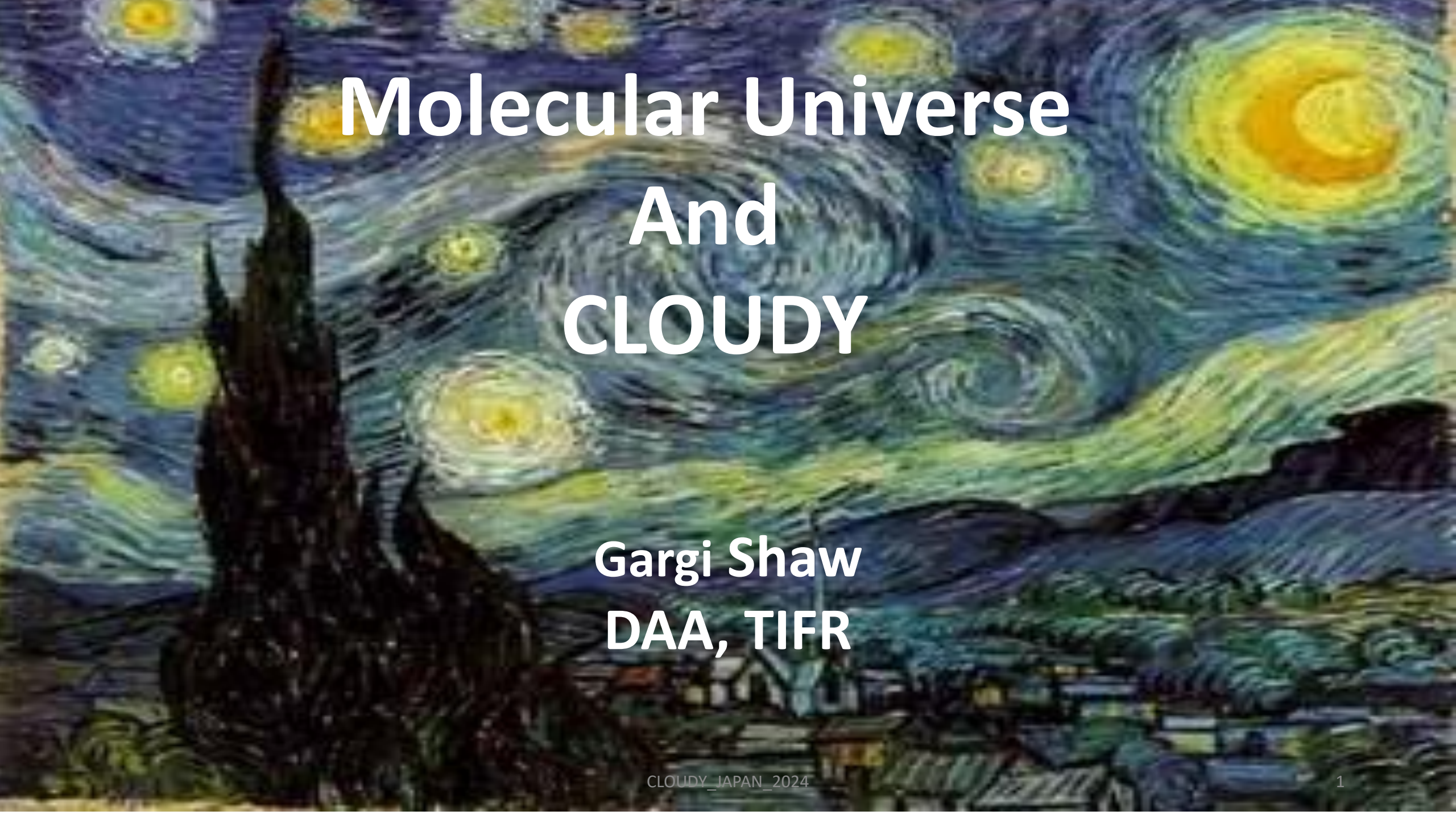


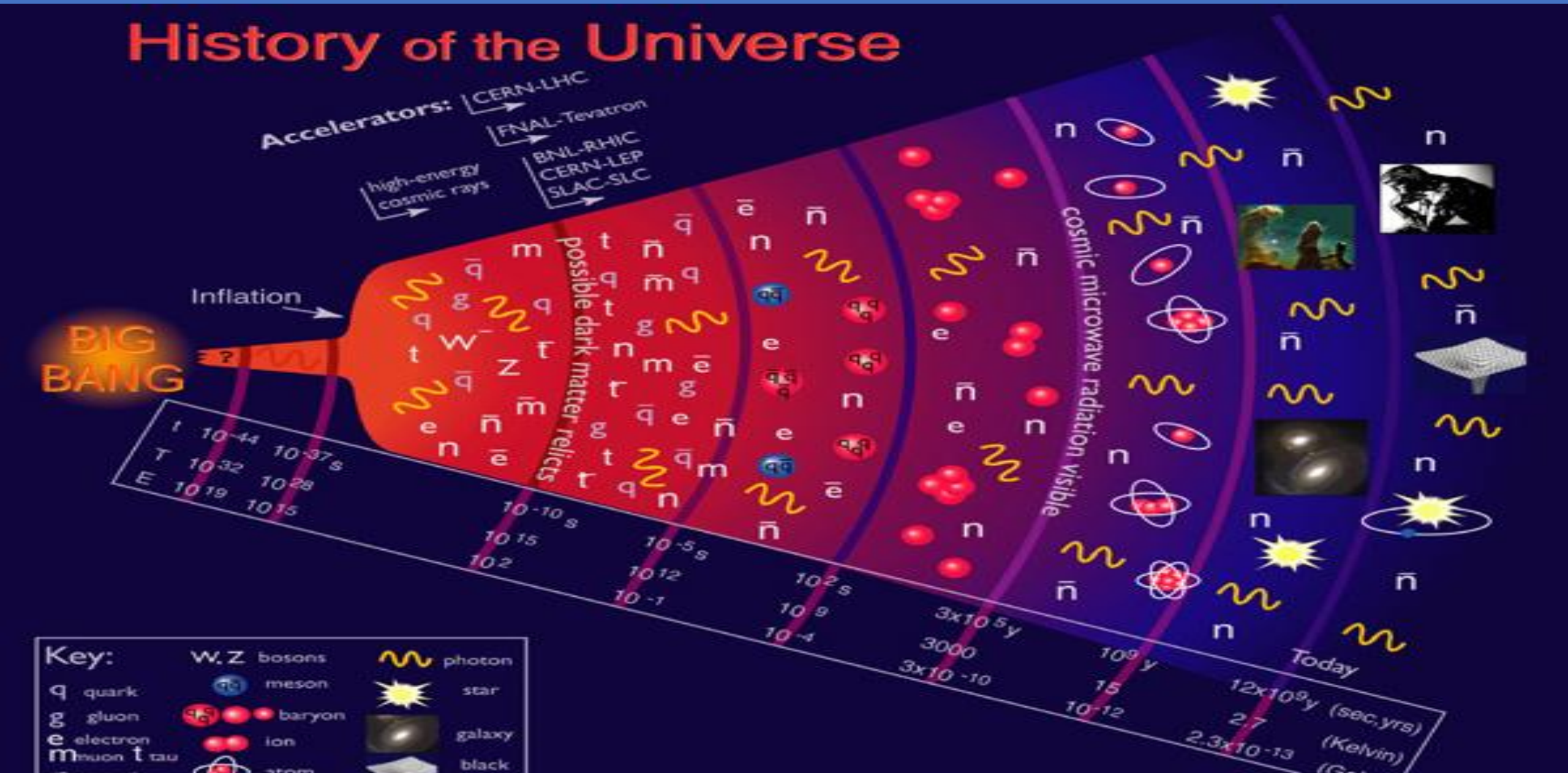
Molecular Universe And CLOUDY

Gargi Shaw
DAA, TIFR

Outline

- A brief introduction to molecules and its importance
- Molecular network of CLOUDY
  - H_2
  - Other molecules
- How to include new molecules in CLOUDY

Molecules formed much later

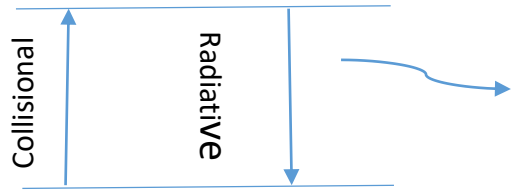


Why molecules are important?

❖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

