Extragalactic Astrochemistry: from nearby to high redshift galaxies

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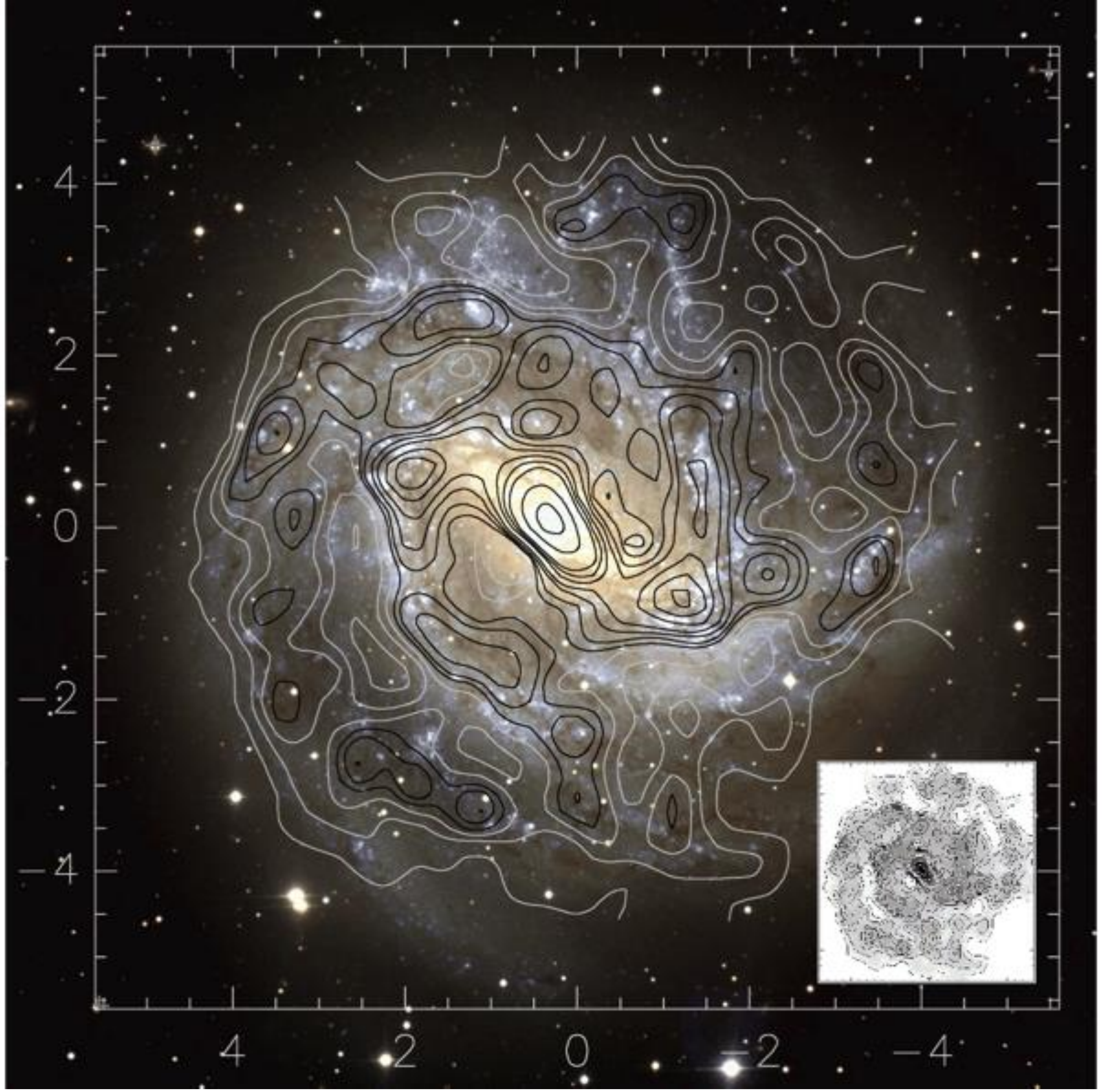
JWST Pillars of creation

Why are molecules important in astronomy?

- Cosmic gases at temperatures (T) less than a few thousand K and with number densities (n_H) greater than one hydrogen atom/cm^3 are likely to contain some molecules
- If T < 100-200 K and n_H > 1000 cm^{-3} gas almost entirely molecular
- Molecular regions are relatively small in volume compared to hot gas in structures such as galactic jets or extended regions of very hot X-ray emitting gas in interstellar space
- However their much higher density offsets that disparity, and so compact dense objects are often more massive than large tenuous regions.

Types of gas and physical characteristics (however note that this classification was done with our own galaxy in mind)

Region	n_H (cm^{-3})	T (K)
Coronal gas	$< 10^{-2}$	$5{\times}10^5$
HII regions	> 100	$1{\times}10^4$
Diffuse gas	100-300	70
Molecular clouds	10^4	10
Pre-stellar cores	10^5-10^6	10-30
Star Forming Regions	10^7-10^8	100-300
Protoplanetary disks	10^4(outer)-10^{10}(inner)	10(outer)-500(inner)
Envelopes of Evolved stars	10^{10}	2000-3500



Velocity-integrated CO(J=1-0) intensity as contours superposed on a map produced from images in B, V, and R of M83, a nearby spiral galaxy.

- The CO is associated with small regions of higher densities ($\leq 10^3$--10^5 cm^{-3}) and temperatures ~ 50 K.
- We use CO to measure the molecular mass of the Galaxy
- We shall see why along the way during this lecture but do start to think of **why** this is the case…..

The importance of dense (> 1000 cm^{-3}) gas

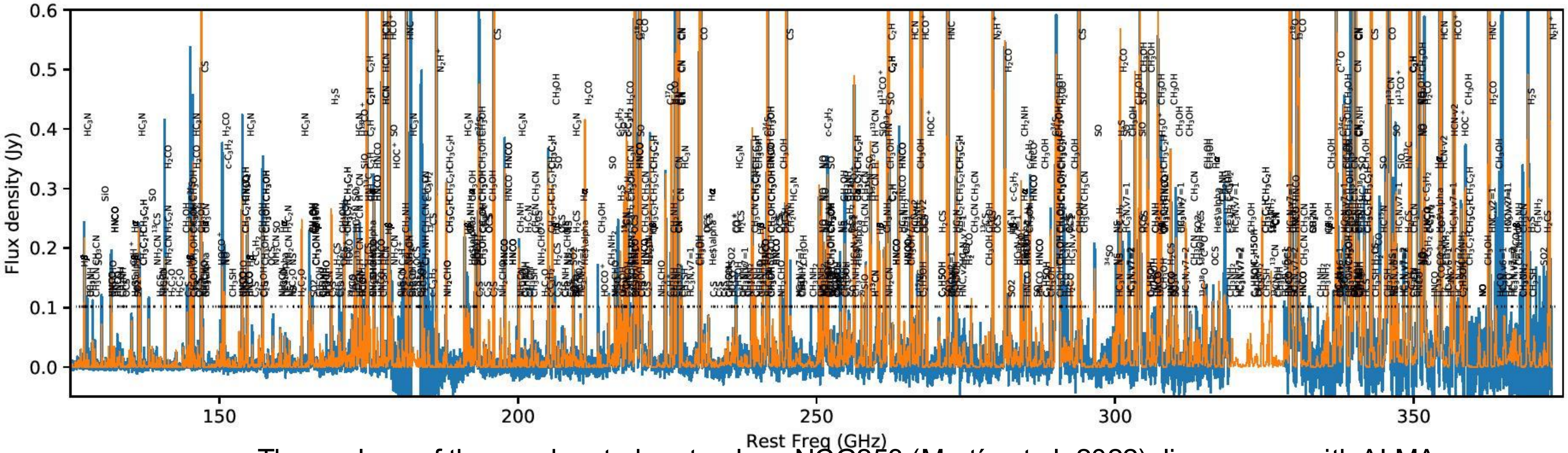
1. Dense, cool gas is the *only* reservoir of matter for future star formation →tenuous gas collapses to a dense core which has a specific molecular signature. At the end of that collapse, the newly-formed star irradiates any surrounding debris that was not incorporated into the star, and generates a new chemistry that provides new molecular signatures.
2. Dense gas helps us to understand galaxy evolution → measuring the mass of this gas and comparing with the existing stellar mass give some indication of the evolutionary state of that galaxy.

The importance of dense (> 1000 cm^{-3}) gas

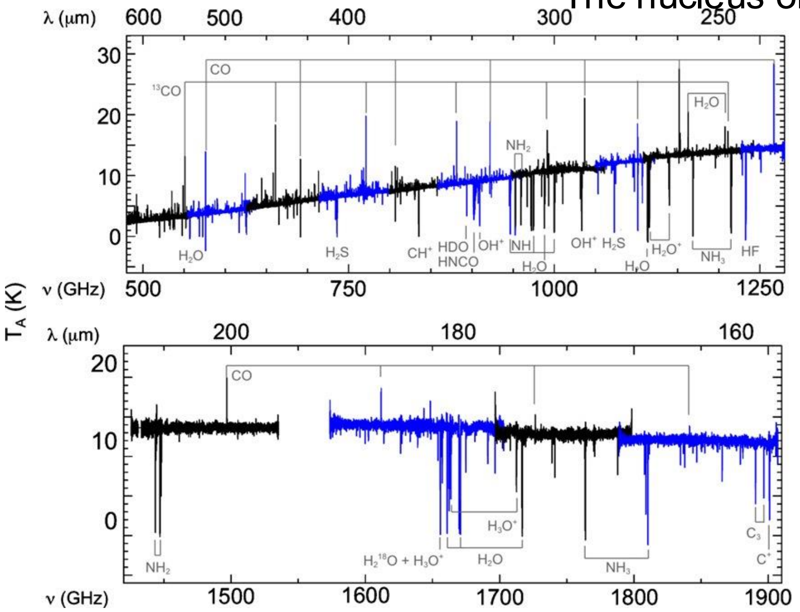
3. Dense gas helps us understanding AGN feedback → the interaction of an outflow from an active galactic nucleus with cool dense gas in the galaxy produces a signature chemistry that through its specific molecular emissions reveal important details of the outflow, such as its mass loss rate.

→ many processes of topical interest in modern Astronomy involve cold dense gas and/or the interaction of radiation and/or of violent processes with cold dense gas.

Observing Molecules in Space



The nucleus of the nearby starburst galaxy NCG253 (Martín et al. 2022): line survey with ALMA



Herschel line survey of Sagittarius B2(N) (Neil et al. 2014)

Our knowledge of the conditions of dense gas comes from observations of molecules mainly in the **infrared** and in the **(sub)millimetre**

The ingredients of cosmic chemistry: Gas and Dust

Gas

Solar elemental abundances relative to the *total number of hydrogen nuclei*.

Notation: a(-b) means a x 10 $^{-b}$

H	1
He	9(-2)
O	5(-4)
C	3(-4)
N	7(-5)
Si	3(-5)
Mg	4(-5)
Fe	3(-5)
S	1(-5)
Na, Ca	2(-6)

- All elements apart from H are formed in stellar nucleosynthesis and distributed by novae and supernovae (see SSE course)
- Gas with these solar abundances is said to have solar *metallicity*
- Metallicity may vary from galaxy to galaxy → depends on the star formation rates and efficiencies
- Also, supernovae of different masses may lead to different relative abundances

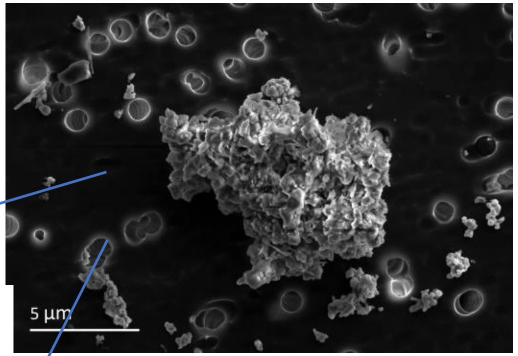
It is important to understand the difference between metallicity and relative abundances

Dust

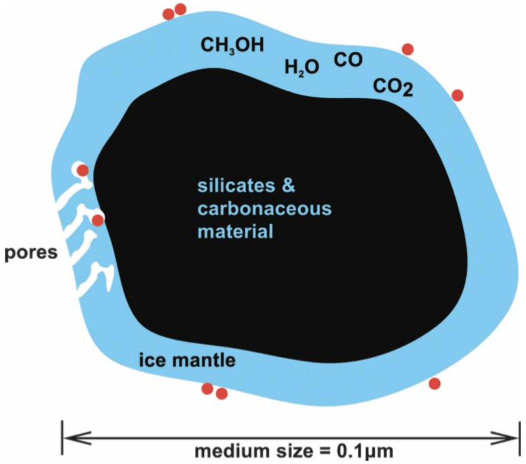
- Dust grows and nucleate in the envelopes of cool stars, in novae and in supernovae
- The dust-to-gas ratio in our own Galaxy is ~ 1:100; this can vary across galaxies
- Dust sizes range from nanometre to ~ 1μm and generally follow a distribution of this type:

$$n_d(a)da \sim a^{-3.5}da$$

= Number density in the range of sizes a to a+da

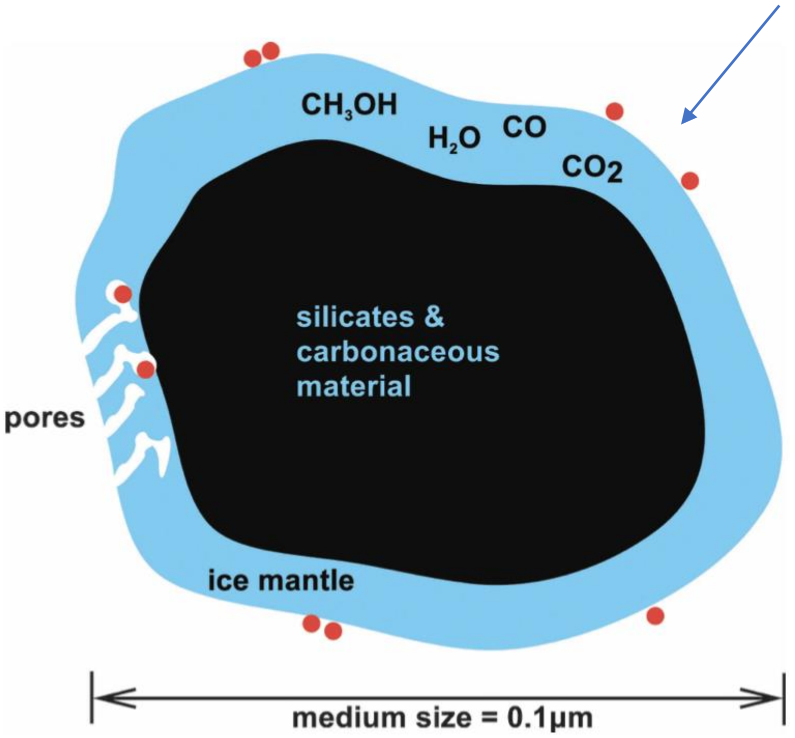


Hope Ishii, University of Hawai‘i



Karssemeijer et al. (2012)

- The core of the dust is made of silicates and carbonaceous material
- Most of the "metals" i.e Mg, Fe, Si are incorporated in the dust (cf solar abundances)
- Dust is important because it acts as a "catalyst" and allows atoms to form molecules, in particular H_2
- In dense and cold environments, gas phase species condense on the surface of the dust grains and form the so called "icy mantles"



Roles of molecules:

Observations of molecules → local conditions in interstellar clouds

1. They <u>trace</u> interstellar gas:
    - relatively cool ($T \leq 10^3$ K)
    - relatively dense ($n_H > 100$ cm^{-3}) (note: star forming clouds have a density of $10^5 – 10^7$ cm^{-3})
    - This gas contains nearly all non-stellar baryonic mass in the Galaxy → <u>molecules are tools to understand interstellar conditions</u>

2. Main coolants in denser interstellar gas:
    - radiate at long wavelengths (typically mm);
    - transitions corresponding to low temperatures
    - molecular radiation allows collapse under gravity of gas clouds in formation of galaxies, globular clusters and star formation (potential energy radiated away)

3. Control level of ionization:

e.g. $HCO^+ + e^- \rightarrow H + CO$ <u>fast</u> ,
$Mg^+ + e^- \rightarrow Mg + h\nu$ <u>slow</u>

Link magnetic field to gas:

- High ionization → ions tied to field lines, many ion-neutral collisions so neutral and field fixed together so magnetic pressure.
- Low ionization → neutral gas weakly tied to magnetic field → no magnetic pressure

Now…look at again at the physical conditions of the “dense” gas…..

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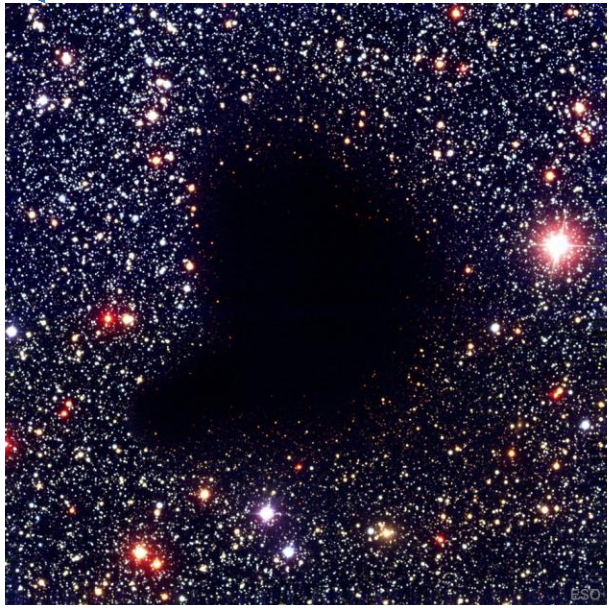
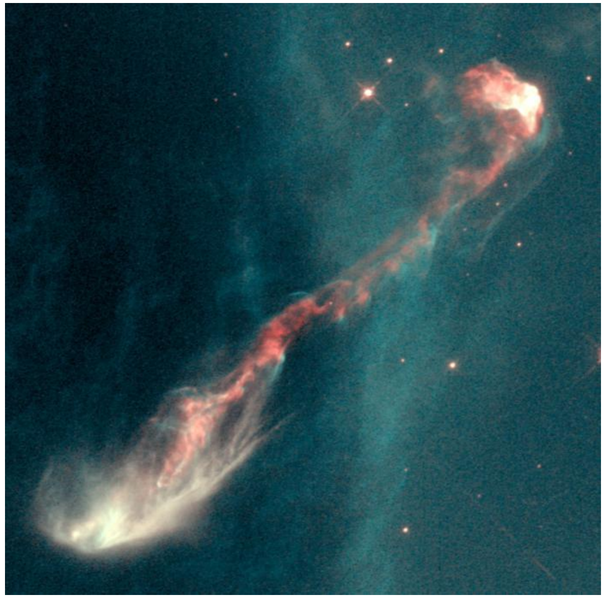
What drives cosmic chemistry?

