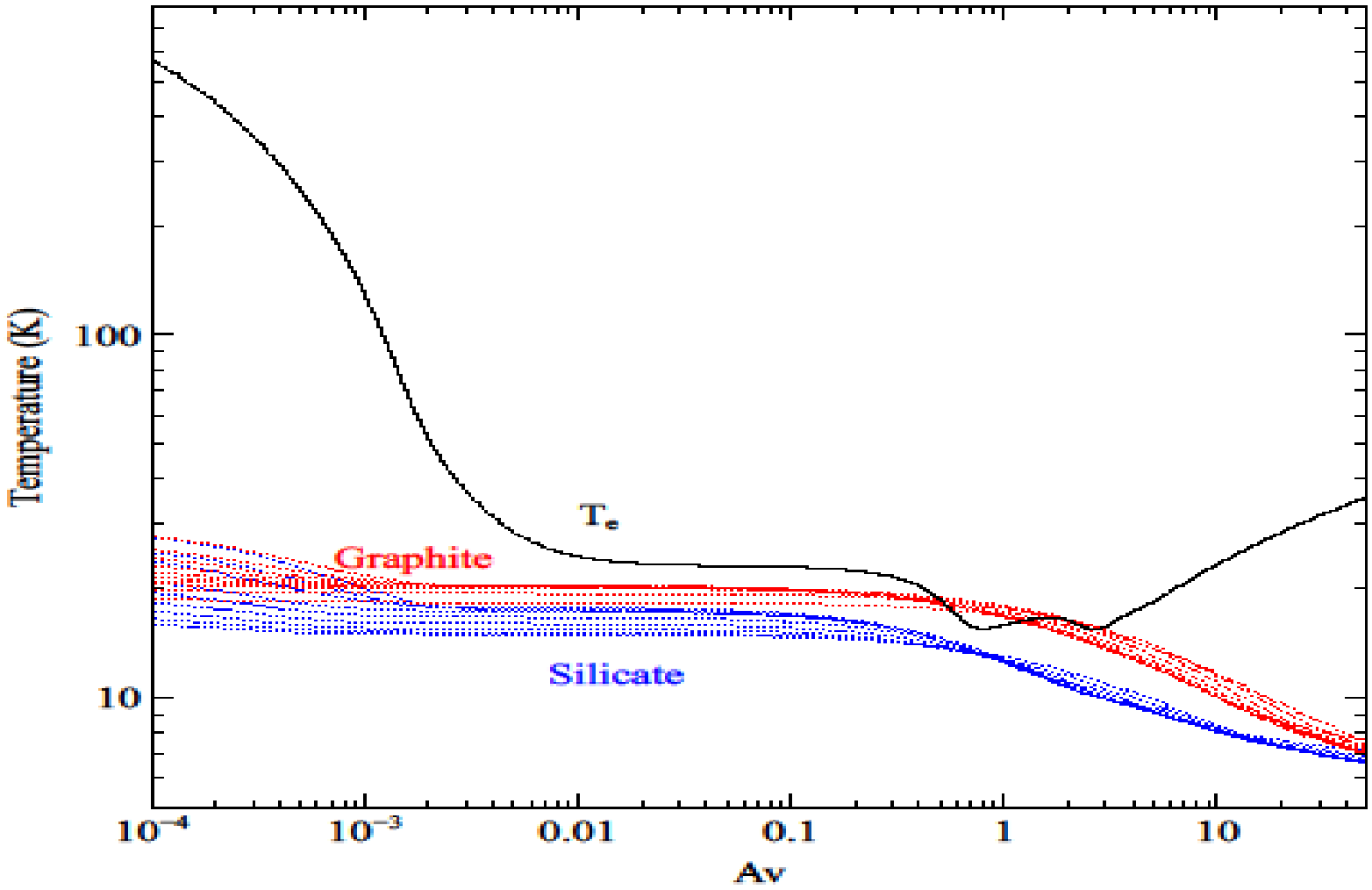
Test model (output)

```
==== H      compounds ====          Log10 column densities [cm^-2]
 H2        : 22.658   H2*        : 14.376   H2+        : 13.426   H3+        : 15.604
==== He     compounds ====
 HeH+      :  9.623
=== Li     compounds ====
 LiH       :  4.073   LiH+       :  1.911
==== C      compounds ====
 CH        : 16.889   CH+        : 12.356   CH2        : 16.016   CH2+       : 12.332   CH3        : 15.048   CH3+       : 13.624   CH4        : 14.725   CH4+       :  9.686
CH5+       : 10.854   C2         : 17.369   C2+        : 11.561   C2H        : 16.458   C2H+       : 11.595   C2H2       : 12.090   C2H2+      : 12.887   C2H3+      :  9.298
C3         : 15.276   C3+        :  9.429   C3H        : 12.938   C3H+       : 11.499
==== N      compounds ====
 NH        : 15.509   NH+        : 10.989   NH2        : 15.153   NH2+       : 11.617   NH3        : 14.231   NH3+       : 12.516   NH4+       :  9.682   CN         : 16.126
CN+        :  9.751   HCN        : 15.789   HCN+       : 10.389   HNC        : 15.865   HCNH+      : 12.142   HC3N       : 14.817   N2         : 18.004   N2+        : 13.071
N2H+       : 13.181
==== O      compounds ====
OH         : 15.333   OH+        : 11.435   OHgrn      : 15.249   H2O        : 15.977   H2O+       : 11.359   H2Ogrn     : 19.538   H3O+       : 12.418   CO         : 18.763
CO+        :  9.895   COgrn      : 18.390   HCO+       : 13.447   H2CO       :  9.902   CH3OH      :-19.493   NO         : 14.720   NO+        : 10.327   HNO        : 12.133
HNO+       :  9.220   OCN        : 10.396   OCN+       :  8.325   N2O        :  8.447   O2         : 14.285   O2+        :  9.375   NO2        :  9.936   NO2+       :  2.570
==== F      compounds ====
HF         : 14.292   HF+        :  6.045   H2F+       :  9.962   CF+        : 10.820
==== Ne     compounds ====
NeH+       : 12.913