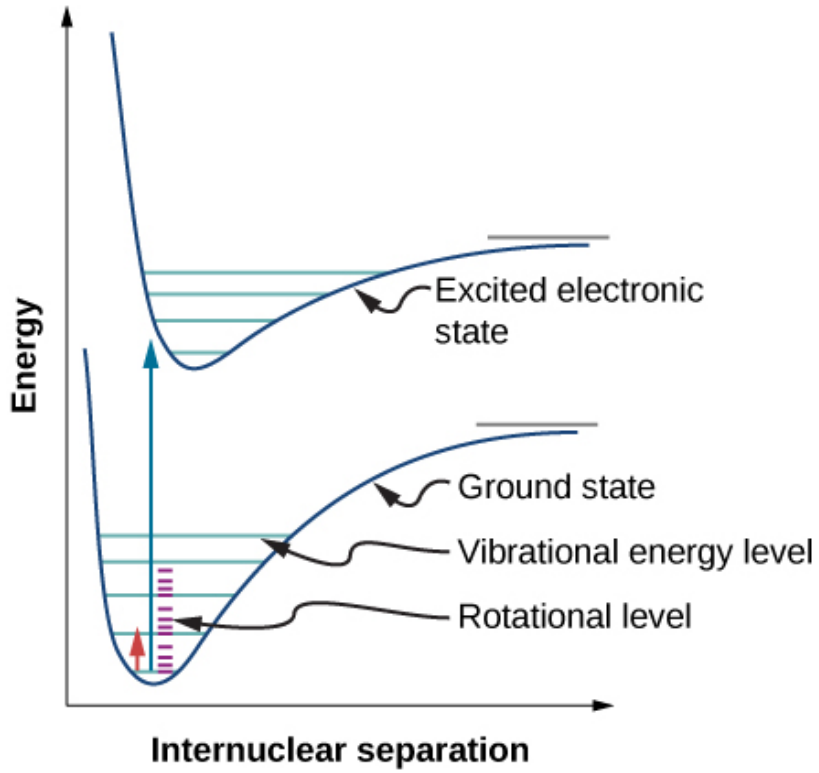
temperature T_{kin}

density n_H

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



List of Molecules predicted by CLOUDY

H_2, H_2^+, H_3^+
HeH^+
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^+
NeH^+
SiH, SiH_2^+, SiN, SiN^+, SiO, SiO^+, $SiOH^+$
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^+
ArH^+
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^+, $HTiS^+$

Work on P-related chemistry is now in progress.