- Interstellar chemistry needs to be `driven' → a gas at low density and low temperature, of cosmic composition, left to its own devices, will not generate an extensive chemistry that produces useful tracer molecules.

- <u>Drivers</u>: starlight, cosmic rays, grain catalysis, and gas dynamics.





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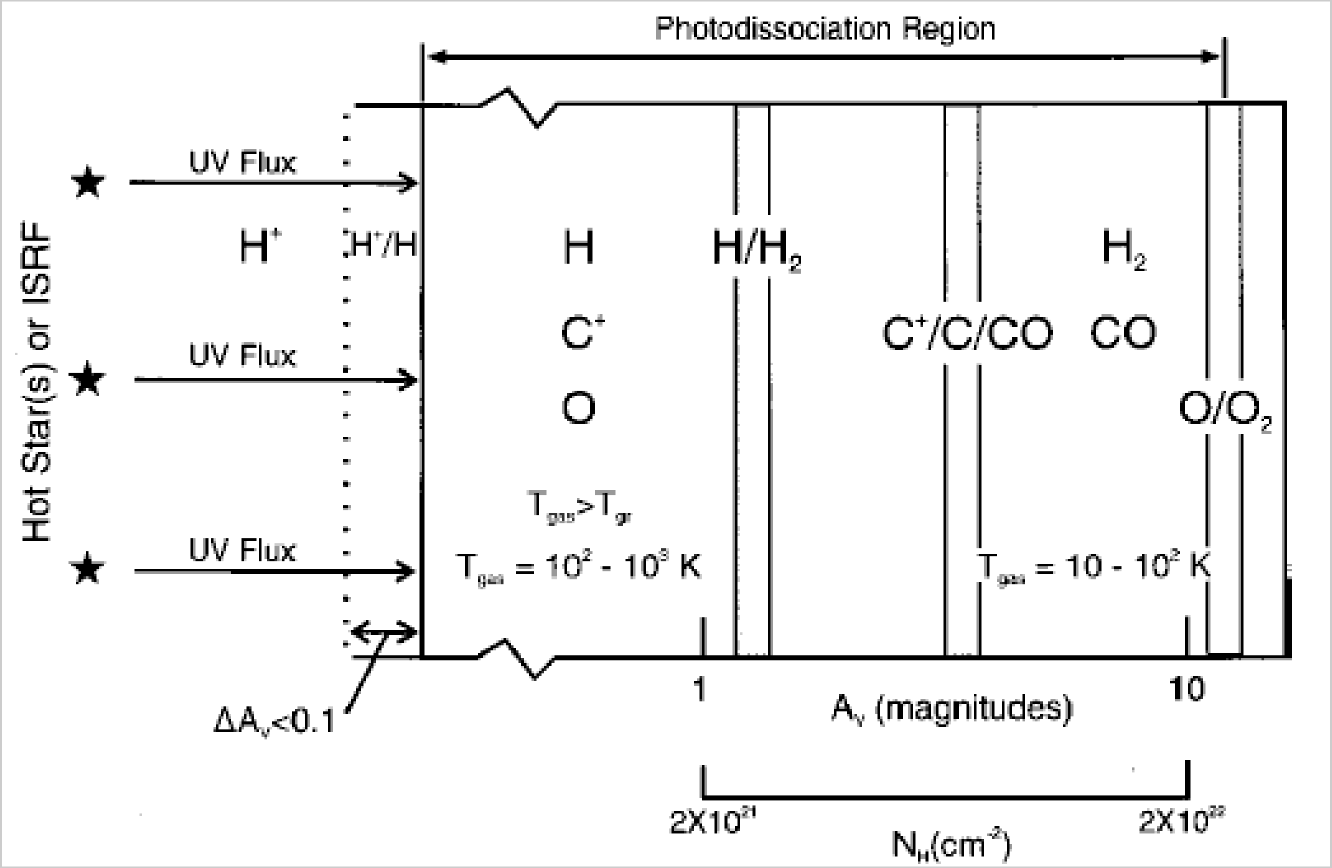
UV-dominated regions or PDR

The interstellar radiation field impinging on an interstellar cloud is dominated by the contribution from O and B stars.



See later lectures

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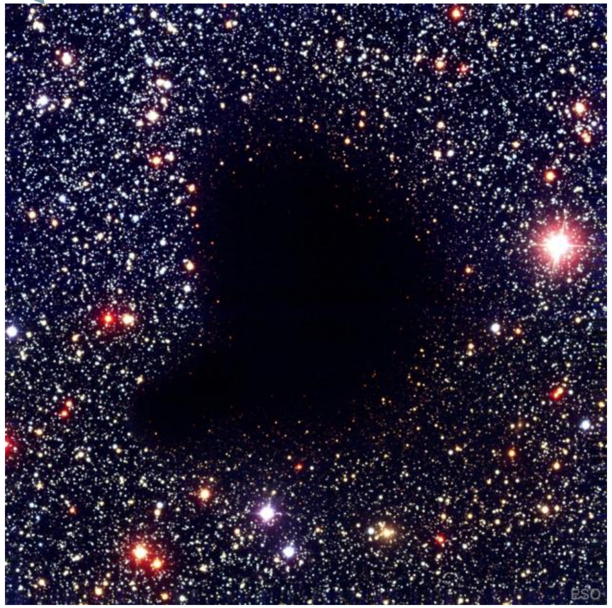

- Cosmic rays are important drivers of interstellar chemistry.
- These fast particles, mostly H and He nuclei, **collide** with and **ionise** atoms and molecules.
- They also heat the gas through the kinetic energy given to the ejected electrons.
- The most effective cosmic rays in ionizing the gas are those with energies of **a few MeV**
- The flux of these relatively low energy cosmic rays is not easily determined at Earth because of modulation by the solar wind
- The actual interstellar cosmic ray ionization rate in the Milky Way is still somewhat uncertain → **10^{-17}-10^{-16} s^{-1}**

$$\mathrm{H} + \mathrm{cr} \rightarrow \mathrm{H}^+ + \mathrm{e} + \mathrm{cr}$$

$$\mathrm{He} + \mathrm{cr} \rightarrow \mathrm{He}^+ + \mathrm{e} + \mathrm{cr}$$

$$\mathrm{H}_2 + \mathrm{cr} \rightarrow \mathrm{H}_2^+ + \mathrm{e} + \mathrm{cr}$$

Cosmic ray affect the atoms and molecules that are not affected by UV → cosmic rays can penetrate the cloud (unlike UV)

- Cosmic rays are (mostly) unaffected by the loss of some tens of eV given to the ejected electron in each ionization[1] → ionization rate not significantly attenuated by depth into a cloud
- The creation by cosmic rays of the three ions **H^+, He^+, and H_2^+**, drives the rest of the interstellar chemistry.
- Ion-molecule chemistry is rapid, occurring on almost every collision, whereas neutral exchanges may be forbidden at low temperatures → ionization encourages a rapid chemistry to proceed, even in gas at low temperatures.

[1] Recent work has challenged this assumption and shows that there is indeed some dependency.

- Details of the chemistry are not covered here but few key points to remember:

  1. Chemistry initiated by cosmic rays begins with the conversion of *oxygen* and *carbon* to several of their hydrides
  2. Molecules are being continually formed and destroyed
  3. At the same time, destructive reactions such as those with He^+ (e.g. $CO + He^+ \rightarrow C^+ + O + He$) tend to return material to simpler (atomic) components.
  4. The network of reactions may reach a chemical steady-state if circumstances permit.

These networks very rarely lead to molecules with more than few atoms. Yet, we observe very large molecules in space (e.g CH_3COOH*)* → ***can you think of how these molecules can form?***

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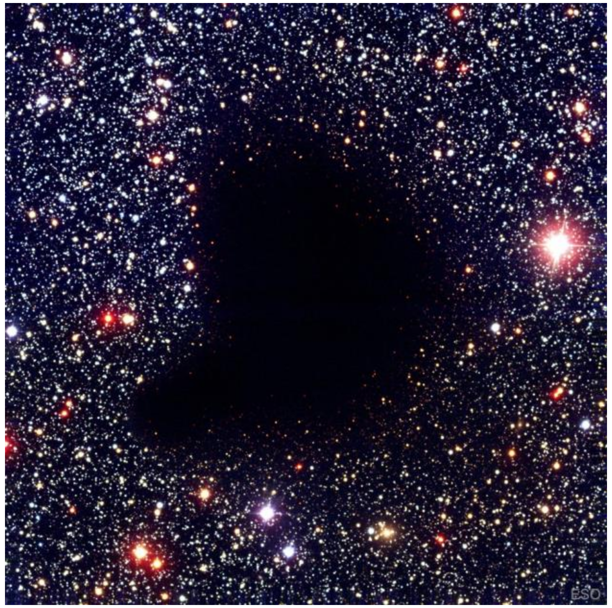
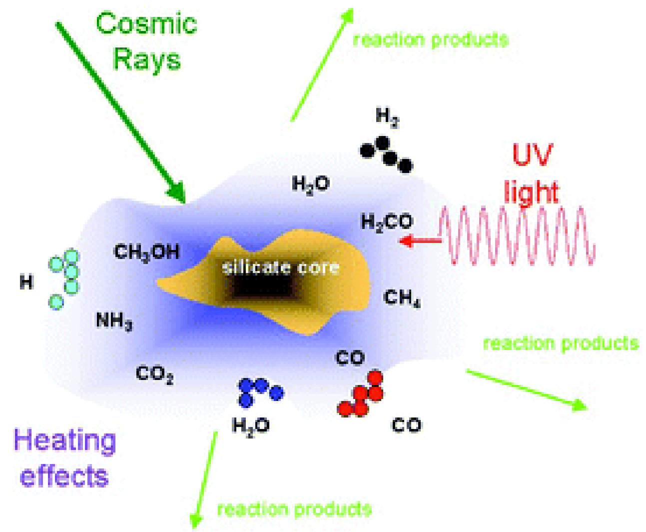
- Drivers: starlight, cosmic rays, grain catalysis, and gas dynamics.



The role of dust

- The most abundant molecule in the Universe is H_2
- In the Milky Way H_2 is formed (almost entirely) in reactions that occur on the surface of dust grains → dust acts as a catalyst
- The function of the dust grain is to trap one H-atom long enough for a second H-atom to arrive at the surface, locate the first, and react with it.
- This reaction releases ~ 4.5 eV per molecule



- It is now well known that many molecules form on the surface of dust grains → at low temperatures most species ”freeze” to the dust
- If an oxygen atom freezes to the dust it is likely to meet an hydrogen atom → hydrogenation until saturation occurs → H_2O, NH_3, CH_4 etc
- **Ices accumulated while the gas is cold reflect the local conditions and evolutionary history**
- Ices can be removed non-thermally and thermally (~ 100K) e.g. near a new born star.
- When the dust is warmed up ices sublimate and go back to the gas phase

The gas before and after the star is born will ”look” different

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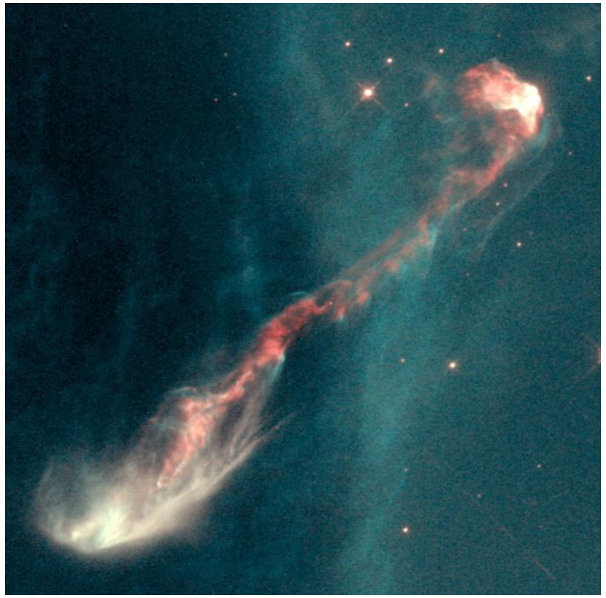
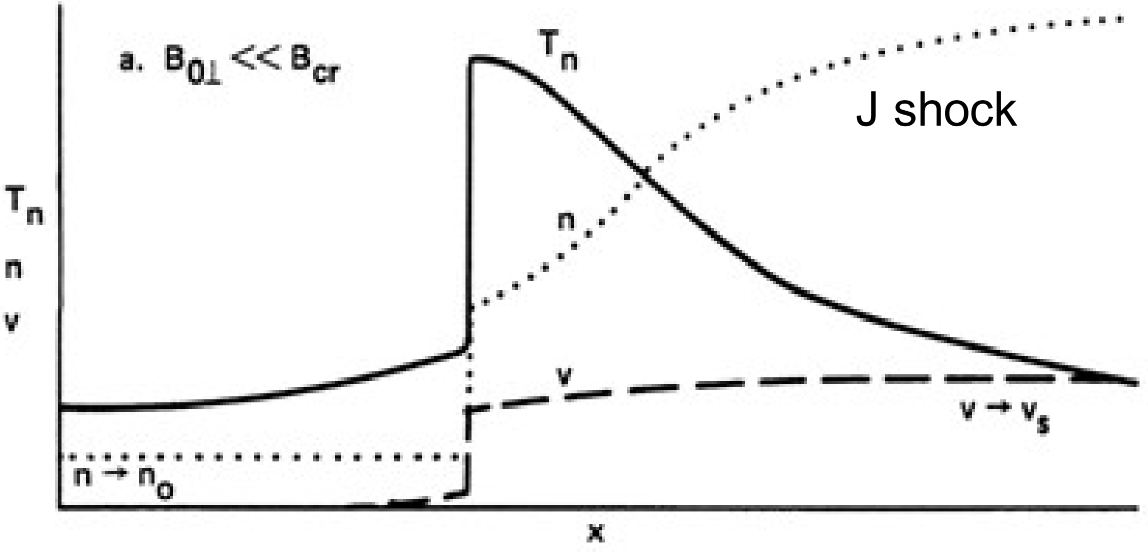


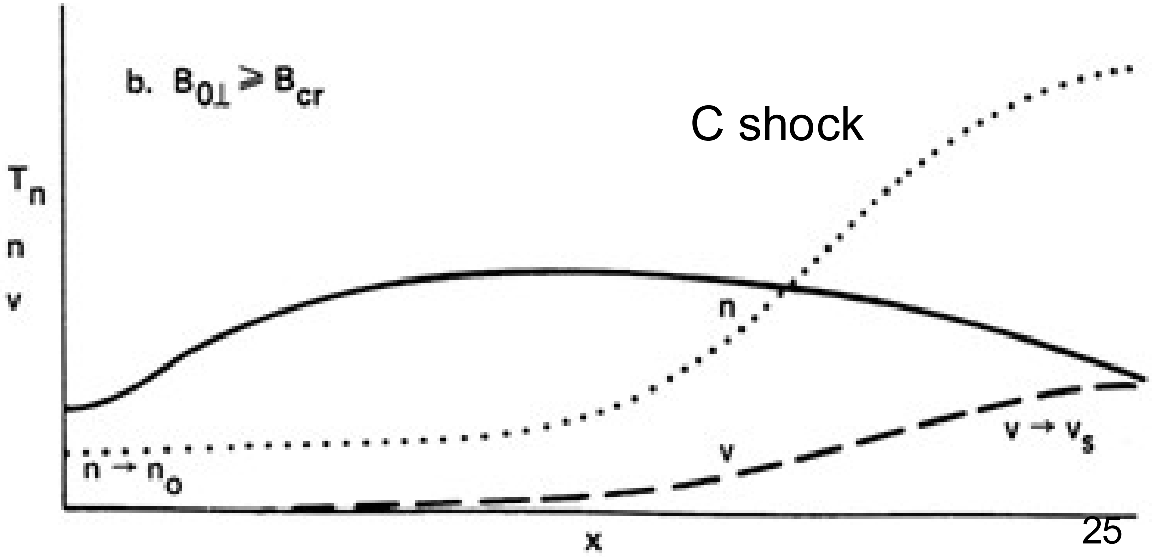
Chemistry initiated by gas dynamics → Shocks

A shock arises when an external event (e.g. a collision of one interstellar cloud on another, impact of a rapidly expanding HII region on a nearby cloud of cold neutral gas etc) drives a perturbation *faster than the local sound speed*.

→ kinetic energy of bulk motion is converted to internal thermal energy, and the shocked gas is heated and compressed.



By looking at their effects on the chemistry of the dust and gas, it is possible to study the shock driver(s) as well as the shock history.