==== Si     compounds ====
SiH        : 12.400   SiH2       :-18.584   SiH2+      :  9.593   SiC        :-35.930   SiC+       : 15.506   SiCH2+     :-35.930   SiC2       :-35.930   SiC2+      : -8.209
SiN        : 13.402   SiN+       : 11.305   SiNC       :-15.010   SiNC+      :  9.060   SiO        : 16.019   SiO+       : 10.384   SiOH+      : 11.490
==== P      compounds ====
PH         : 11.627   PH+        : 11.238   PH2        : 10.265   PH2+       :  8.958   PH3        :  9.716   PH3+       :  6.549   CP         : 11.519   CP+        :  5.278
HCP        :-35.930   HCP+       :  6.559   PN         : 15.213   PN+        : 10.413   PO         : 12.651   PO+        :  9.565
==== S      compounds ====
 HS        : 13.990   HS+        : 12.844   CS         : 17.593   CS+        : 12.070   HCS+       : 13.816   NS         : 13.885   NS+        : 10.431   SO         : 14.020
SO+        : 10.121   OCS        : 12.705   OCS+       :  8.787   SO2        :-20.470   SiS        : 14.271   SiS+       :  8.409   HSiS       :-35.930   HSiS+      : 10.416
S2         :-12.181   S2+        :-13.798
==== Cl     compounds ====
HCl        : 14.186   HCl+       : 10.689   H2Cl+      : 11.416   CCl        : 10.948   CCl+       :  9.924   H2CCl+     :  6.951   ClO        :-28.998   ClO+       :-34.061
==== Ar     compounds ====
ArH+       :  9.501
==== Ti     compounds ====
TiH        :  8.407   TiH+       : 10.432   TiH2       :-35.930   TiH2+      :  7.572   TiC        : 13.992   TiC+       :  9.264   HCTi       : 14.111   HCTi+      : 10.948
TiC2       : 10.128   TiC2+      : 10.165   TiN        : 14.054   TiN+       : 10.172   HNTi       :-35.930   HNTi+      :  8.808   TiNC       :-35.930   TiNC+      : 10.038
TiO        : 13.190   TiO+       :  8.928   TiOH+      :  9.487   TiO2       :  9.819   TiF+       :  9.384   TiS        :  7.621   TiS+       :  5.901   HTiS+      :  4.388
```