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

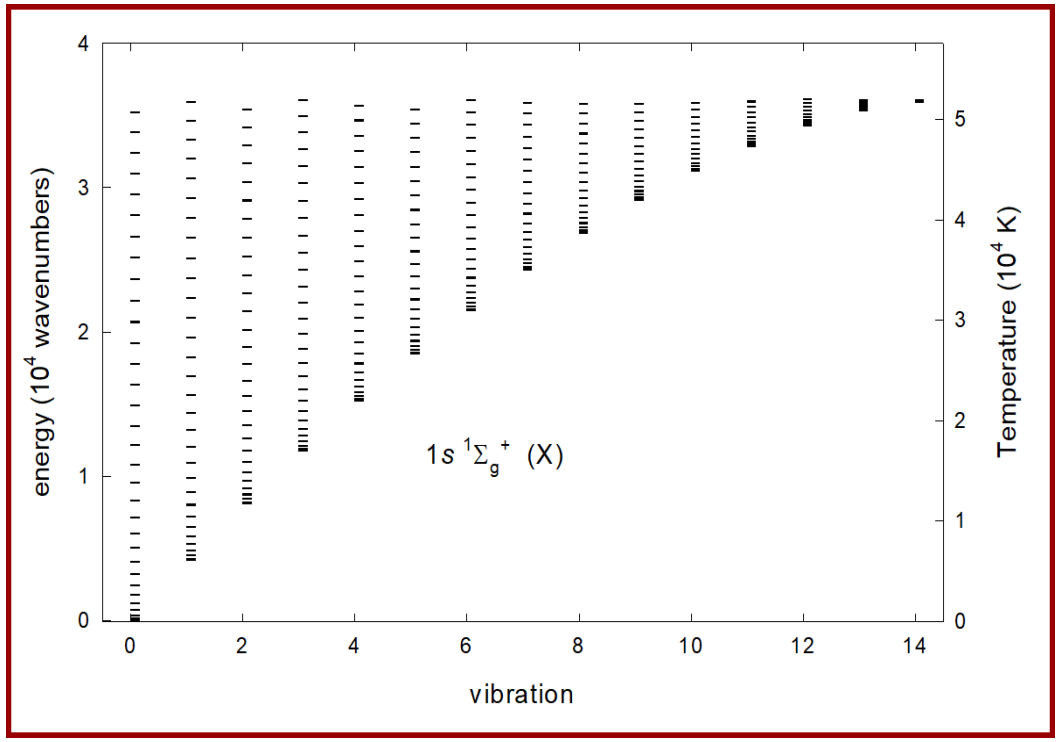
  - In the interstellar gas, the formation of molecular hydrogen controls
    * Ionization
    * Thermal balance
    * Mechanism of star formation.

  - 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.