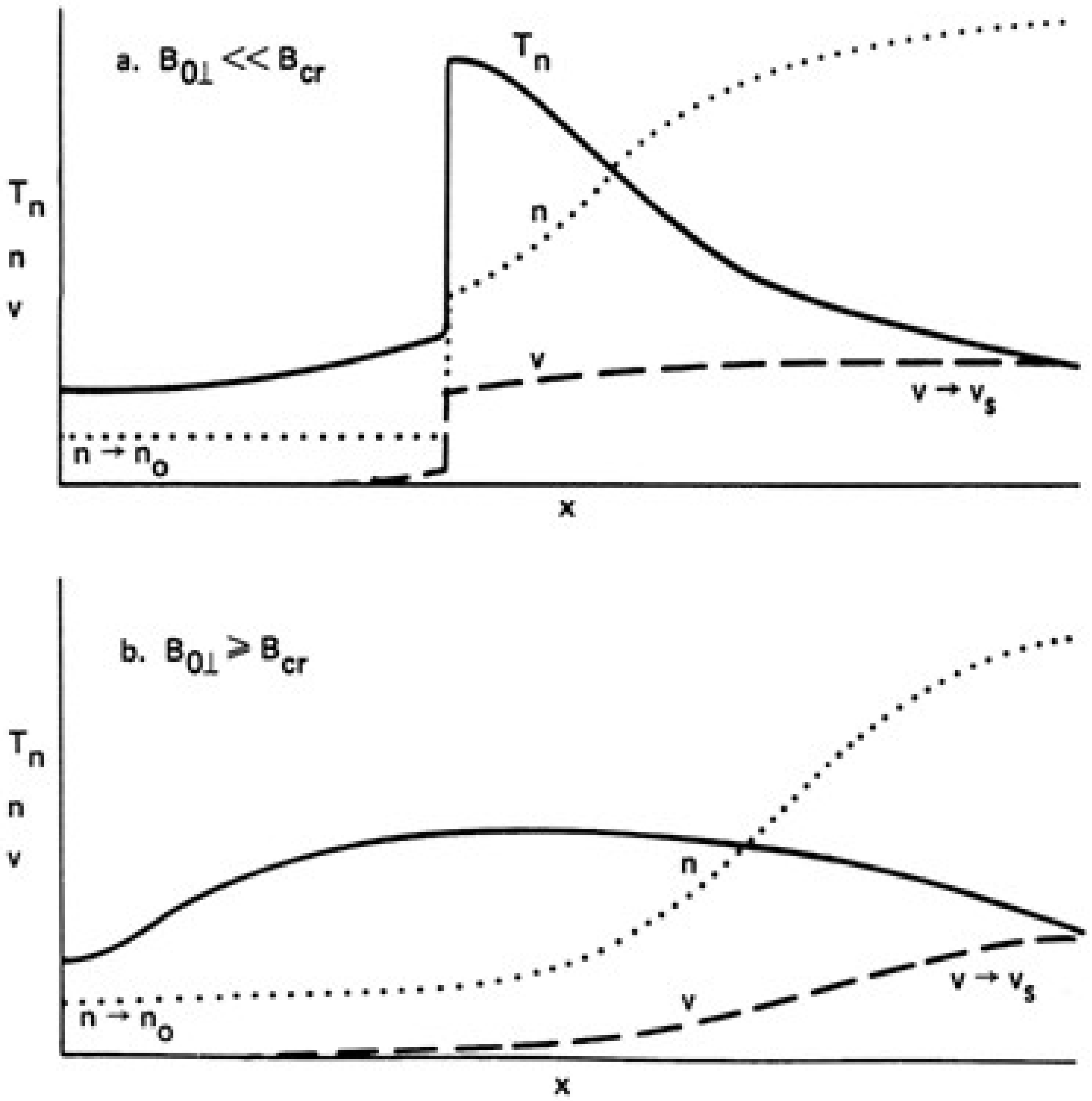
<u>Simplest case: J shock</u>

→energy conversion at the shock wave is abrupt compared to other timescales in the gas, and the temperature and density **jumps** are effectively discrete.
→Short period where T is very high
→In post-shock gas radiative cooling occurs:

$$T_{ps} \sim 5 \times 10^3 (v_s/10)^2$$

<u>Magnetic fields present: C shock</u>

→ions drift through the mainly neutral gas, depositing energy in the gas over a much wider range than in the simple J shock case.
→Because the energy in a C shock is dumped over a larger physical extent than in a J shock, the resulting temperatures are generally lower



Non dissociative shocks

At T > 500-1000 K the reactions:

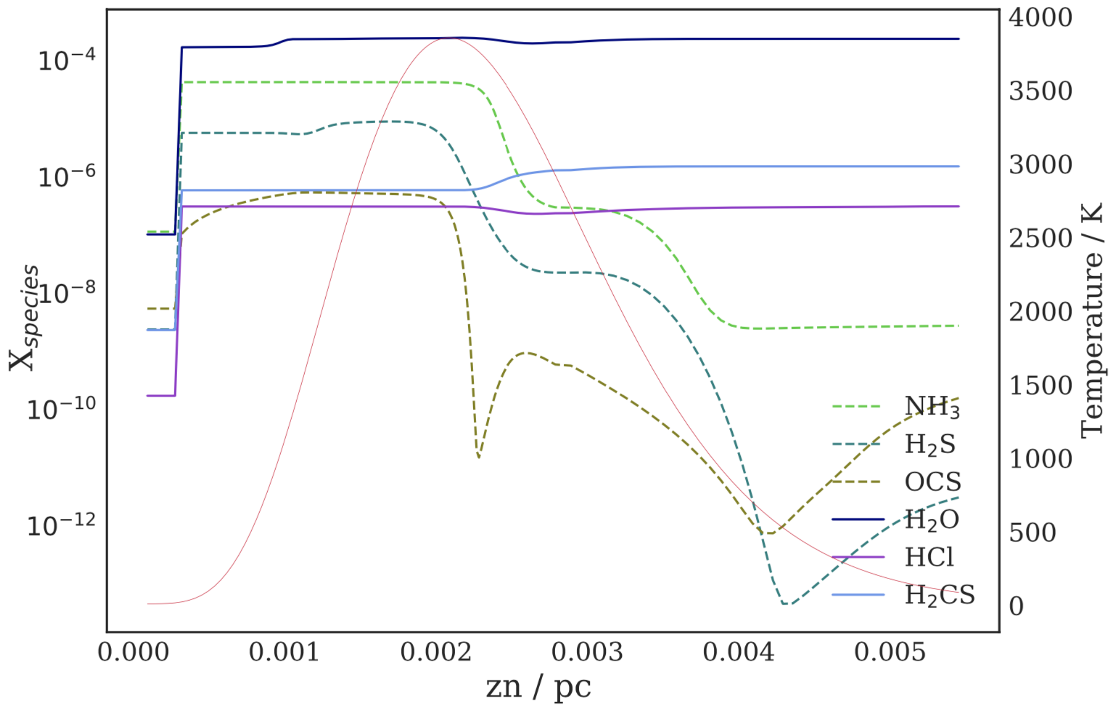
$O + H_2 \rightarrow OH + H$
$OH + H_2 \rightarrow H_2O + H$
$C + H_2 \rightarrow CH + H$

…are no longer slow → dissipation in shocks is one of the mechanisms that can heat the gas

$$k = \alpha \left(\frac{T}{300}\right)^{\beta} \exp\left(\frac{-\gamma}{T}\right) \text{cm}^3\,\text{s}^{-1},$$

Two key points to remember:

- High temperature can lead to molecule **formation** but also to molecule **destruction**



$V_s = 45 \text{kms}^{-1}$; $n_H = 10^5 \text{ cm}^{-3}$

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Two key points to remember:

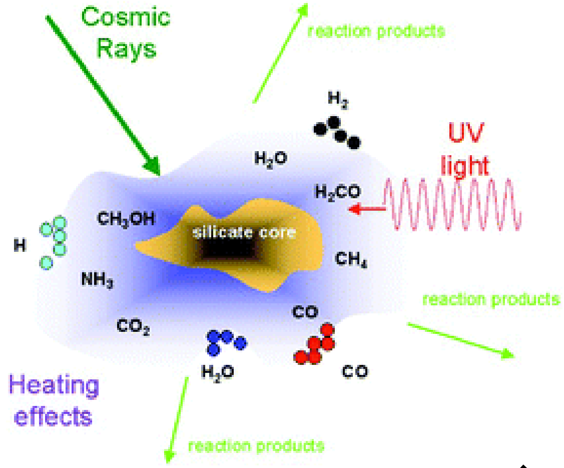
- High temperature can lead to molecule **formation** but also to molecule **destruction**
- While the increase in temperature is caused directly by the shock, the cooling is determined by **molecules** → radiative cooling depends on the post-shock chemical structure

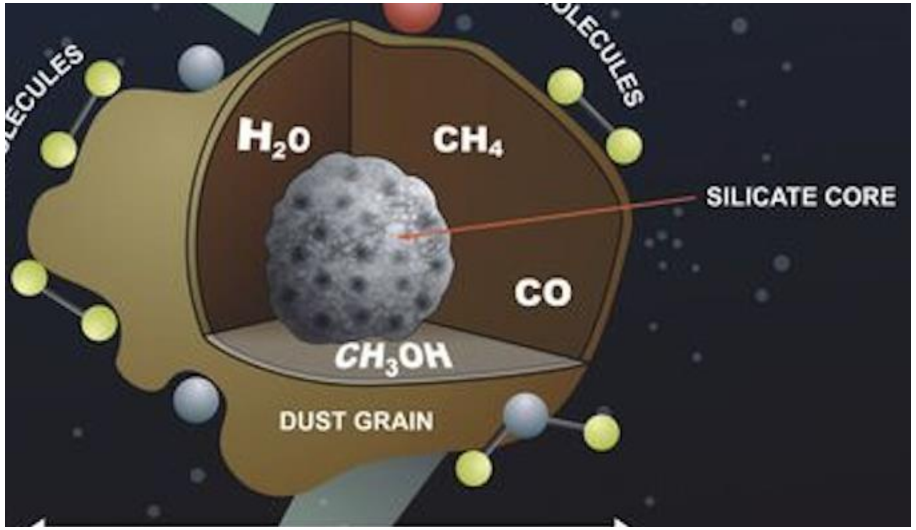
$O + H_2 \rightarrow OH + H$
$OH + H_2 \rightarrow H_2O + H$
$OH + h\nu \rightarrow O + H$
$H_2O + h\nu \rightarrow OH + H$

} All very efficient in cooling, with the last two in regions with strong UV field

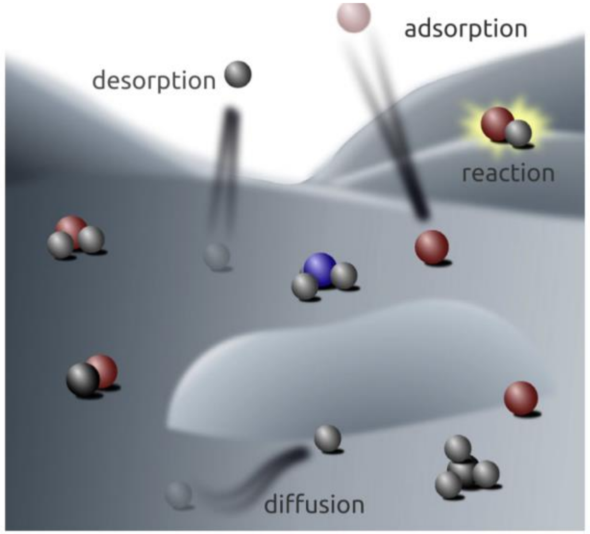
What about the dust? Remember that before shocks impact on the ISM, depending on the density, many molecules are “frozen” on top of the grains (icy mantles) and many atoms are “stuck” in the core of the grains

→ **Shocks lead to dust sputtering**



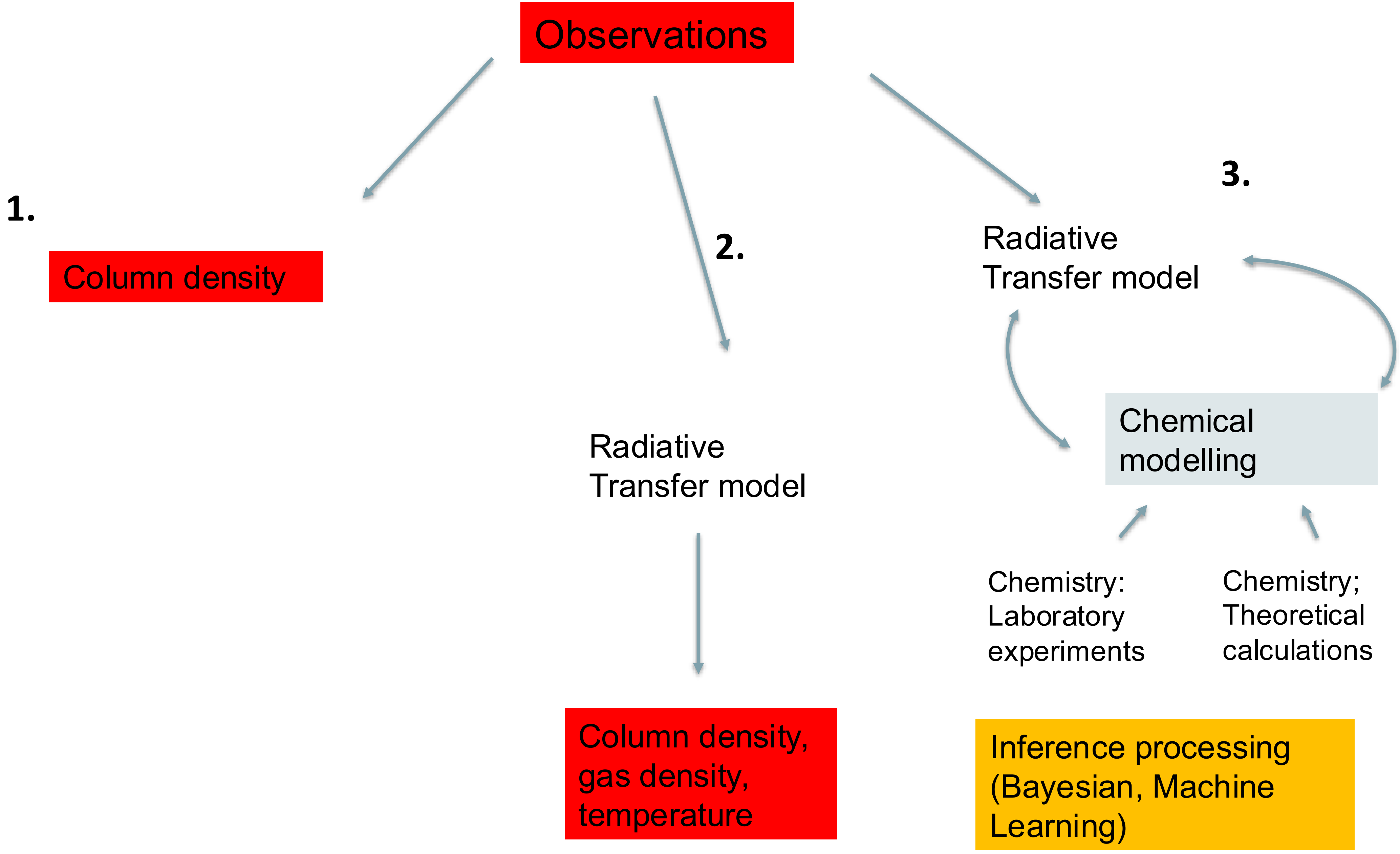


Legacy Astronomical Images, “Shock Front Molecule Production,” *NRAO Archives*, accessed June 14, 2022, https://www.nrao.edu/archives/items/show/33585.



Cuppen et al. (2017)

How to "decipher" the messages from molecular observations? The jargon…



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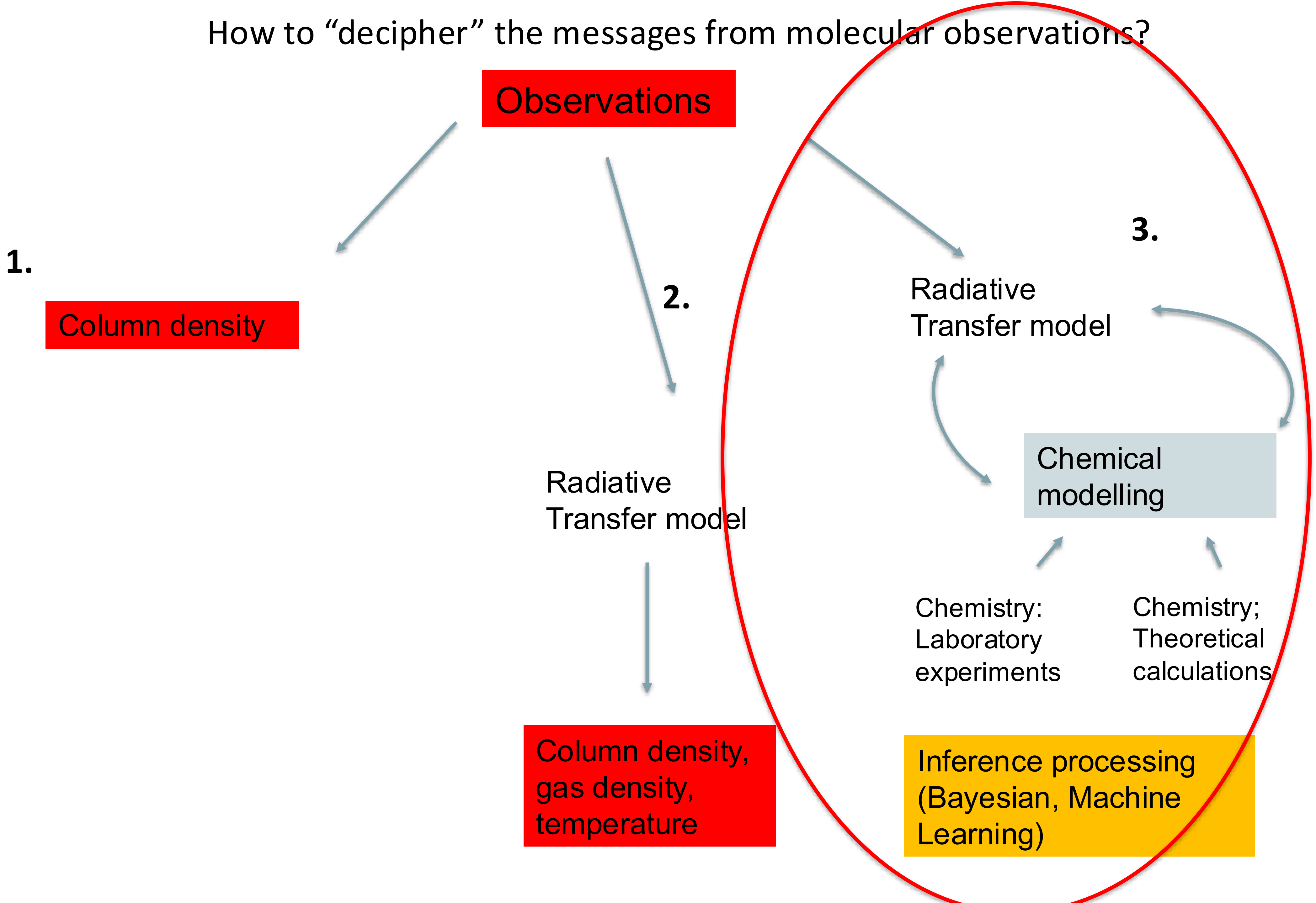

What type of spectra are most common in the molecular gas in galaxies?