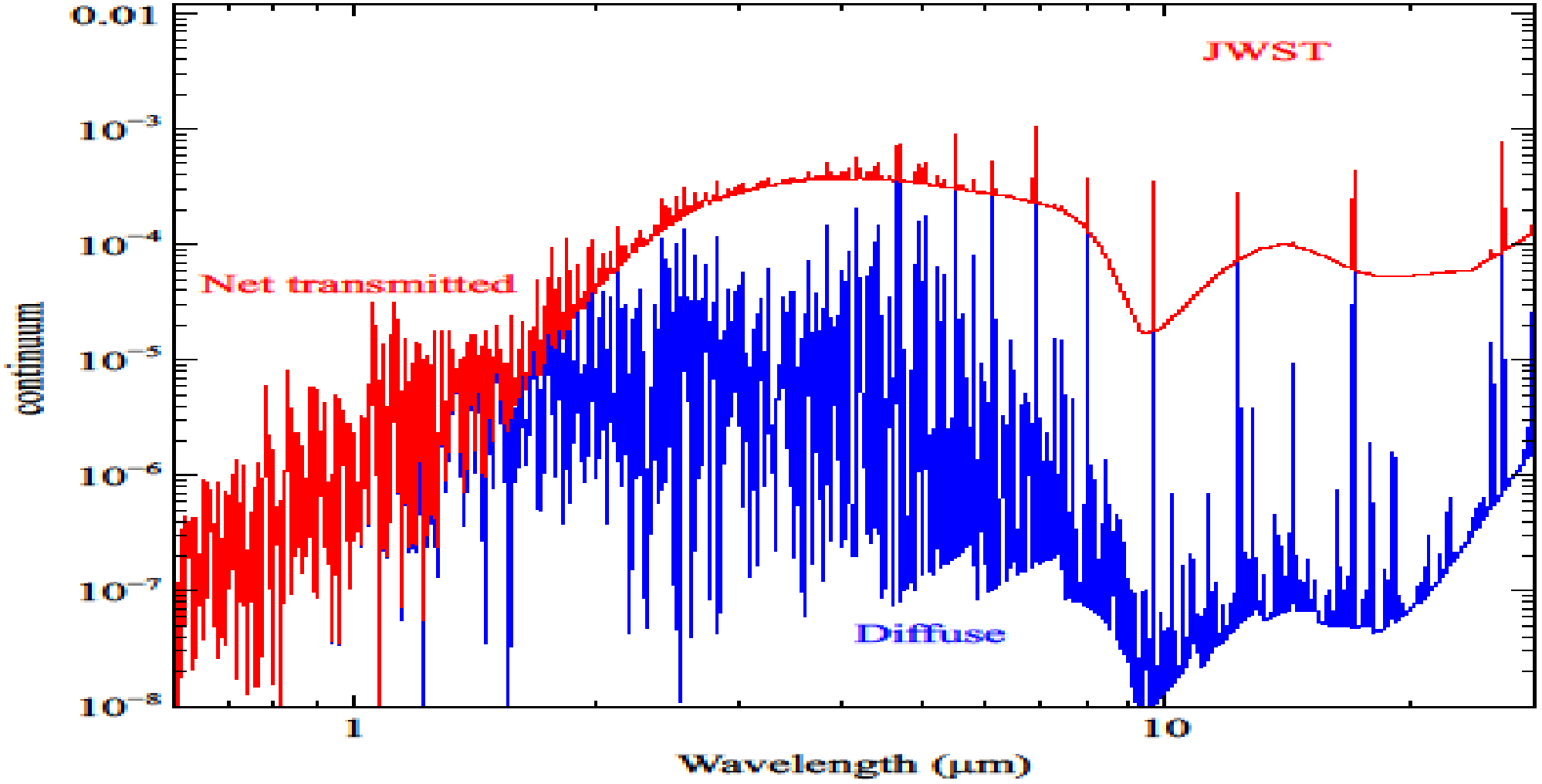
Test model (output)