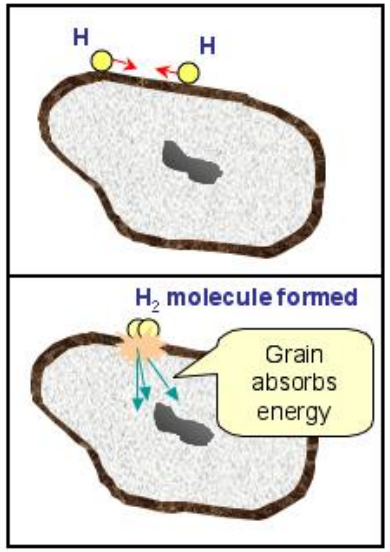
Micro-physics of H_2

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

FORMATION OF H_2

Catalysis on grain surfaces



H + H + grain → H_2 + grain

Other processes

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

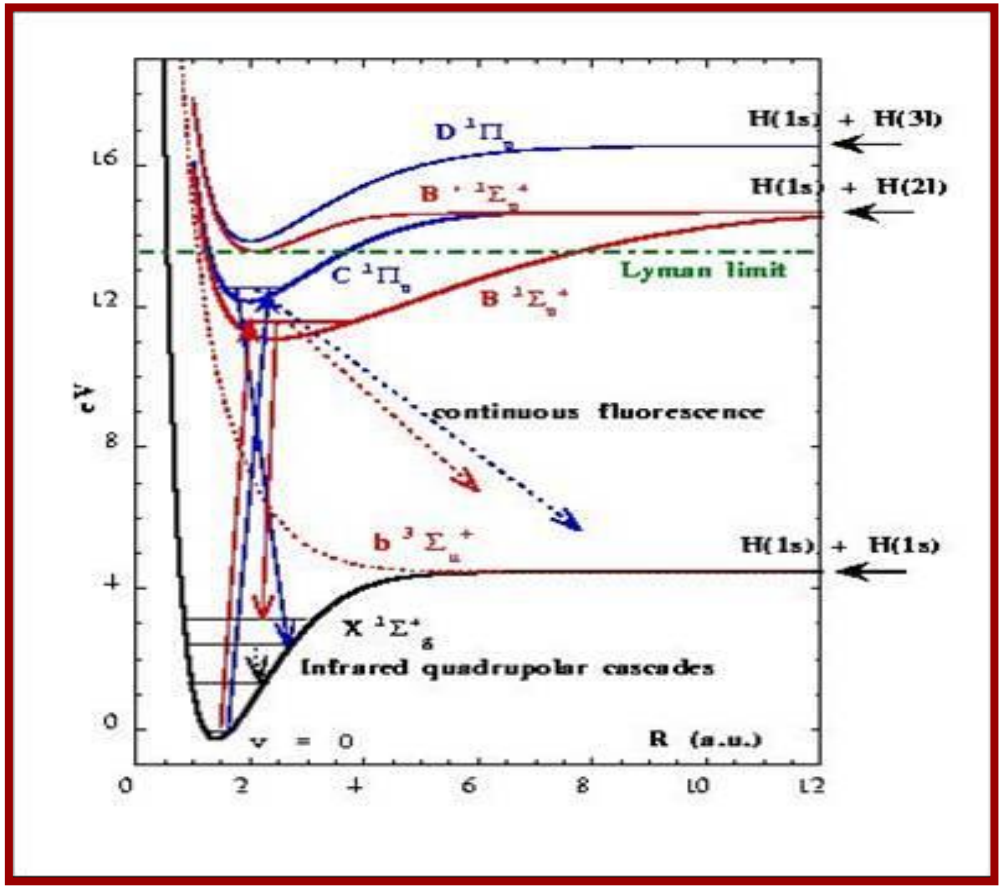
ii. $H_2^+ + H \rightarrow H_2 + H^+$

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

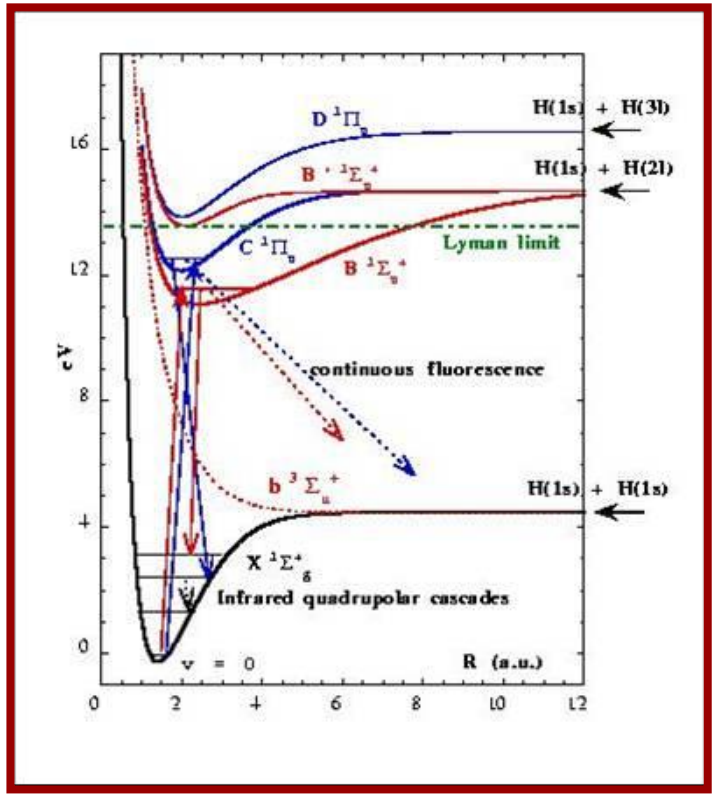
  Molecular hydrogen is excited to $B^1\Sigma u^+$ or $C^1\Pi_u^{\pm}$ state by secondary electrons.

- Excitation to the triplet b state

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

- Cosmic ray ionization

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



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

Molecular Hydrogen

The Astrophysical Journal, 624:794–807, 2005 May 10

MOLECULAR HYDROGEN IN STAR-FORMING REGIONS: IMPLEMENTATION OF ITS MICROPHYSICS IN CLOUDY

G. Shaw,[1] G. J. Ferland,[1] N. P. Abel,[1] P. C. Stancil,[2] and P. A. M. van Hoof[3]
Received 2004 August 30; accepted 2005 January 16

RNAAS RESEARCH NOTES OF THE AAS

Cosmic Ray Dissociation of Molecular Hydrogen and Dense Cloud Chemistry

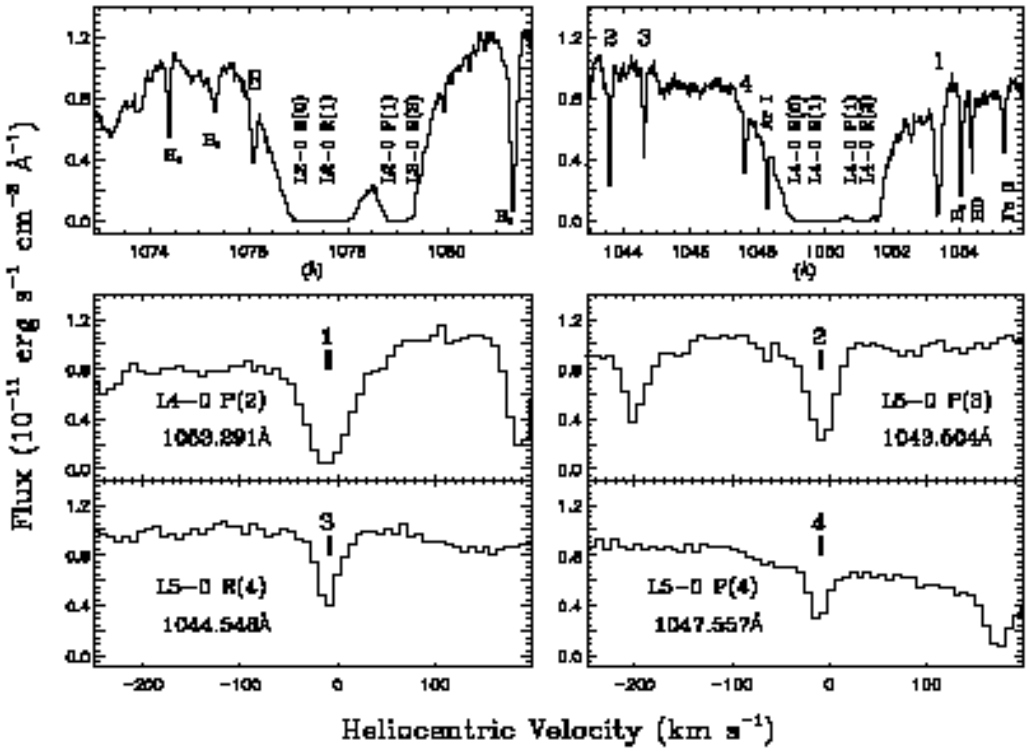
Gargi Shaw[1], G. J. Ferland[2], and S. Ploeckinger[3]
Published June 2020 • © 2020. The American Astronomical Society. All rights reserved.
Research Notes of the AAS, Volume 4, Number 6
Citation Gargi Shaw *et al* 2020 *Res. Notes AAS* **4** 78
DOI 10.3847/2515-5172/ab97ae