- By far the most detections have been made in the millimetre and sub-millimetre, corresponding to pure rotational transitions, almost always of molecules in their ground electronic state and lowest vibrational level. *[But note that there are also some other types of transition (e.g., in OH and NH_3) that do not fit this pattern]*

- In order to extract information from an astronomical spectrum we need to get acquainted with some of the spectroscopic notation for diatomic as well as polyatomic molecules.

- Two of the key "concepts" that we have to understand are: the energy level of a transition (E) and the rotational quantum number (J)

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This information will give you an indication of the temperature and density of the gas

Molecular Transitions

- For a transition to occur the electric dipole moment, $\boldsymbol{\mu}$, must change when the atoms are displaced relative to one another (the strength or energy of the interaction depends on the dipole)
- This only happens for heteronuclear diatomic molecules, since homonuclear molecules have the charges distributed symmetrically.
- *Vibrational and rotational spectra of homonuclear diatomics can only be obtained if an electronic transition also occurs.*

What are the major consequences of the statements above for us?

→ H_2 can only be observed when an electronic transition occurs i.e *not* in the cold interstellar medium and *not* in the submm

The key concept of critical density

- One can define the critical density as: the density for which the net radiative decay rate from j → i equals the rate of collisional depopulation out of the upper level j for a multilevel system.

- **A molecule decays radiatively if the timescale for this process is smaller than the timescale for collisional de-excitation**

- At densities **higher** than the critical density, the upper state is normally de-excited in collisions.

- At densities **lower** than the critical density, the population in the upper state is not highly populated.

- But at densities **near** to the critical density, maximum emission occurs → *this is why each transition will tend to trace gas at a particular density near to the critical density for that transition, and one can use different molecules and transitions to map different parts of a cloud where density is not uniform*

The key concepts of Excitation Temperature and of LTE

- So molecular lines can appear in *emission* or in *absorption* and this depends on the Critical density as well as on the Excitation Temperature (T_{ex}) of the transition: this is the temperature that gives the observed ratio of two energy levels in a Boltzmann distribution
- An important point to consider is whether a gas is in Local Thermodynamic Equilibrium (LTE) i.e whether we can assume that all the thermodynamical properties have thermodynamic equilibrium values at the local values of temperature and pressures.

The various temperatures encountered in molecular spectroscopy

Excitation temperature (T_{ex}): this is the temperature that gives the observed ratio of two energy levels in a Boltzmann distribution (and depends on the critical density)

Brightness temperature (T_B): In the Rayleigh-Jeans limit, we can define the temperature at which a black body would have to be to give rise to the observed intensity

Kinetic temperature (T_k): this is essentially the **actual** temperature of the gas

Antenna Temperature (T_a): this is what we measure with submillimeter and radio telescopes i.e the temperature of the blackbody that would lead to the equivalent power received by the antenna. This temperature incorporates radiative transfer and possible losses between the source emitting the radiation and the detector.

Main Beam Temperature (T_{MB}): For extended sources, it is often desirable to account for the efficiency of the antenna integrated only over the so called main beam. Or in other words, it is the beam-averaged brightness temperature of an extended source over the solid angle of the main beam.

So whether a molecular transition appears in emission or absorption depends on T_{ex} of the transition:

If $T_{ex} \neq T_B \rightarrow$ i) emission if $T_{ex} > T_B$ and ii) absorption if $T_{ex} < T_B$

How to extract information from a molecular line…or

how to transform observational results into physically meaningful information

- Let's relate what we measure with submillimetre and radio telescopes to the fundamental molecular constants and the relevant astronomical parameters.

- What we would like to know of the local gas are:
  - the column densities of the observed species,
  - the gas temperatures
  - gas densities

- The methods of obtaining this information depend on the types of molecule involved – for a very in-depth explanation please see the article by Goldsmith & Langer 1999 and/or have a look at the Additional-Material.pdf

Molecular Tracers in External Galaxies

- First detections of molecular emission such (e.g. CO and HCN) in external but relatively nearby galaxies were made in the 1970s.
- From the 1990s → CO detected in emission from high redshift objects, culminating in the remarkable identification in 2023 of high excitation CO in a gravitationally-lensed quasar at a redshift z = 7.5 → when the Universe was ~ a few percent of its present age.
- The discovery of molecular emission in such a distant object demonstrated that chemistry was occurring very early in the evolution of the Universe → *molecules must be widespread.*
- it has now been firmly established that chemistry in external galaxies can be complex and well developed.
- So the question arises: **can we use molecular emissions from distant galaxies to explore the physical conditions in them and their likely evolutionary status, as we can do for various regions of the Milky Way?**

Molecules in Galaxies – key facts

There are two important concepts that need to be considered when working with molecules in external galaxies:

1) Apart from the nearest objects, most galaxies will be spatially unresolved → the telescope beam will usually encompass the entire galaxy being observed, so that emissions from many types of region are compounded.

→ the detection of any molecule in a spatially unresolved galaxy does not mean that they occur in the same region of that galaxy → e.g. say you detect CO, SiO and CH_3OH:

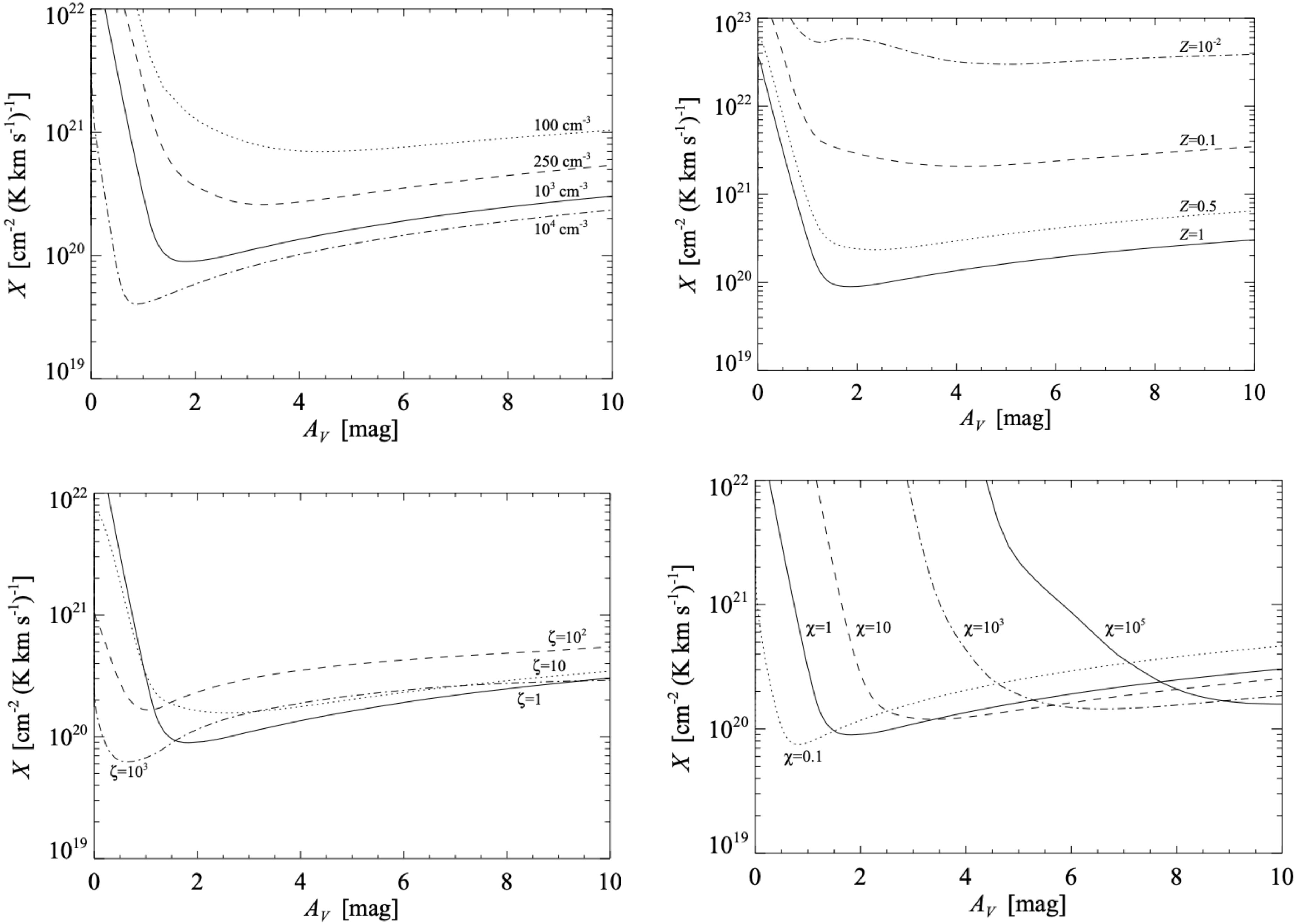
- the first molecule may indicate the presence of cold tenuous clouds
- the second strong shocks
- the third dense star-forming cores.

External galaxies will, in general, contain the variety of regions and sources similar to those that we can identify in the Milky Way.

2) galaxies are found in a variety of shapes, sizes and physical conditions → The range of physical parameters (gas densities, UV fields, cosmic ray ionization rates, dust properties, etc.) that determine the appearance of the Milky Way may be very *different* in other galaxies.

→ we can not necessarily use information about the Milky Way as a bullet-proof guide to the properties of other galaxies, without considering how the chemistry vary according to the physics and energetics of that region → the very same H_2/CO ratio (so needed to determine the molecular mass of a galaxy) might be very different from galaxy to galaxy!

$$X = \frac{N(\mathrm{H_2})}{\int T_\mathrm{A}(\mathrm{CO})\,\mathrm{d}v} \qquad [\mathrm{cm^{-2}\,(K\,km\,s^{-1})^{-1}}],$$

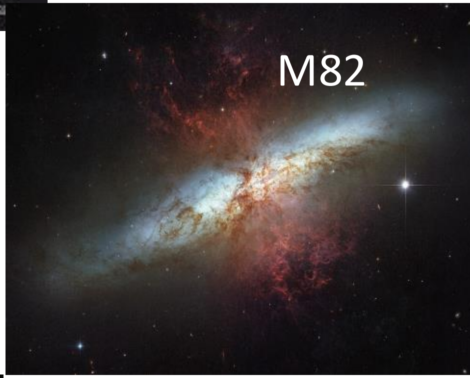


CO/H_2 ratio in different types of galaxies

Bell et al. (2006)

The most observed galaxies (in molecular lines) at a glance…..

Starburst galaxies: very high rates of massive star formation, possibly triggered by mergers between galaxies rich in interstellar matter → short-lived, until the interstellar gas reservoir is significantly depleted → *molecular abundances will be time-dependent!*

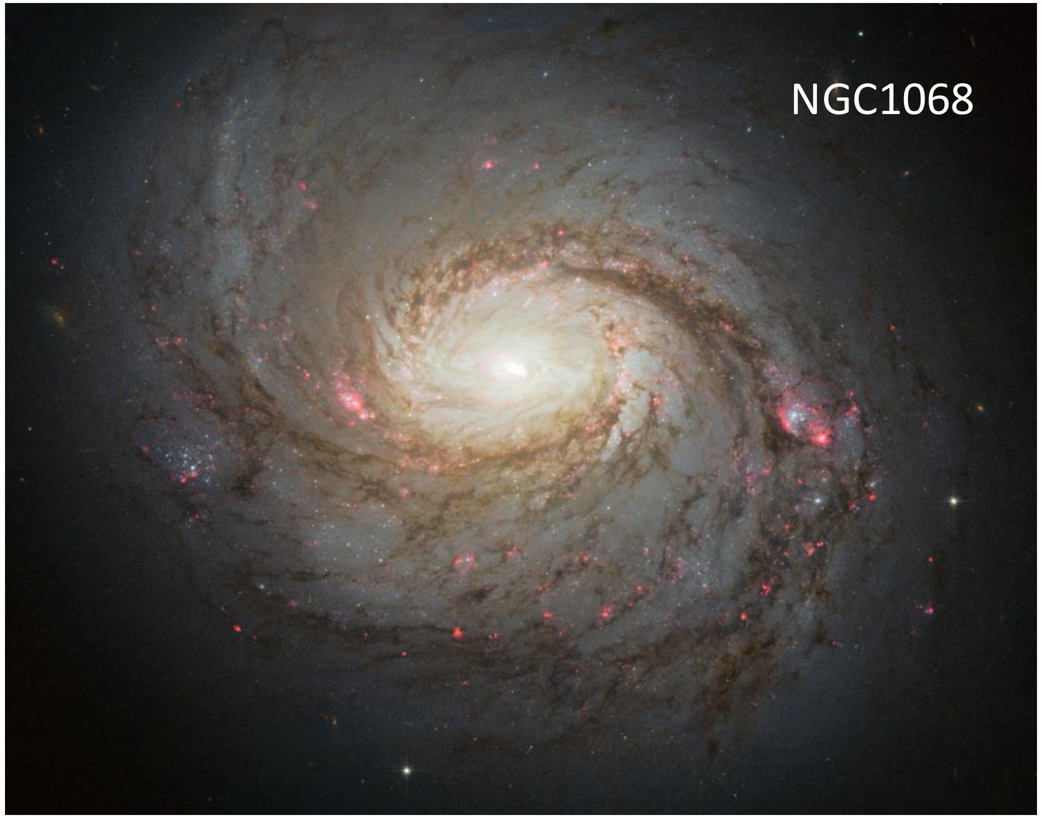


Ultra Luminous InfraRed Galaxies (ULIRG): interstellar medium is dust-rich → much of the UV radiation from the massive stars is absorbed by the dust and re-radiated in the infrared; *these are some of the most powerful infrared sources in the Universe.*

The most observed galaxies (in molecular lines) at a glance…..

Active galaxies/AGN dominated: their central compact regions are highly luminous in *all* wavebands → *powered by the accretion of mass by supermassive black holes at the centre of the galaxies.*

Note: these (and other) classifications of galaxies may not be mutually exclusive. For example, a ULIRG may be re-emitting radiation in the infrared that originated as ultraviolet not only from massive stars in the galaxy but also from an active galactic nucleus (AGN) at its centre or a galaxy may have a very powerful AGN in the centre but a lot of starburst activity in the spiral arms



Multi-Component galaxies

- Single-dish telescope's beam will always encompass many different gas components. E.g. even for M82 (one of the closest starbursts) the beam will encompass few arcsecs → not possible to trace the spatial extent of individual star-forming regions

- Interferometers do better – e.g. ALMA → with the full array in its most extended configuration has a resolution of $\lesssim 0.01''$ arcsecs at wavelengths ~ 0.3 mm. E.g. for M82 this means resolving structures down to 0.15 pc → smaller than a typical star-forming region BUT larger than an individual star-forming core.

Converting angular to linear scales → so that you know how small a region in your galaxy you are observing

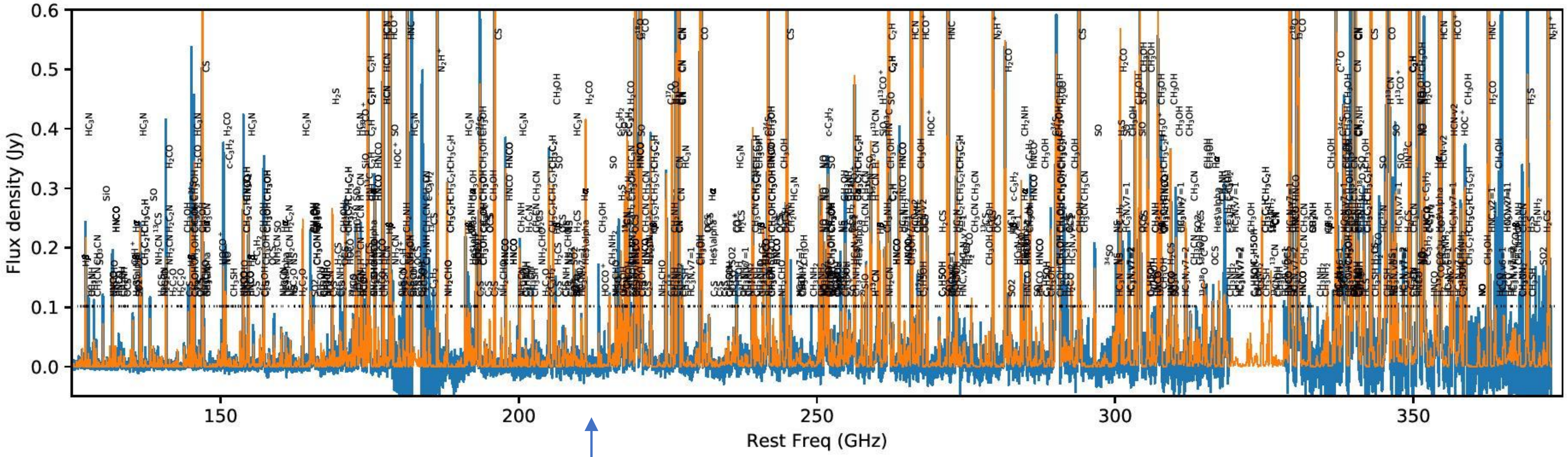
<u>Rule of thumb</u>: 1" ~ 1AU at 1 pc

e.g. M82 is at a distance of 3.3 Mpc so an angular resolution of 0.01" → 33000 AUs → 0.16 pc

(1 pc ~ 206265 AUs)

How can we “disentangle” the different molecular components from the beam?

The chemical diversity and complexity that we find indicates that the molecular emission is not all coming from the same component.



Such chemical complexity can not be explained by a one-component model → relative abundances between molecules may be able to provide insights into the physical distribution of the molecular gas in these galaxies.

Can the measured abundances tell us if some galaxies may be dominated by one or more type of energy source?
i.e <u>can we determine the “driver”?</u>

Normal Spiral Galaxies

- How does a spiral galaxy look like? → a flat, rotating, and relatively thin disk of stars, gas and dust + has spiral arms in the plane of the disk extending out from the centre, together with a concentration of stars towards the centre → bulge.

- This complex structure is surrounded by a much fainter spheroidal halo of stars, including stars in globular clusters.

- Most of the star formation in a spiral galaxy occurs in the spiral arms which are the locations of the giant molecular clouds (GMCs).