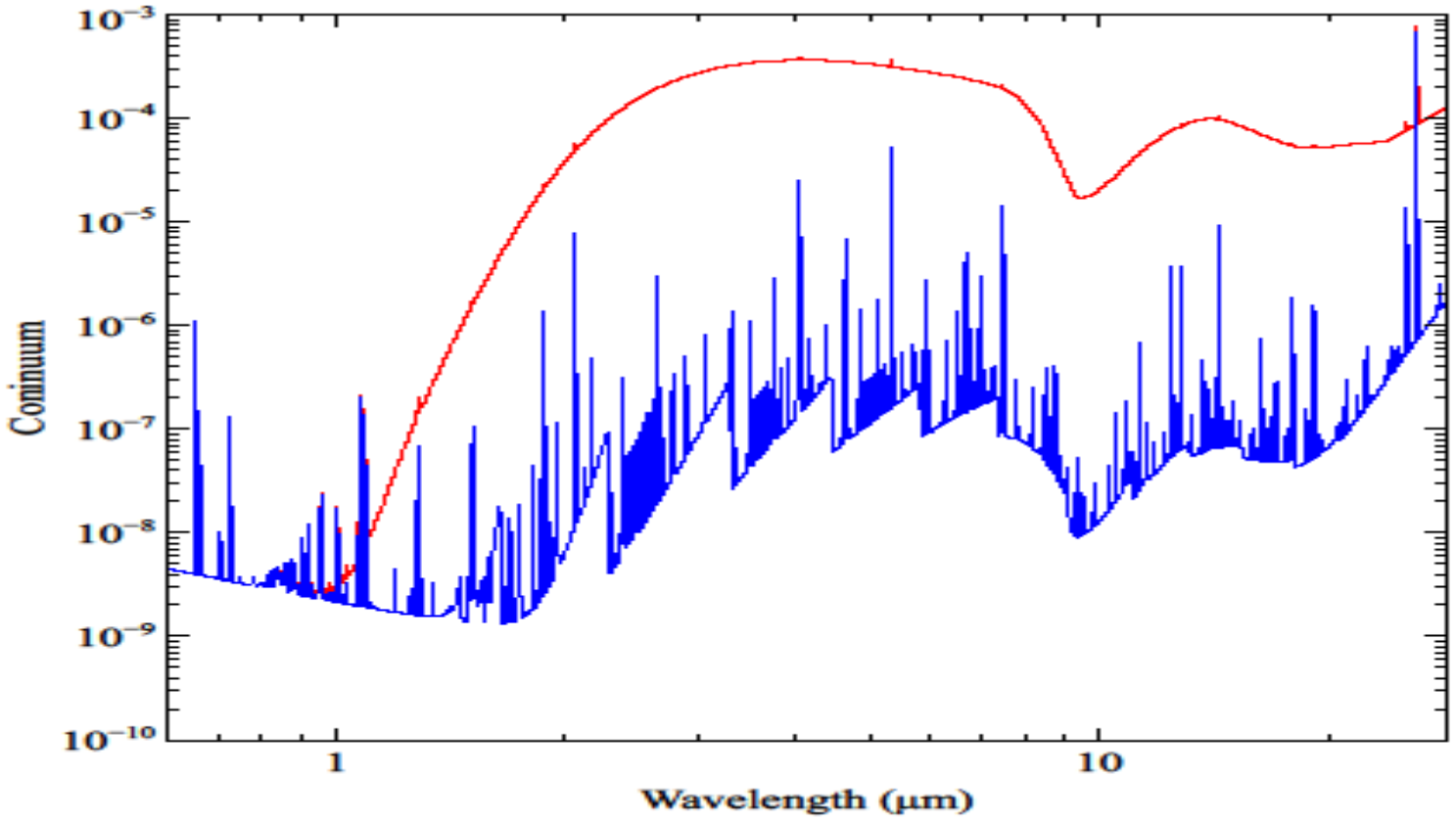
Test model (output)