In the input script include "Database H2"
Section 12.3 of Hazy 1: Database H2 commands

Physical conditions in ISM towards HD185418

HD185418 is a well studied B0.5 V star located at Galactic coordinates (*l*, *b*) = (53°, -2.2°) at a distance of 790 pc.

Large number of molecular, atomic, and ionic absorption lines (Sonnentrucker et al. 2003).



Physical conditions in ISM towards HD185418

In the input script include “Database H2”

Model parameters

Plane parallel geometry

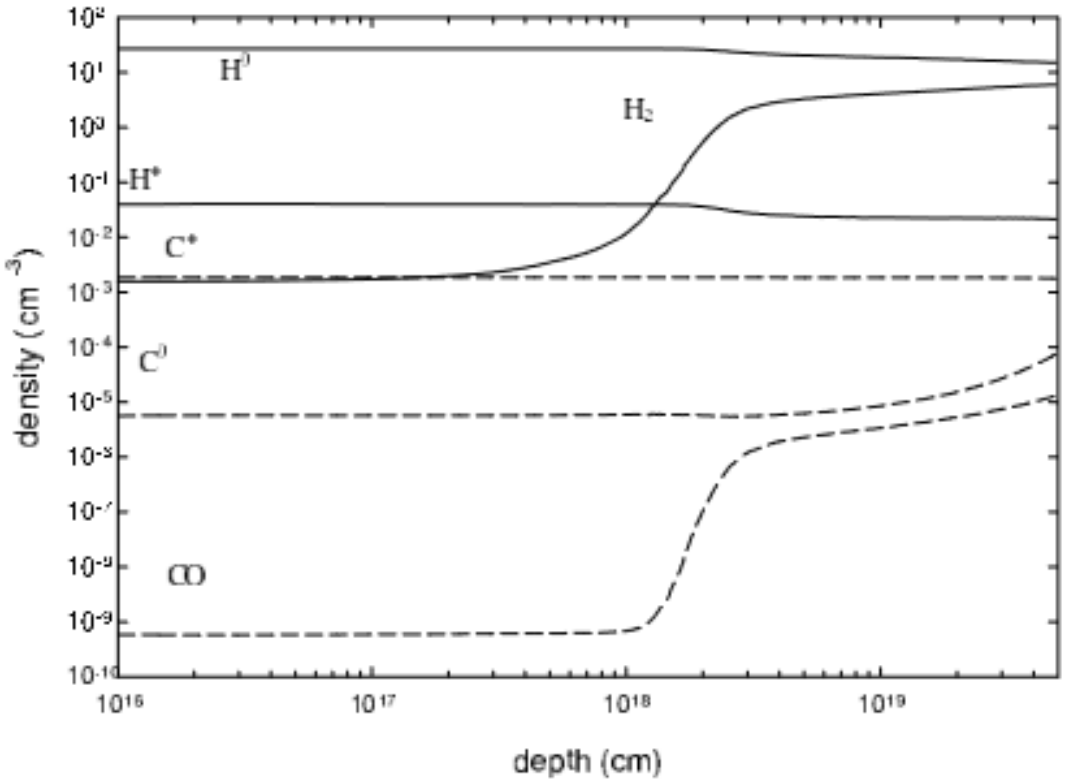
- 1.6 × Black (1987) Galactic background radiation field
- Turbulence = 6.0 km s^{-1}
- n_H = 25 cm^{-3}
- CR = 18 Galactic Background
- T_{10} = 83 K