- These arms can be traced in nearby galaxies by:

❖ the millimetre-wave emission from GMCs,

❖ optical emission from the young massive stars and the HII regions they generate

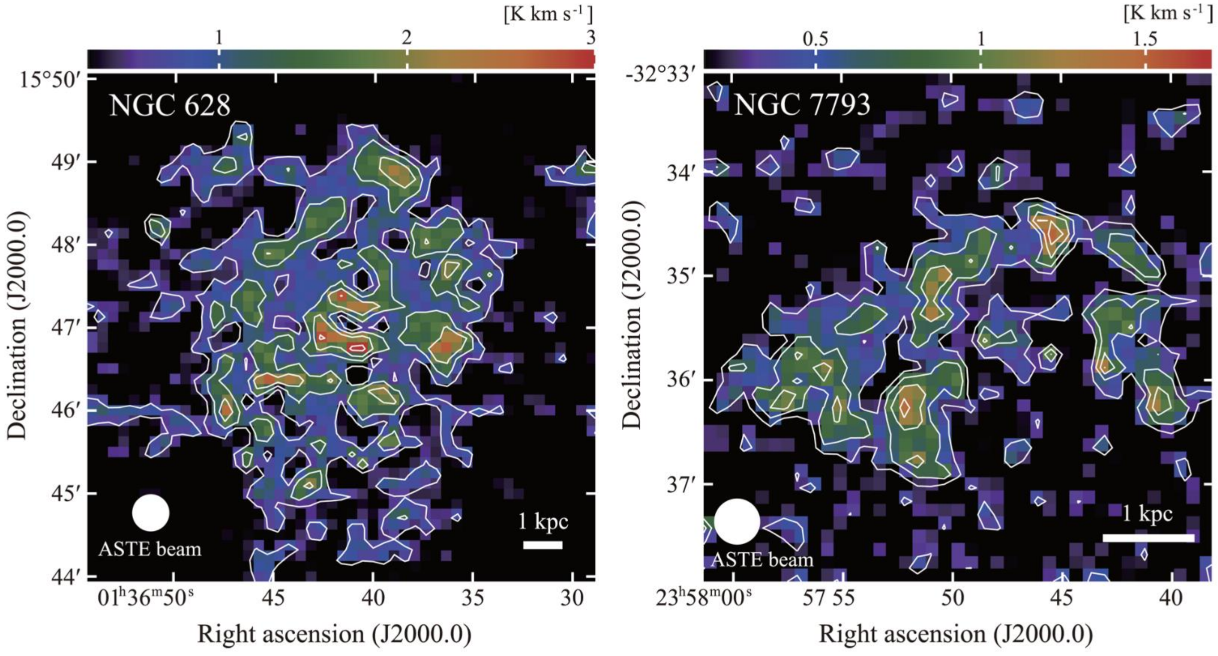
❖ infrared emission from dust heated by stars deeply embedded in dark clouds.

In terms of molecular observations → remarkably little!

Extensively mapped in the millimetre observations of CO → molecular content *varies by large amounts even within the same class of massive spirals.*

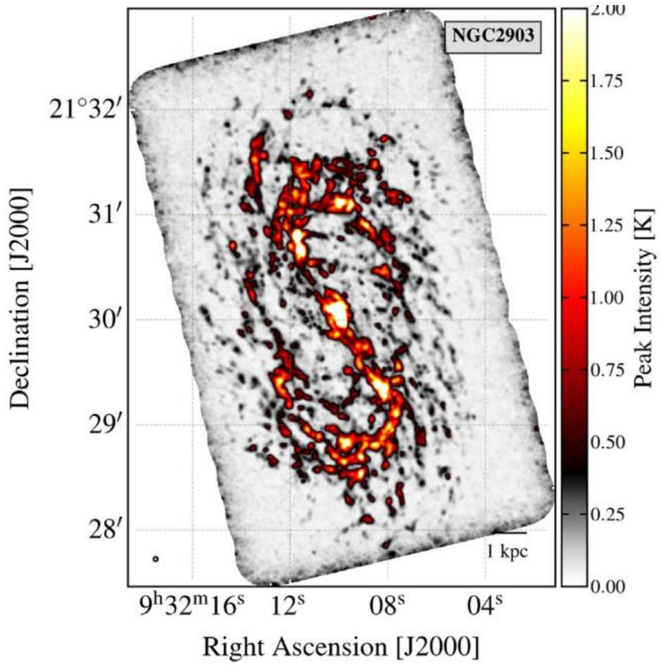
Ex: xCOLD GASS survey (IRAM 30m); PHANGS survey (ALMA)

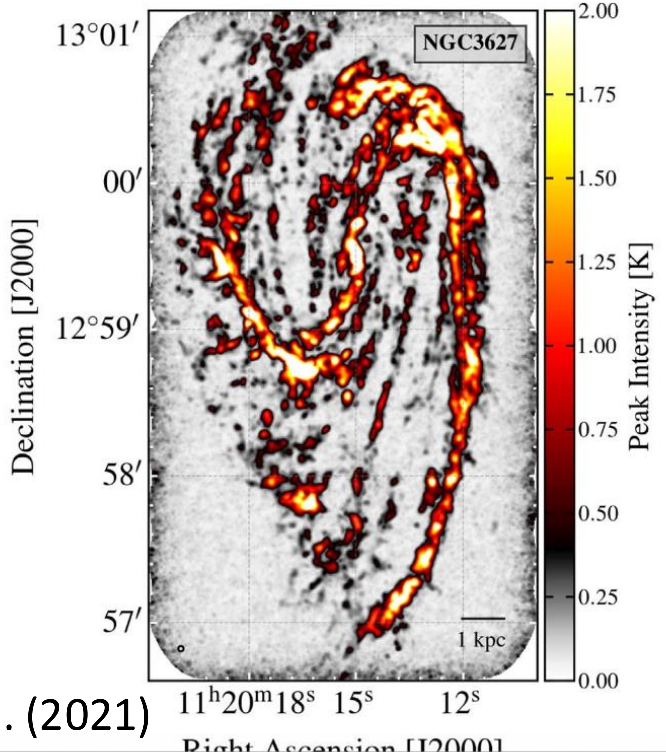
CO (3-2)



Muraoka et al. (2016)

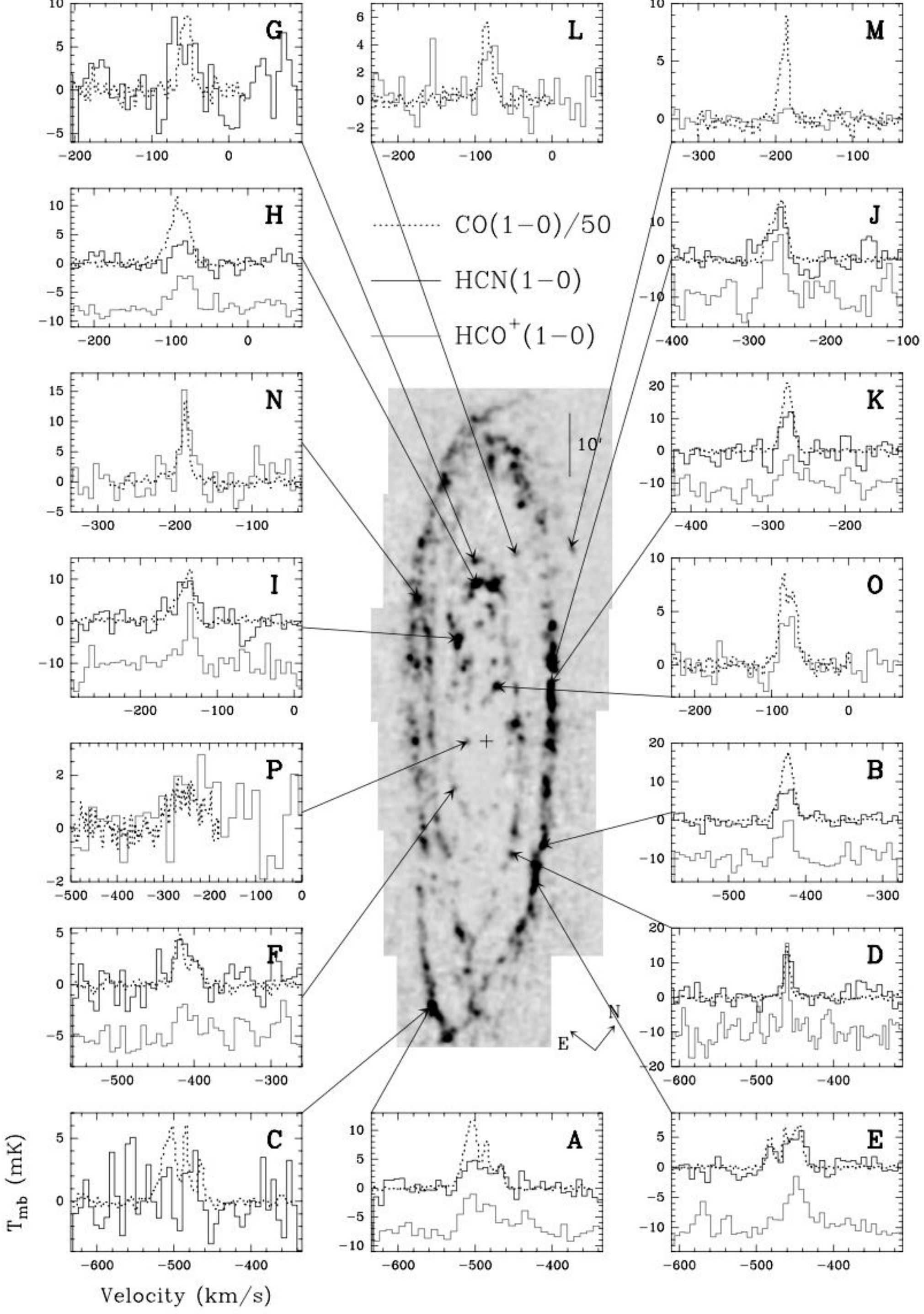
CO (2-1)





PHANGS survey: Leroy et al. (2021)

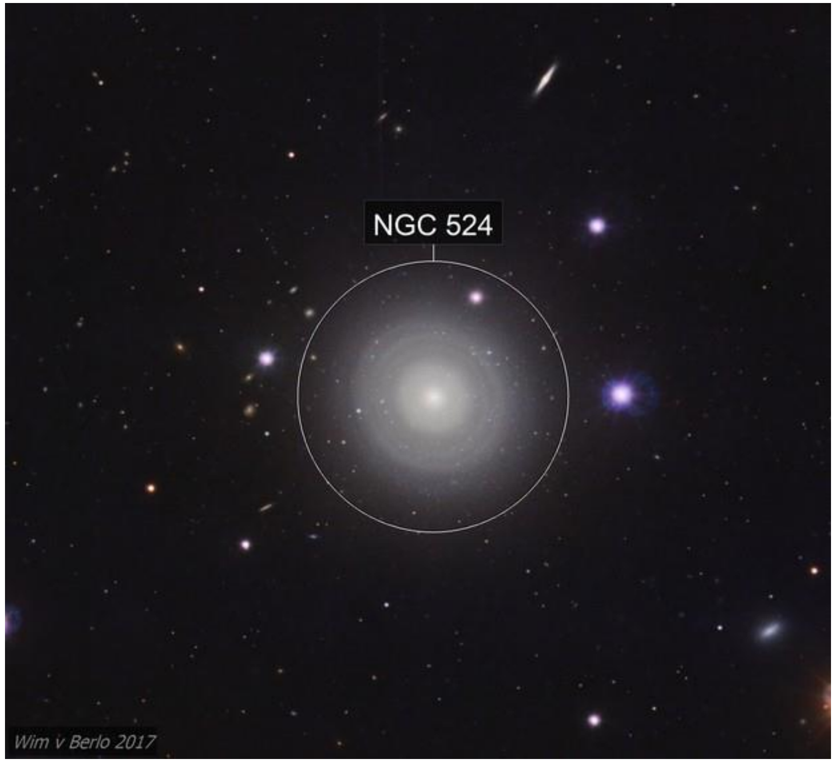
- HCN and HCO^+ have been observed in few normal spiral galaxies, but in particular in several GMCs in M31
- The HCN/HCO^+ ratio is found to be higher than that in the Milky Way galaxy but still well below that found in starbursts

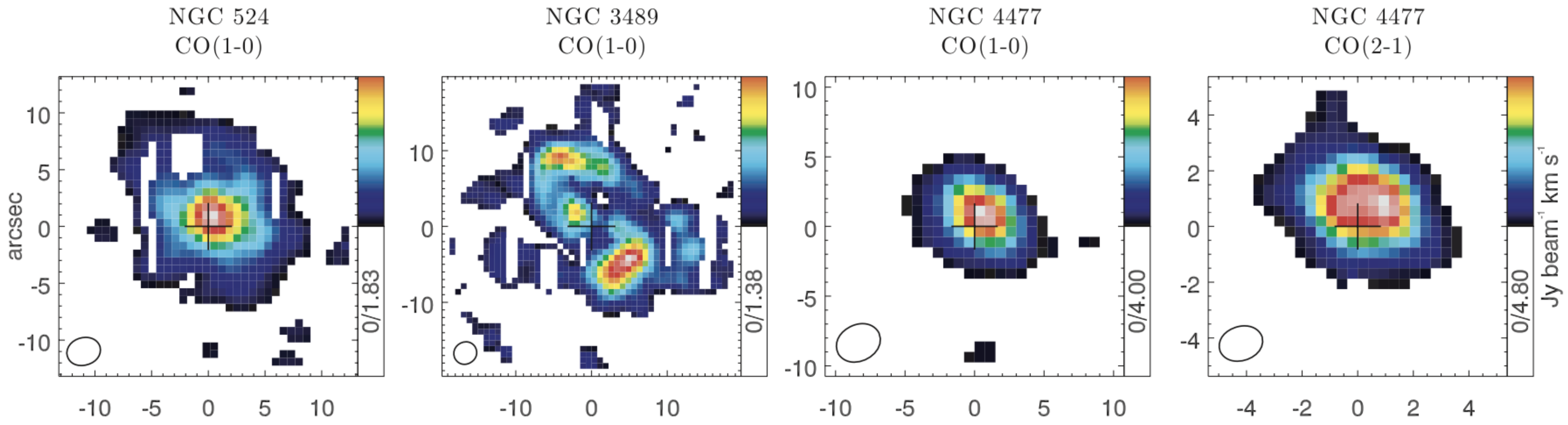


Brouillet et al. (2005)

Early-type galaxies

- Early-type galaxies comprise different types of galaxies → lenticular and elliptical.
- In the past they were thought to be the final step of galaxy evolution and that the fuel for star formation was all consumed/destroyed
- But observations of HI + dust showed that some of these galaxies have cold gas and some star formation.
- In fact a survey of the properties of hundreds early type galaxies has revealed substantial molecular gas reservoirs via CO observations



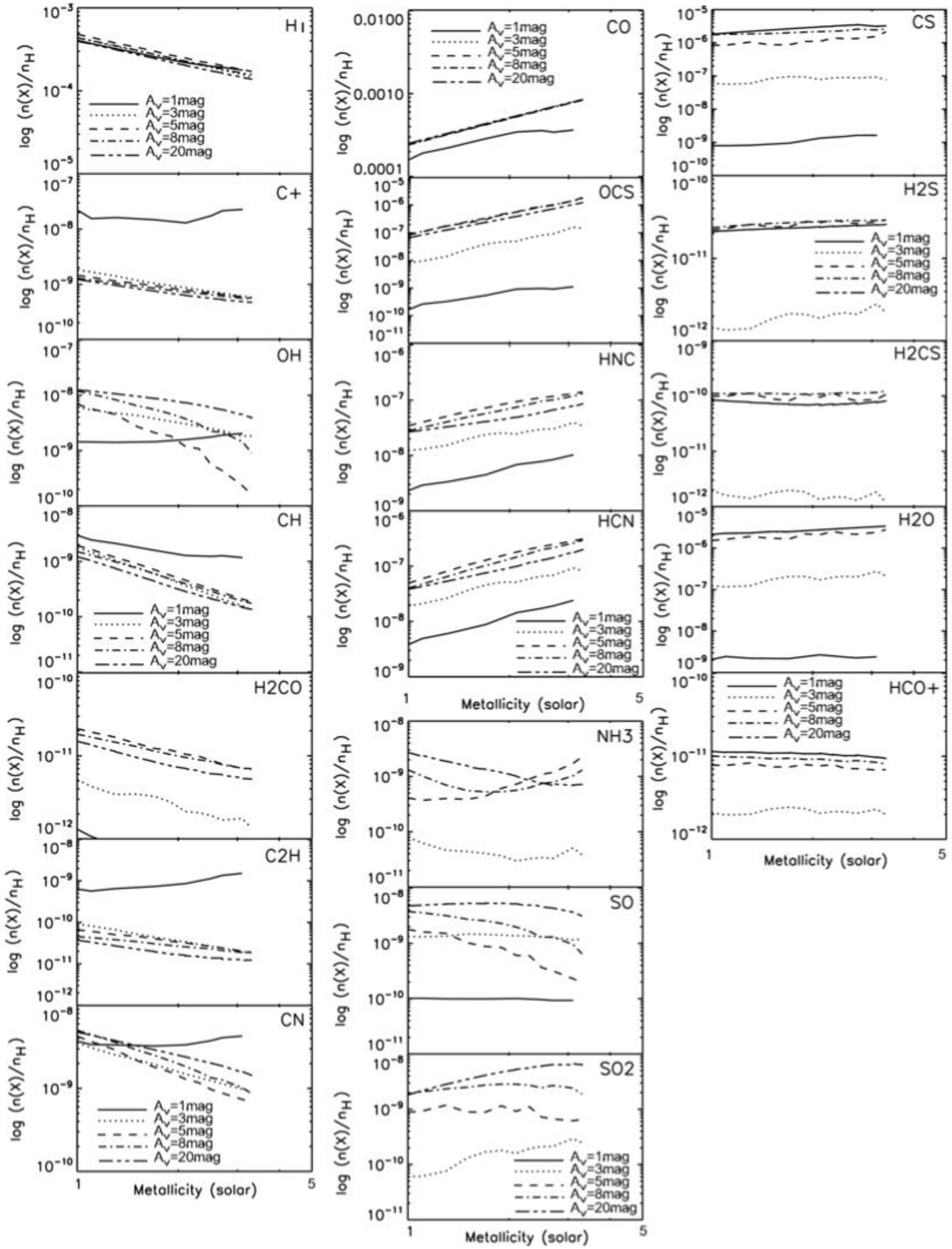


Crocker et al. (2011)