Test model (output)

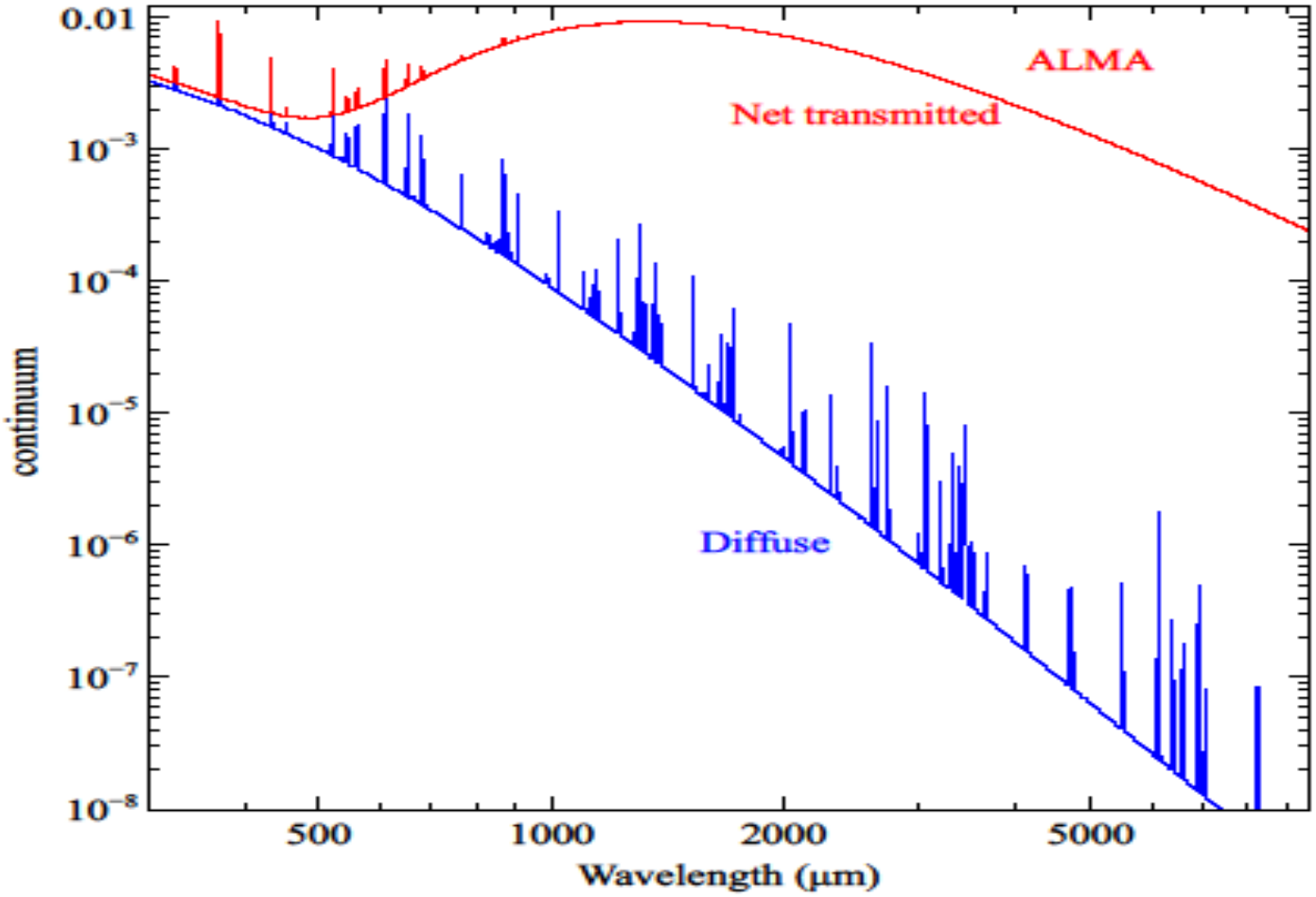


Test model (output)



Database H2 turned off

Test model (output)



Test model (output)

H_2(0,J) column density

vib	rot	Ener(K)	colden	colden/stat wght	LTE colden	LTE colden/stat wght
0	0	0.0	4.258e+22	4.258e+22	4.406e+22	4.406e+22
0	1	170.5	2.922e+21	3.246e+20	1.443e+21	1.603e+20
0	2	509.9	1.117e+17	2.234e+16	3.153e+16	6.305e+15
0	3	1015.1	7.200e+16	3.428e+15	2.138e+14	1.018e+13
0	4	1681.6	5.316e+15	5.906e+14	8.449e+12	9.388e+11
0	5	2503.7	3.297e+15	9.990e+13	4.655e+12	1.411e+11