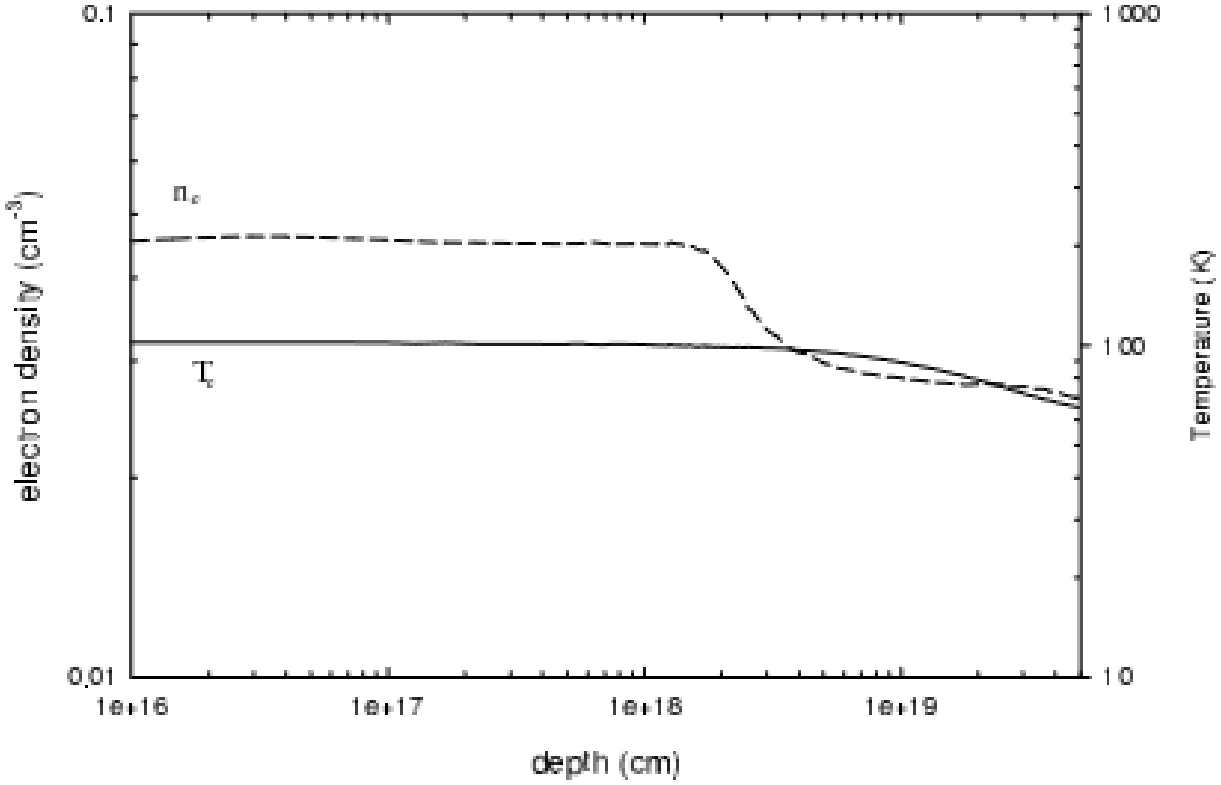
$$T_{10} = -170.5 \left\{ \ln \left[\frac{N(J=1)}{9N(J=0)} \right] \right\}^{-1},$$

Physical conditions in ISM towards HD185418

Chemical elements	Observed log N (cm^{-2}) Sonnentrucker et al. 2003	Predicted log N(cm^{-2})
C I	15.53 ± 0.09	15.52
C I*	14.45 ± 0.08	14.61
C I**	13.59 ± 0.08	13.75
O I	18.15 ± 0.09	18.15
O I*	12.61 ± 0.16	12.67
O I**	≤ 12.40	12.18
CO	14.70 ± 0.10	14.73
H_2 (J=0)	20.30 ± 0.10	20.38
H_2 (J=1)	20.50 ± 0.10	20.44
H_2 (J=2)	18.34 ± 0.10	18.34
H_2 (J=3)	16.20 ± 0.15	16.20
H_2 (J=4)	15.00 ± 0.20	14.30
H_2 (J=5)	14.30 ± 0.80	13.94
H I	21.11 ± 0.15	21.22
N I	17.30 ± 0.09	17.33
C II	≤ 17.75	17.05
C II*	14.93 ± 0.10	14.90

Physical conditions in ISM towards HD185418





H_3^+ chemistry, electron density, ζ(H2)

Cosmic-ray ionization of H_2

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

Proton abstraction reaction

$$H_2^+ + H_2 \Rightarrow H_3^+ + H$$

Electronic dissociative recombination

$$H_3^+ + e^- \Rightarrow H + H + H \text{ or } H_2 + H$$

In a steady state,

$$\zeta(H_2)\, n(H_2) = k_e\, n(e^-)\, n(H_3^+)$$

where k_e is electron recombination co-efficient rate of H_3^+.

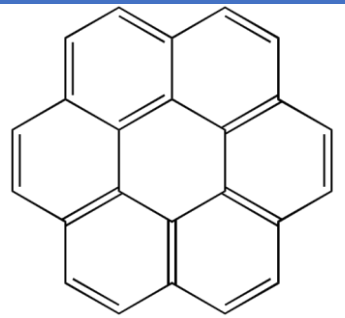
For a constant density cloud with length L,

$\zeta(H_2) = 2k_e n(e^-)N(H_3^+)/fN(H)[\ s^{-1}]$ where, $f = 2N(H_2)/N(H)$.

$n(e^-)$ plays a crucial role in determining the value of $\zeta(H_2)$.

k_e was measured by Oka & McCall (2004), but n_e is not observed directly.

Polycyclic Aromatic Hydrocarbons



- PAHs are ubiquities in the Galaxy.
- PAHs has benzene like structure.
- The abundances of C atoms locked up in PAHs containing 20–100 C atoms are 14 parts per million H atom (Tielens 2008)
- PAHs absorbs electrons very effectively.
- Electron density depends on the presence of PAHs.
- $\zeta(H_2)$ depends on the abundance of PAHs.
- $\zeta(H_2)$ is higher in the absance of PAHs

Include **grains PAHs** in the input script
Check SET PAH options in HAZY

HF, CF^+, HC_3N, ArH^+, HCl, HCN, CN, CH, CH_2, SiS, TiO and Ti-related molecules

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

OPEN ACCESS

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

Gargi Shaw[1], G. J. Ferland[2], and M. Chatzikos[2]
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To appear in *Revista Mexicana de Astronomía y Astrofísica*