- Early type galaxies should be metal-rich (i.e > solar metallicity)
- Models of this molecular gas show that the abundances of some species are insensitive to increases in metallicity:
    - e.g. CS, H_2S, H_2CS, H_2O, H_3O^+, HCO^+ and H_2CN

whereas other appear to be sensitive:

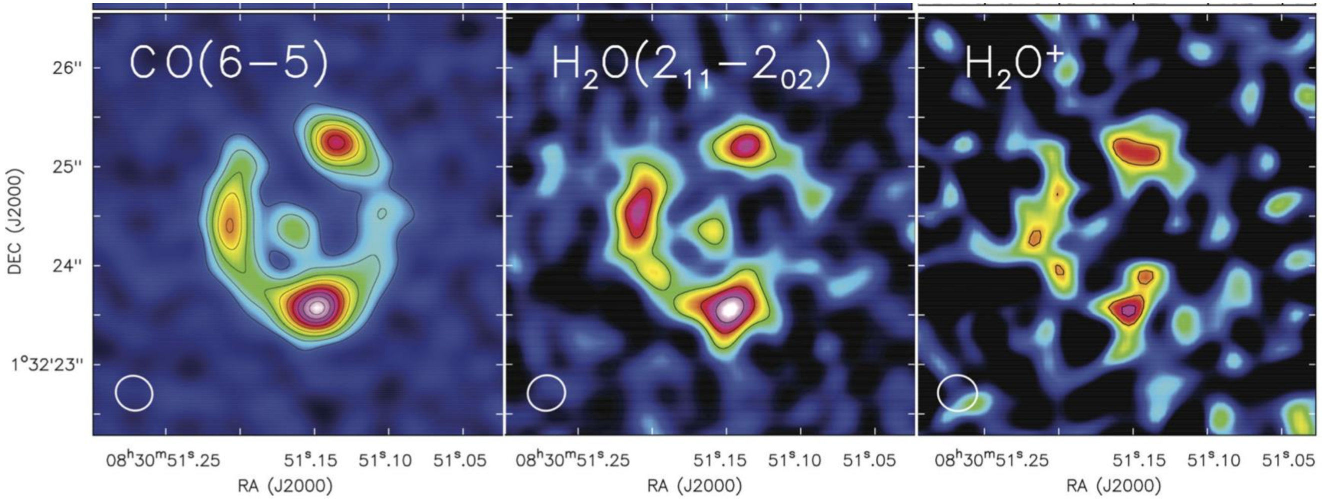
- e.g. C^+, CO, C_2H, CN, HCN, HNC and OCS



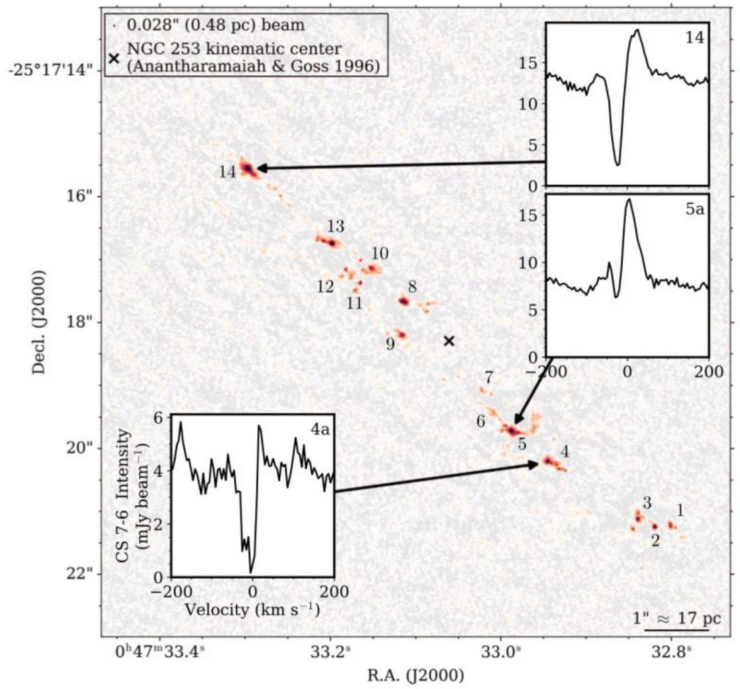
Starburst galaxies

Starburst galaxies

- Starburst galaxies are very luminous galaxies, powered by bursts of massive star formation.
- Massive stars occur in clusters and are embedded in dusty molecular clouds.
- Lifetimes of massive stars are ~ short (see SSE course) → periodical bursts of massive star formation → active chemistry in the surrounding gas.
- Starburst events are detected indirectly in a variety of ways, all due to the effects of the hot massive stars present in them.
- What causes the bursts is still debatable → possibly mergers of galaxies or gas flows in barred galaxies
- To date there are many observations of starburst galaxies in the millimetre waveband with many molecular species detected e.g.



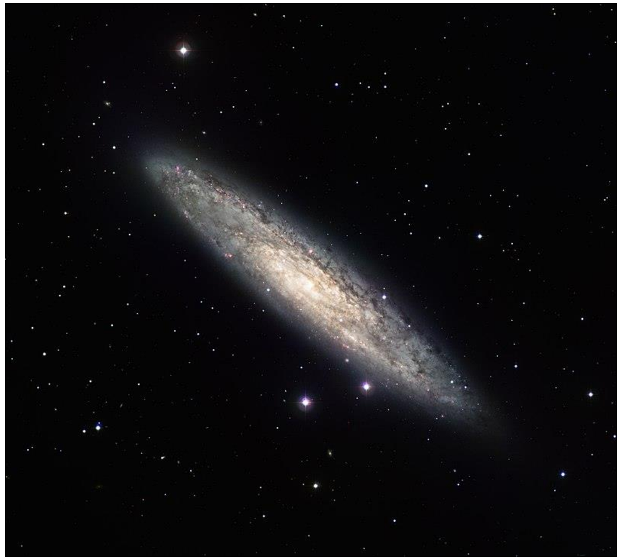
Yang et al. (2019), strongly lenses starburst at z=3.63



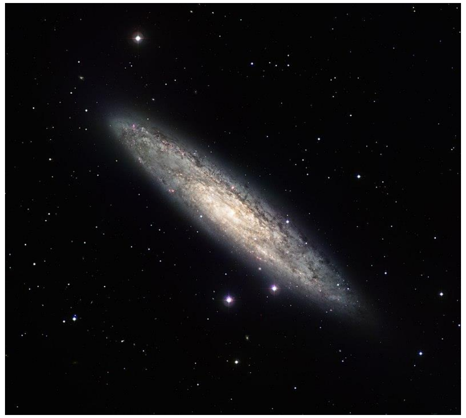
Levy et al. (2021), NGC 253

What physical characteristics can we deduce from molecular observations of starburst galaxies

- Starburst galaxies are among the most luminous in CO
- CO luminosity is strongly correlated with to the far infrared flux →at large scale one can deduce a star formation rate (with the appropriate CO/H_2 conversion factor)
- Many other molecules have been observed in starburst galaxies with **M82 and NGC 253** being the most studied starburst galaxies.
- We shall take these two galaxies to draw some examples of what you can do with molecules



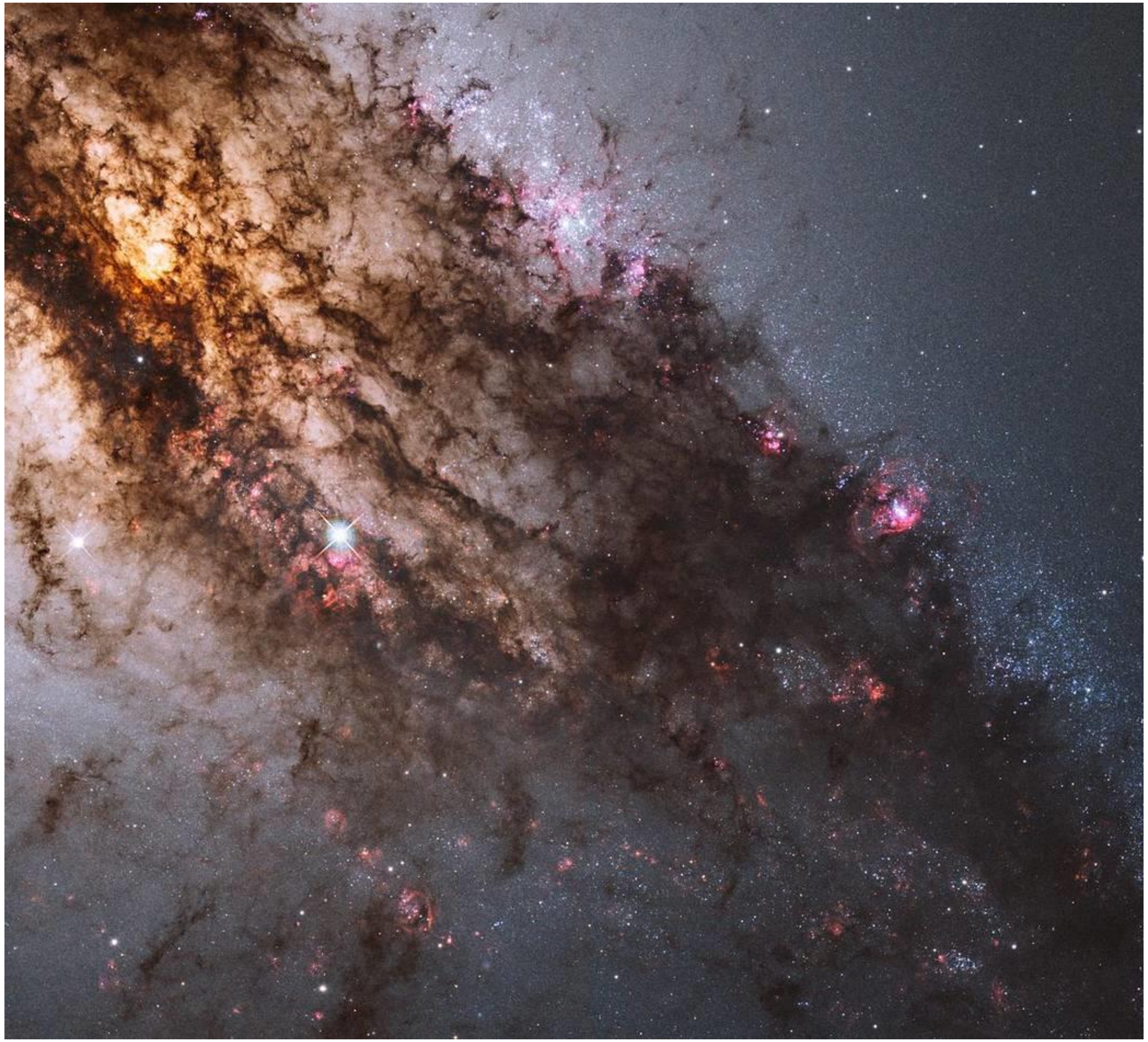
Comparison of molecular large scale Molecular observations of NGC 253 and M82 →



- NGC 253 central region's heating dominated by large-scale low-velocity shocks.
- NGC 253 is at an earlier evolutionary stage than M82
- The abundances of molecules such as SiO, CH_3OH, HNCO, CH_3CN and NH_3 are systematically lower in M82 than in NGC 253
- Species such as HCO and C_3H_2 are more abundant
- This implies M82 has more spatially extended PDRs than NGC253
- Consistent with M82 having many more HII regions than NGC253 → intense UV radiation from massive stars
- HOC^+, CO^+, and H_3O^+ also more abundant in M82 → high ionization rates in large PDRs formed as a consequence of its extended evolved nuclear starburst.

AGN-dominated galaxies

- Some galaxies have powerful AGN in their centres, as well as extended bursts of star formation.
- For these objects the connection between the starburst phenomenon and the central AGN is not well understood, but the presence of large amounts of circumnuclear gas → interaction between the molecular gas that fuels star formation with centres of the gravitational potentials where the AGN resides.



HST multi-wavelength image of Centaurus A

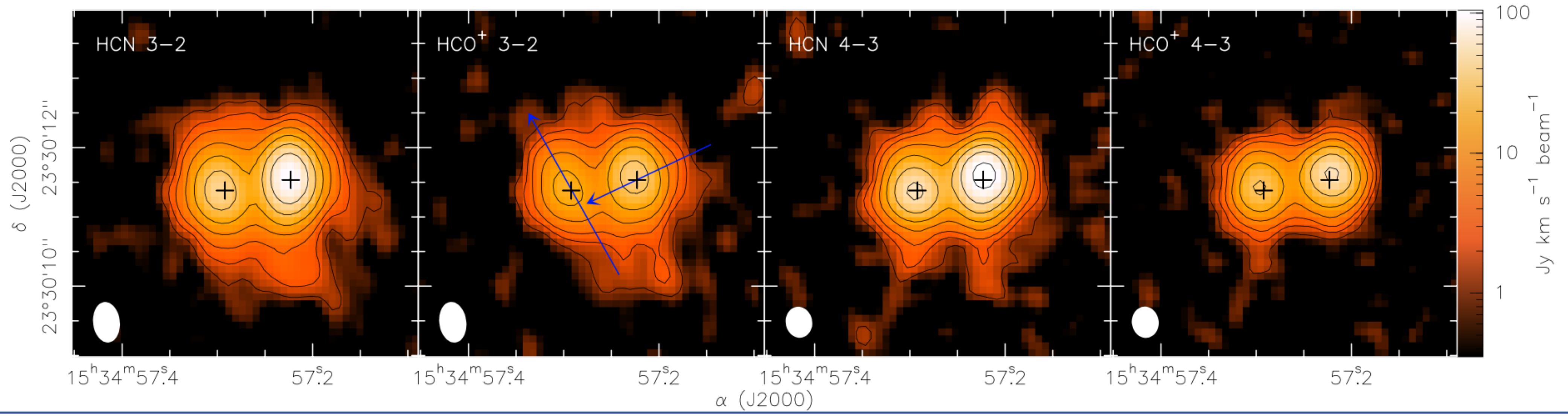
- Such galaxies have an enhanced (by maybe a factor of 100) cosmic ray ionization rate with respect to normal spiral galaxies, as well as a high intensity radiation field ($\sim 10^3$ higher than the galactic interstellar radiation field) but likely "acting" on different locations of the galaxies
- The "bad news" is that there is no unique molecular tracer of such environment
- Ratios of specific molecules, such as HCN/HCO^+, may help to trace the energetic processes that dominate the circumnuclear material.
- But we know that HCO^+ is highly sensitive to parameter changes → it can vary in abundance by several orders of magnitude because of variations in the cosmic ray and UV field rates, as well as time.

Ultra Luminous Infrared Galaxies (ULIRGs)

- ULIRGs are generally very dusty objects → UV radiation produced by the obscured protostars is absorbed by the dust and re-radiated in the infrared at wavelengths of ~ 100 μm.
- These objects can be more than 100 times more luminous in the infrared than in the optical.
- ULIRGs are powered by AGNs as well as starbursts
- Molecular studies of their interstellar gas show signatures of both
- CO very abundant → star formation efficiency of 20-200 $L_\odot/M_\odot$ (compared to the 4 $L_\odot/M_\odot$ in normal spiral galaxies) → larger than those found in some starburst galaxies such as M82.
- PAHs and silicate dust → the presence of (sometimes 'buried') AGN.

Let us take as an example Arp220:

Credit: ALMA(ESO/NAOJ/NRAO)/NASA/ESA and The Hubble Heritage Team (STScI/AURA)



- High spatial resolution emission of the CO(1-0) and also HCN and HCO+ emission → 90% of the dynamical mass of the system and 75% of the molecular mass is confined to a central core of 600 pc in diameter.
- HCN and HCO+ observations also imply high density gas (> 10^5 cm^{-3})
- The CO (2-1) distribution also shows that there are three dense peaks: two in the double nucleus and one in an extended disc structure separate from the dust lanes observed in the optical
- *Here high vibrational lines of various molecules have been observed (HCN in particular)*
- HCN traces higher dense gas than HCO+
- H_3O^+ also observed here (2-10 x 10^{-9} in abundance) → probably traces X-ray "driver"

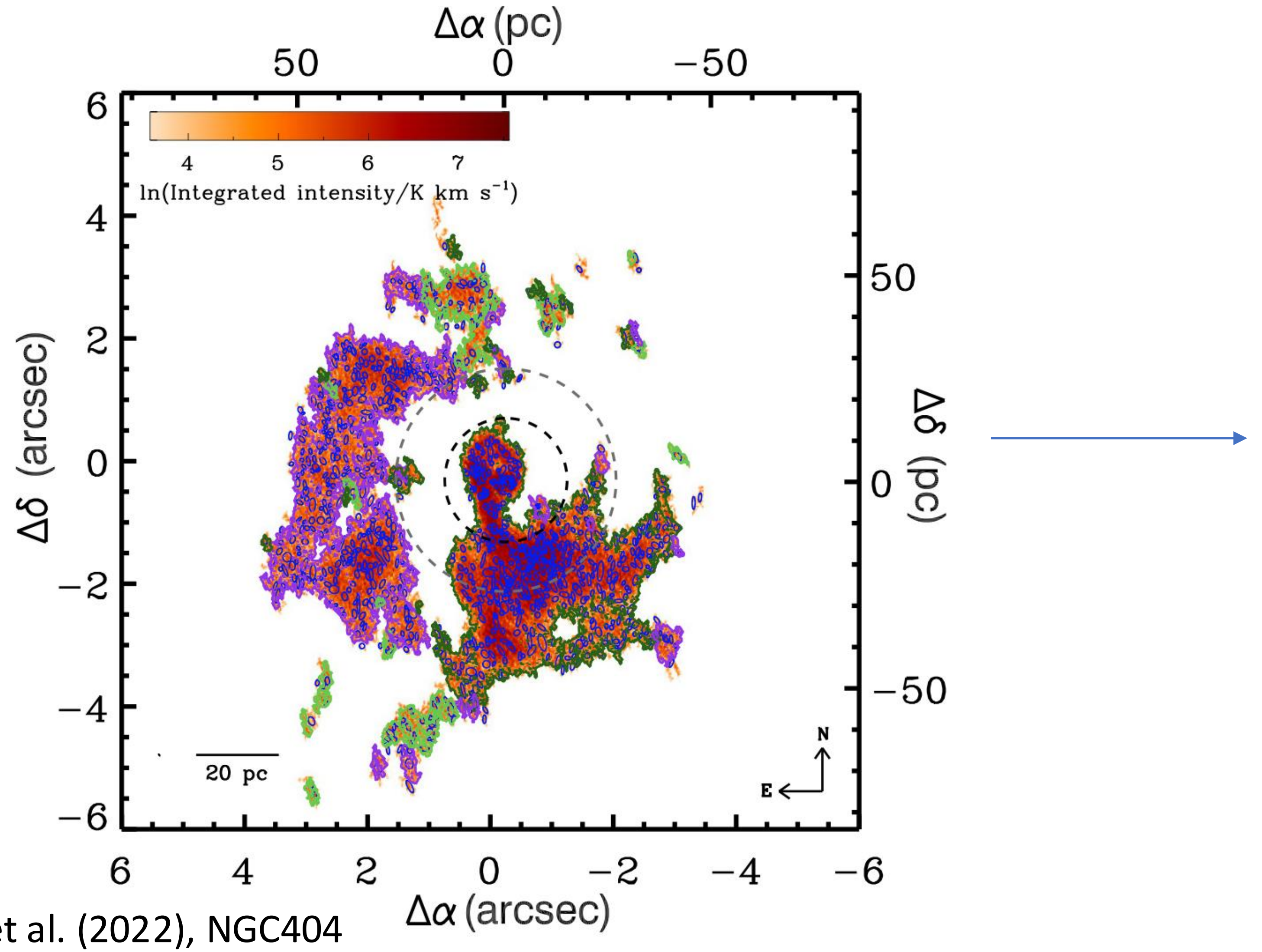
Dwarf Galaxies

- Low mass galaxies with overabundant atomic gas, low metallicity, high gas mass fraction
- Despite the fact that many dwarf galaxies do form stars (→ interstellar gas must be present) molecular detections in such objects have been scarce until very recently.
- It is yet not clear whether the lack of widespread CO implies a lack of molecular hydrogen or whether in these objects *CO becomes a poor tracer of* H_2 → also found that non-detections are correlated with metal-poor low-mass galaxies, implying - maybe - that in this regime CO does not trace molecular hydrogen.