Test model (output)

#H2 line	Ehi	Vhi	Jhi	Elo	Vlo	Jlo	wl(ang)	wl(lab)	log L or I	I/Inorm
0-0 S(0)	0	0	2	0	0	0	282111.469	28.2111m	-6.683	0.04573
0-0 S(1)	0	0	3	0	0	1	170302.047	17.0302m	-5.403	0.8715
0-0 S(2)	0	0	4	0	0	2	122752.656	12.2753m	-5.626	0.5223
0-0 S(3)	0	0	5	0	0	3	96622.766	9.66228m	-5.176	1.469
0-0 S(4)	0	0	6	0	0	4	80228.539	8.02285m	-5.581	0.5782
0-0 S(5)	0	0	7	0	0	5	69076.25	6.90763m	-5.155	1.542
0-0 S(6)	0	0	8	0	0	6	61068.984	6.10690m	-5.623	0.5257
1-0 O(2)	0	1	0	0	0	2	26261.666	2.62617m	-5.985	0.2283
1-0 Q(1)	0	1	1	0	0	1	24059.354	2.40594m	-5.874	0.2948
1-0 O(3)	0	1	1	0	0	3	28017.521	2.80175m	-5.942	0.2522
1-0 S(0)	0	1	2	0	0	0	22226.836	2.22268m	-6.062	0.1912
1-0 Q(2)	0	1	2	0	0	2	24127.805	2.41278m	-5.894	0.2815
1-0 O(4)	0	1	2	0	0	4	30030.49	3.00305m	-6.012	0.2147
1-0 S(1)	0	1	3	0	0	1	21212.547	2.12125m	-5.658	0.4844

Future plans

- ✓ Currently only 47 out of the 191 molecules included in Cloudy have associated spectral lines. In the future, we plan to incorporate internal structures for the remaining molecules to enable the prediction of their spectral lines.
- ✓ In addition, we will include higher vibrational and rotational levels in the molecular models to better support the JWST observations.
- ✓ Currently we do not include formation of molecules on dust grains (except H2). In future, we would like to include formation of molecules on dust grains.

Molecular Hydrogen

THE ASTROPHYSICAL JOURNAL, 624:794–807, 2005 May 10
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MOLECULAR HYDROGEN IN STAR-FORMING REGIONS: IMPLEMENTATION OF ITS MICROPHYSICS IN CLOUDY

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Received 2004 August 30; accepted 2005 January 16

RNAAS RESEARCH NOTES OF THE AAS

Cosmic Ray Dissociation of Molecular Hydrogen and Dense Cloud Chemistry

Gargi Shaw[1], G. J. Ferland[2], and S. Ploeckinger[3]
Published June 2020 • © 2020. The American Astronomical Society. All rights reserved.
Research Notes of the AAS, Volume 4, Number 6
Citation Gargi Shaw *et al* 2020 *Res. Notes AAS* **4** 78
DOI 10.3847/2515-5172/ab97ae

Recent Molecular updates

The Astrophysical Journal, 934:53 (21pp), 2022 July 20
https://doi.org/10.3847/1538-4357/ac7789
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OPEN ACCESS

Recent Updates to the Gas-phase Chemical Reactions and Molecular Lines in CLOUDY: Their Effects on Millimeter and Submillimeter Molecular Line Predictions

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Received 2021 September 11; revised 2022 June 2; accepted 2022 June 8; published 2022 July 25

To appear in *Revista Mexicana de Astronomía y Astrofísica*

RECENT UPDATE OF GAS-PHASE CHEMICAL REACTIONS AND MOLECULAR LINES OF TiO IN CLOUDY

Gargi Shaw[1], Gary J. Ferland[2], Phillip Stancil [3], Ryan Porter [4]

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Recent Updates of Gas-phase Chemical Reactions and Molecular Lines of SiS in CLOUDY

Gargi Shaw[1], Gary Ferland[2], and M. Chatzikos[2]
Published March 2023 • © 2023. The Author(s). Published by the American Astronomical Society.
Research Notes of the AAS, Volume 7, Number 3
Citation Gargi Shaw *et al* 2023 *Res. Notes AAS* **7** 45
DOI 10.3847/2515-5172/acc1ea

Thank you