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

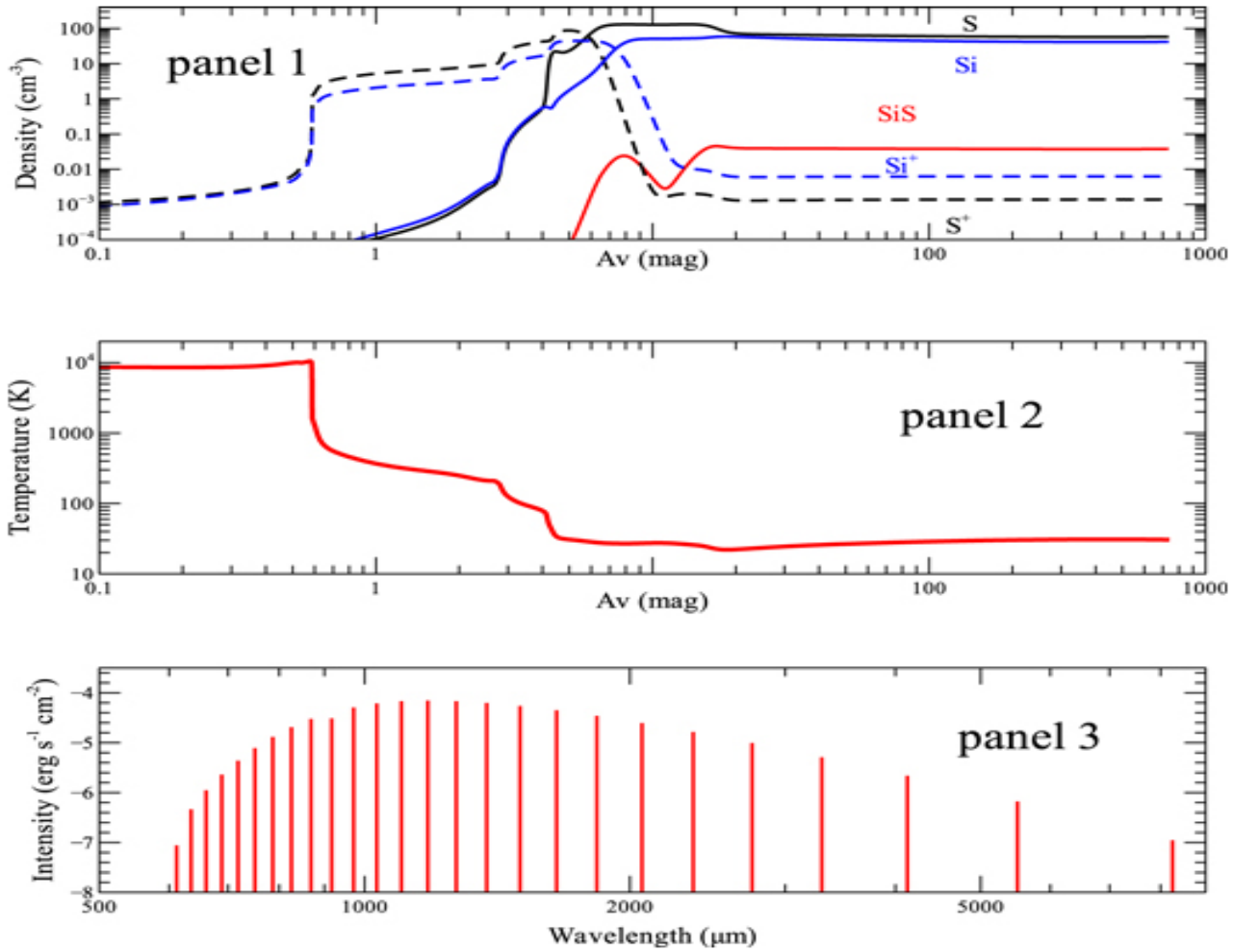
Gargi Shaw[1], Gary J. Ferland[2], Phillip Stancil [3], Ryan Porter [4]

OPEN ACCESS

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

Abundances of SiS for a generic HII region and a PDR



Our model is described by Shaw et al. (2022), and the input script of this model, "h2_Orion_hii_pdr.in,"