What is CO-dark gas?

- It is now well known that some of the H2 in molecular clouds is *not* traced by CO
- This is because CO is not as efficient at shielding itself from FUV radiation as H2 → the transition from C^+ to CO occurs at higher Avs than the transition from H to H_2 → extended diffuse envelope of "CO-dark" H2.

- Molecular structures (clumps and clouds) are quite different from those in the Milky Way and Local Group galaxies but observations are limited to a small number of galaxies.
- Dwarf galaxies may be the crucial building blocks of much larger galaxies
- Example:

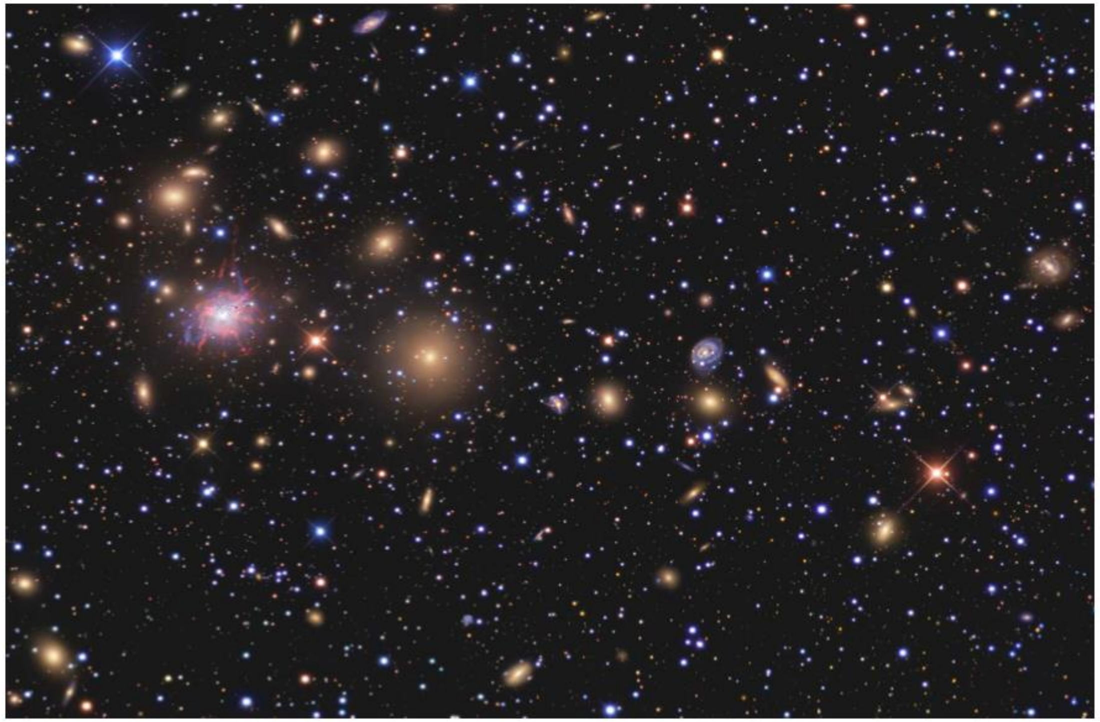


Liu et al. (2022), NGC404

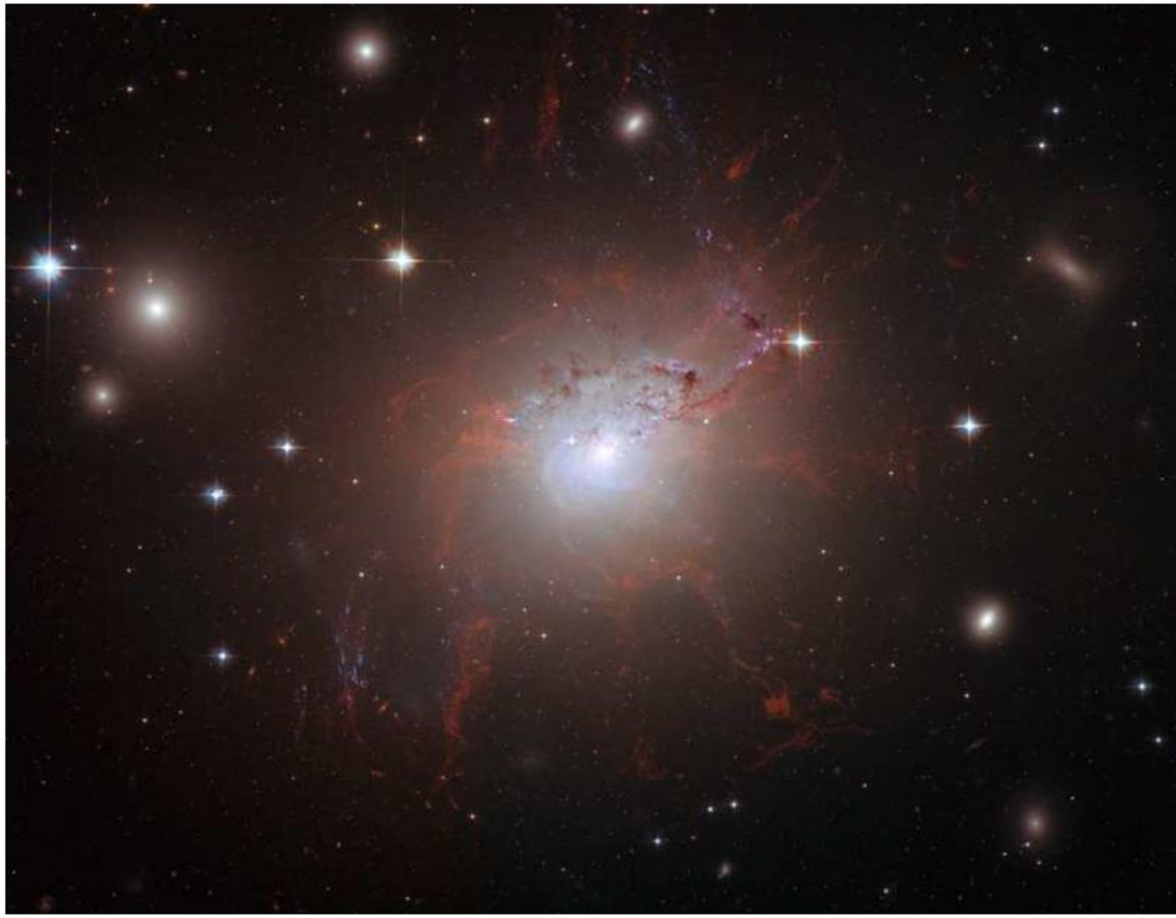
- Very clumpy structures.
- Here CO seem to be tracing turbulence at large scale (→ dynamical "driver"?)

Clusters of galaxies

- Interacting galaxies may give rise to starbursts, by abruptly feeding new interstellar matter into the star forming process.
- Large clusters of interacting galaxies may have even more dramatic consequences: they may generate a new phenomenon not present in single or double galaxies.
- The best studied galaxy cluster is the Perseus Cluster
- This cluster generates powerful X-ray and radio emission as a result of infalling material.

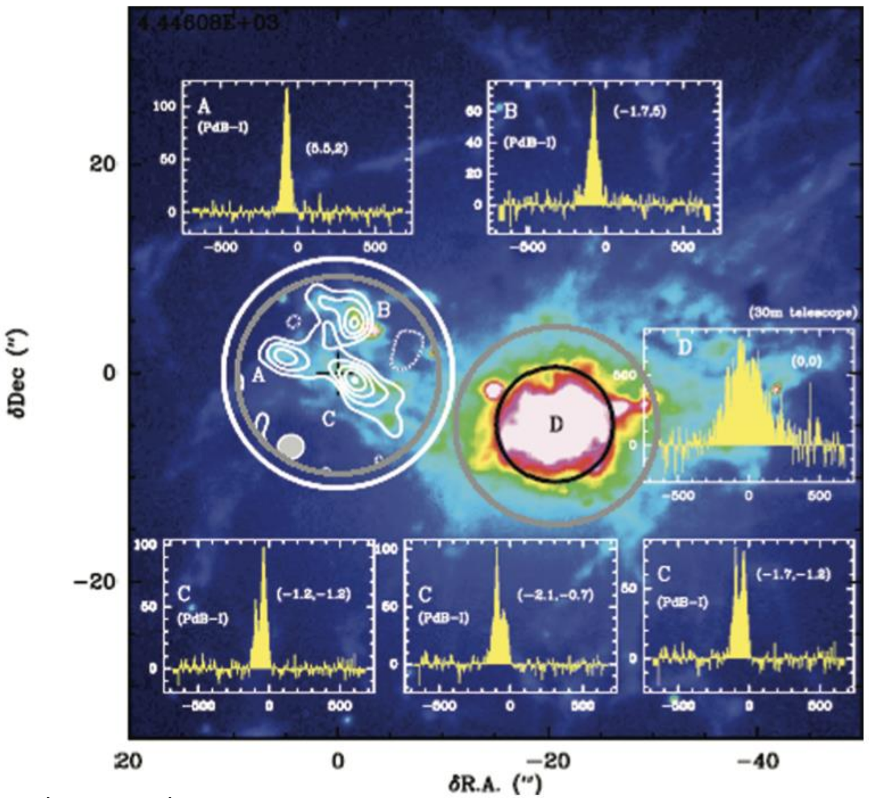


- The central galaxy of the Perseus Cluster is surrounded by ‘filaments’ observed in optical emission lines, in infrared H_2 emission lines, and in CO millimetre-wave emission lines.
- These filaments are about 100 pc thick and extend for many tens of kpc.
- Their origin and excitation remain to be confirmed, but it is likely that they are turbulent mixing layers between very fast diffuse outflows and entrained gas, and that they are heated by dissipation or by cosmic rays.

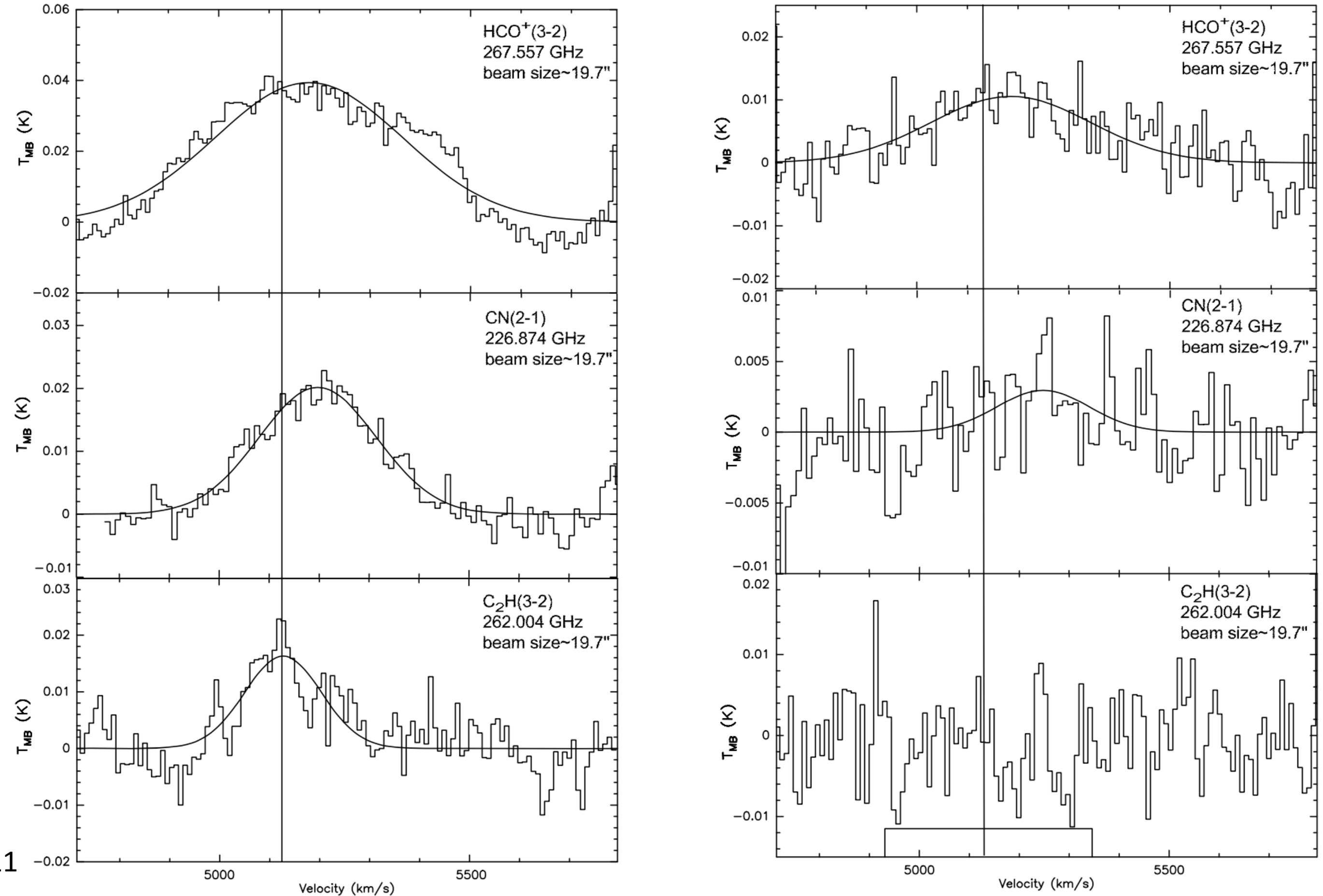


- Heating rates required to maintain the observed emissions from the filaments are very powerful compared to heating rates in Milky Way → molecules could help to determine these rates and identify the heating source.
- CO , CN, HCO^+, and C_2H have been detected and support the view that the main heating in the filaments could be supplied by cosmic rays, at a rate at least two orders of magnitude larger than in the Milky Way Galaxy → *cosmic rays driver?*

Co (2-1)