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

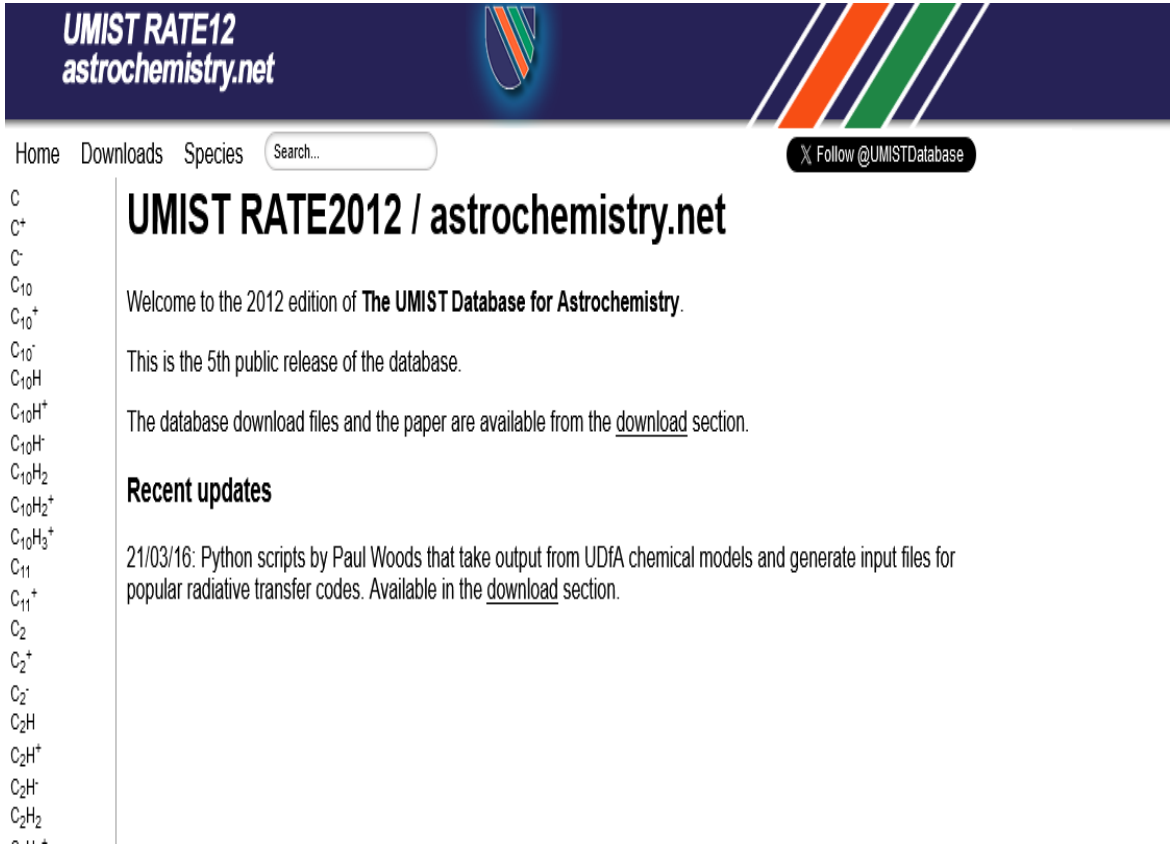
CDMS

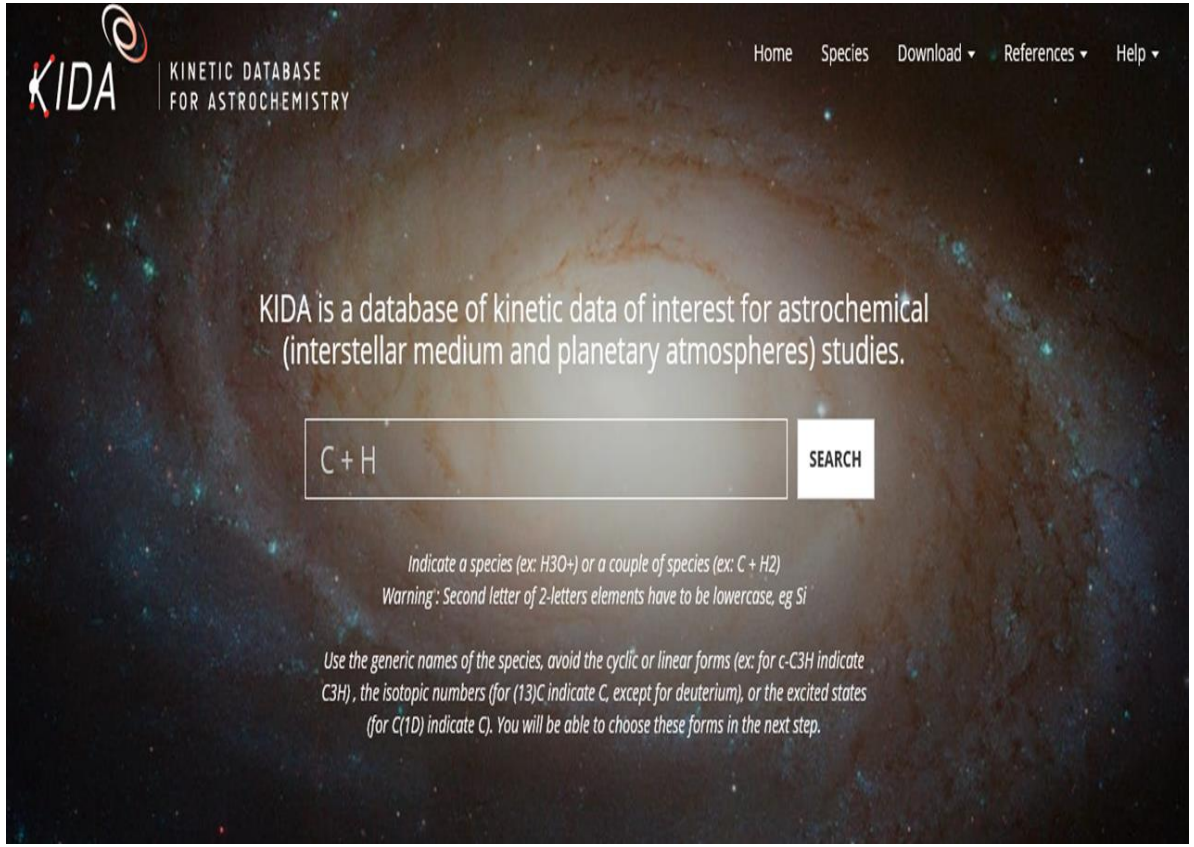
CLASSIC portal

VAMDC consortium

VAMDC portal (beta)

Reaction rate coefficients and databases





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.

Chemical rate coefficients and Temperature

A wide range of temperatures occurs in nature.

Any species' predicted column densities and line intensities depend on the rate coefficients.

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 those reactions with $\gamma < 0$ will become unphysically large at low temperatures.
- For $\gamma < 0$, fix k(T = 10 K) (M. Röllig, 2011)

- Rate coefficients with a positive β can become large at high temperatures.
- For $\beta > 0$, fix k(T = 2500 K) (Shaw et al. 2023)

Uncertainties

- Uncertainties in chemical reaction rate coefficients influence the predicted abundances/column densities of the species involved.
- This effect empirically increases as the number of atoms in the interacting molecule increases . Hence, among all the molecules considered here, we expect results to be most uncertain for HC_3N, as it involves the greatest number of atoms.
- Vasyunin et al. (2007) showed that the dispersion in the column densities is not more than a factor of 4.
- It is important to note that the abundances of multi-atom organic molecules depend on reactions on dust grain surfaces.

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.d

Run tsuite models and check asserts

Thank you