Salome et al. 2008



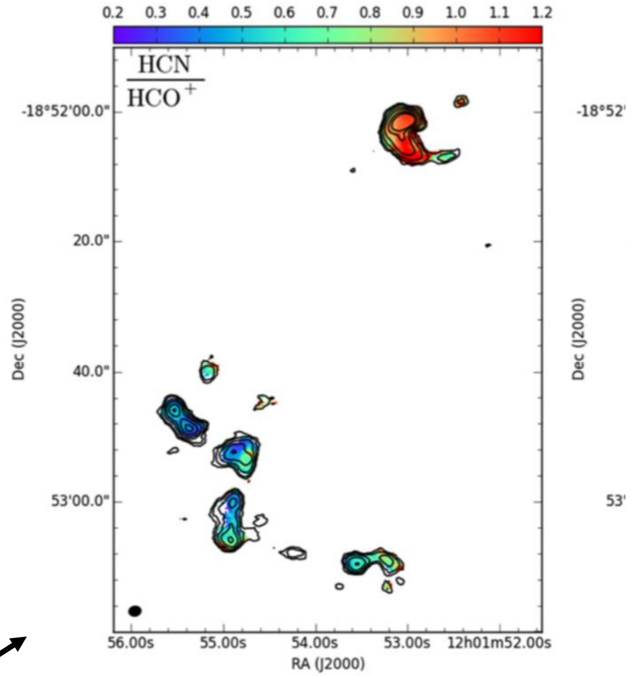
Bayet et al. 2011

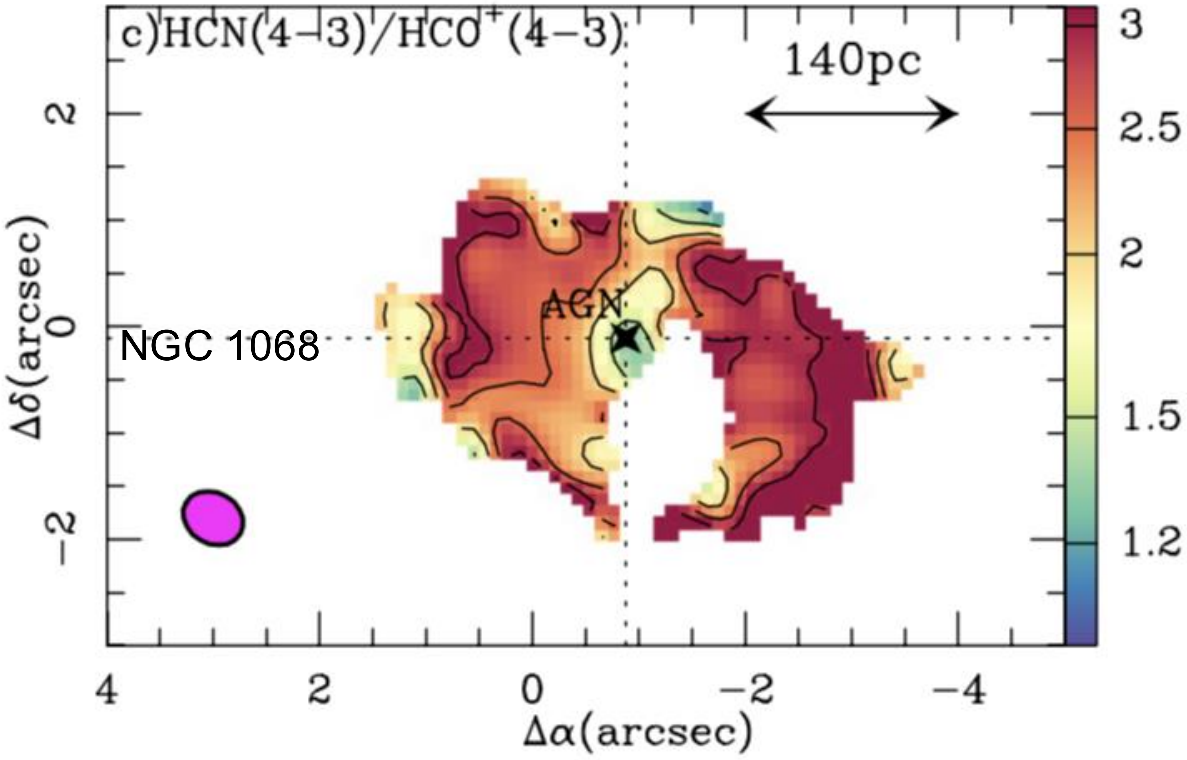
Molecular ratios

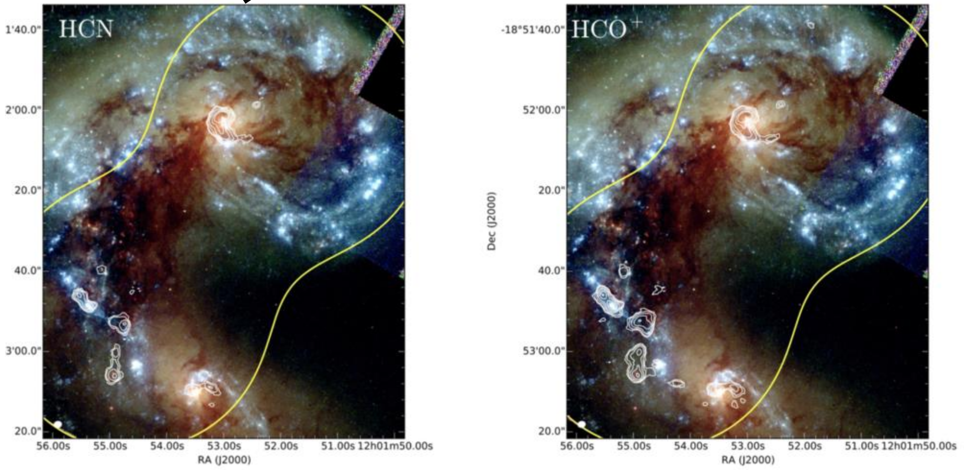
- Observationally, many studies have shown that molecular line ratios, such as HCN/HCO^+ or HCN/CO, differ across different types of galaxies especially between active galactic nuclei (AGN)-dominated galaxies and starburst-dominated galaxies
- On the other hand, other studies have found that enhanced HCN/HCO+ are not unique to AGN environments but can also be found in systems dominated by star formation.
- Moreover, the derived abundance ratios for an individual galaxy also highly differ across studies depending on the transitions observed, available resolution, and method used in deriving the column densities.
- Often used ratios, for example the HCN(4– 3)/HCO^+(4–3) or the HCN(1–0)/HCO^+(1–0), are the same for several models within the accuracy assumed.

It is clear that an understanding of the chemistry behind each molecule and its dependencies on the density and temperature of the gas is essential.

E.g.: HCN/HCO⁺ higher in the nuclei of NGC 4038/9 and NGC 1068 than in overlap region/starburst ring → **AGNs → higher fluxes of cosmic rays and X-rays → leads to an enhancement of the molecule HCN**

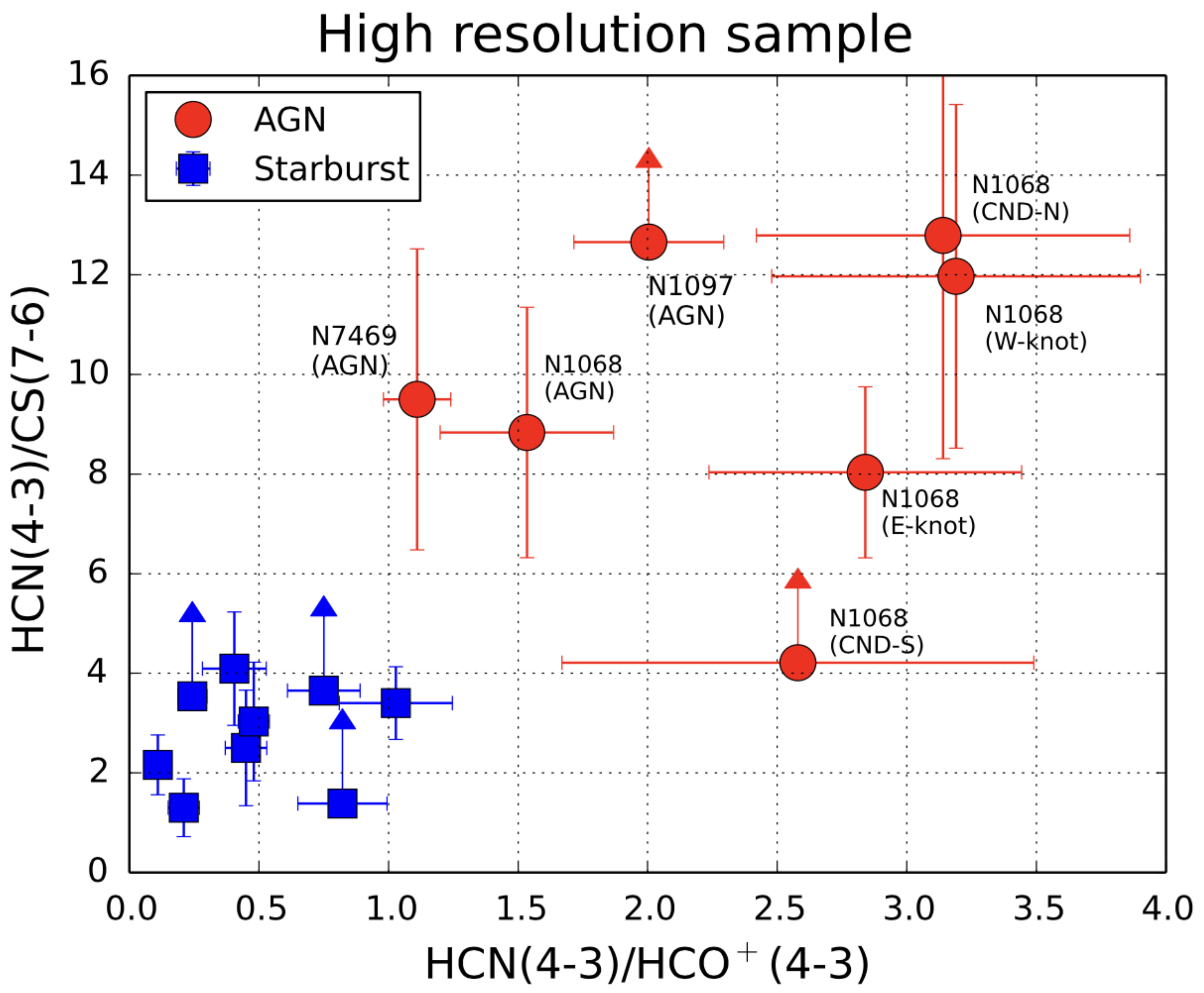






Antennae Galaxies

Schirm et al. (2016)



Izumi et al. (2016)

Molecular ratios

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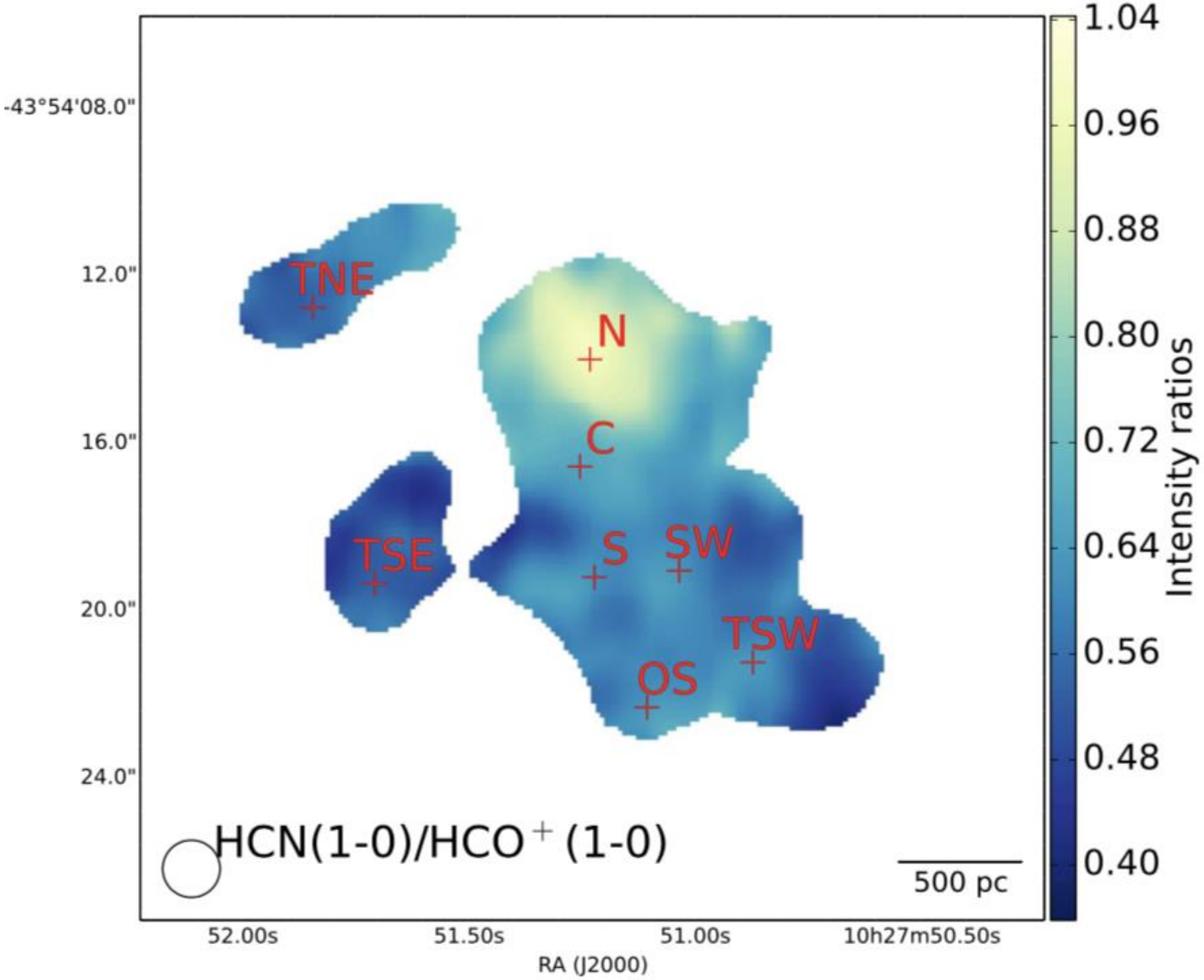
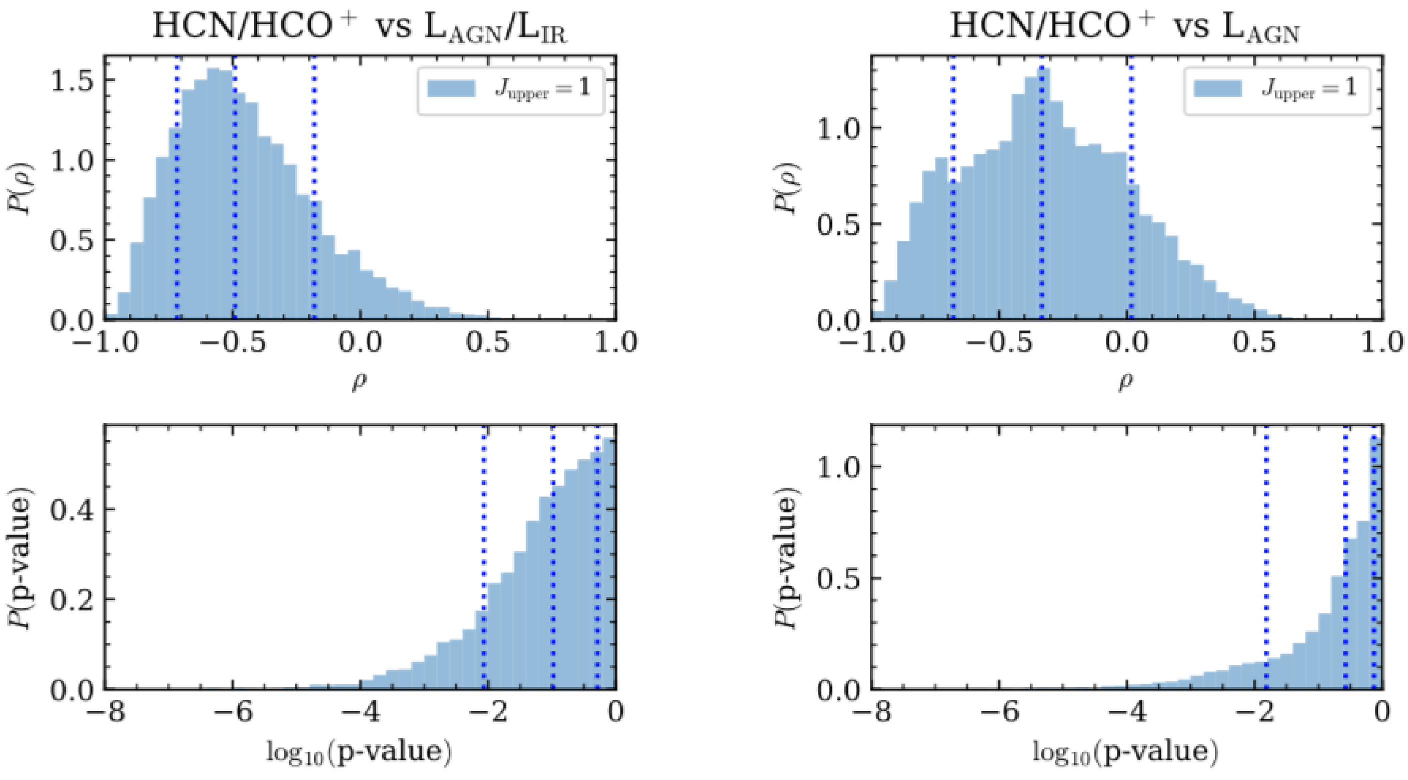
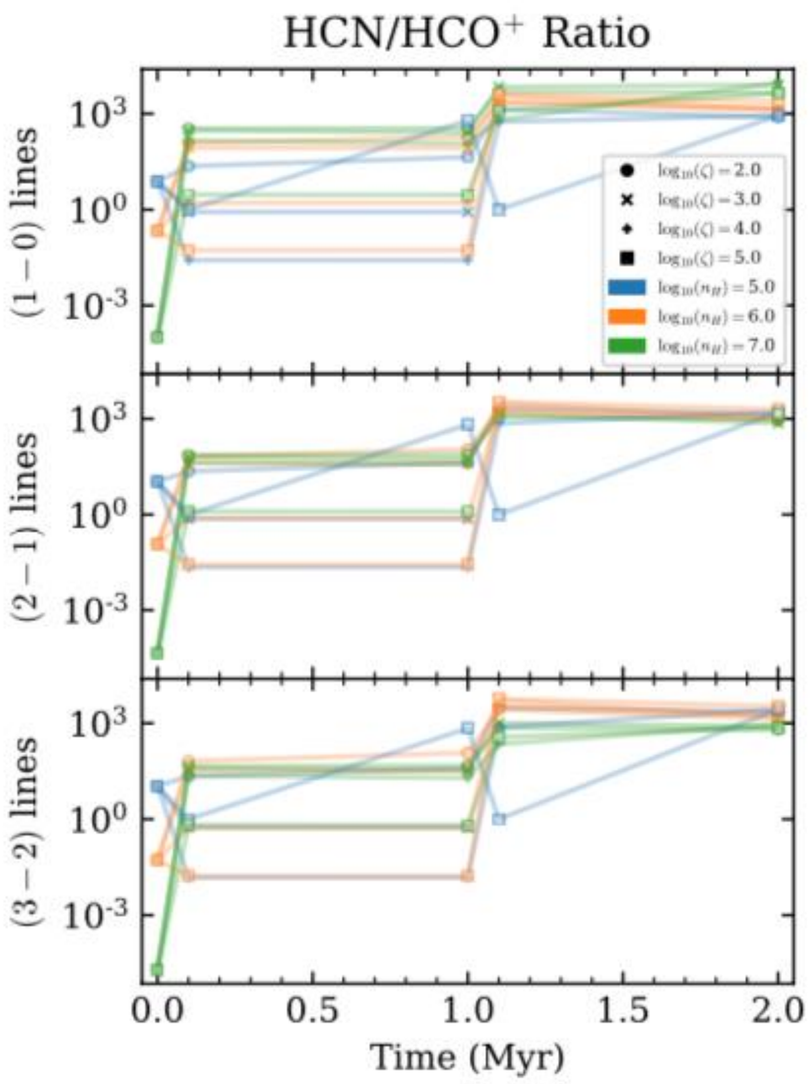
Several studies show no enhancements of HCN/HCO^+ in AGNs (e.g. Costagliola et al. 2011; Privon et al. 2015; Martin et al. 2015; König et al. 2018; Harada et al. 2018)



NGC 3256 Harada et al. (2018)

Theoretical line intensity ratios





Privon et al. (2020): Spearman rank correlation coefficient computed
→ no clear correlation

Molecular ratios

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What would cause the HCN/HCO^+ to increase?

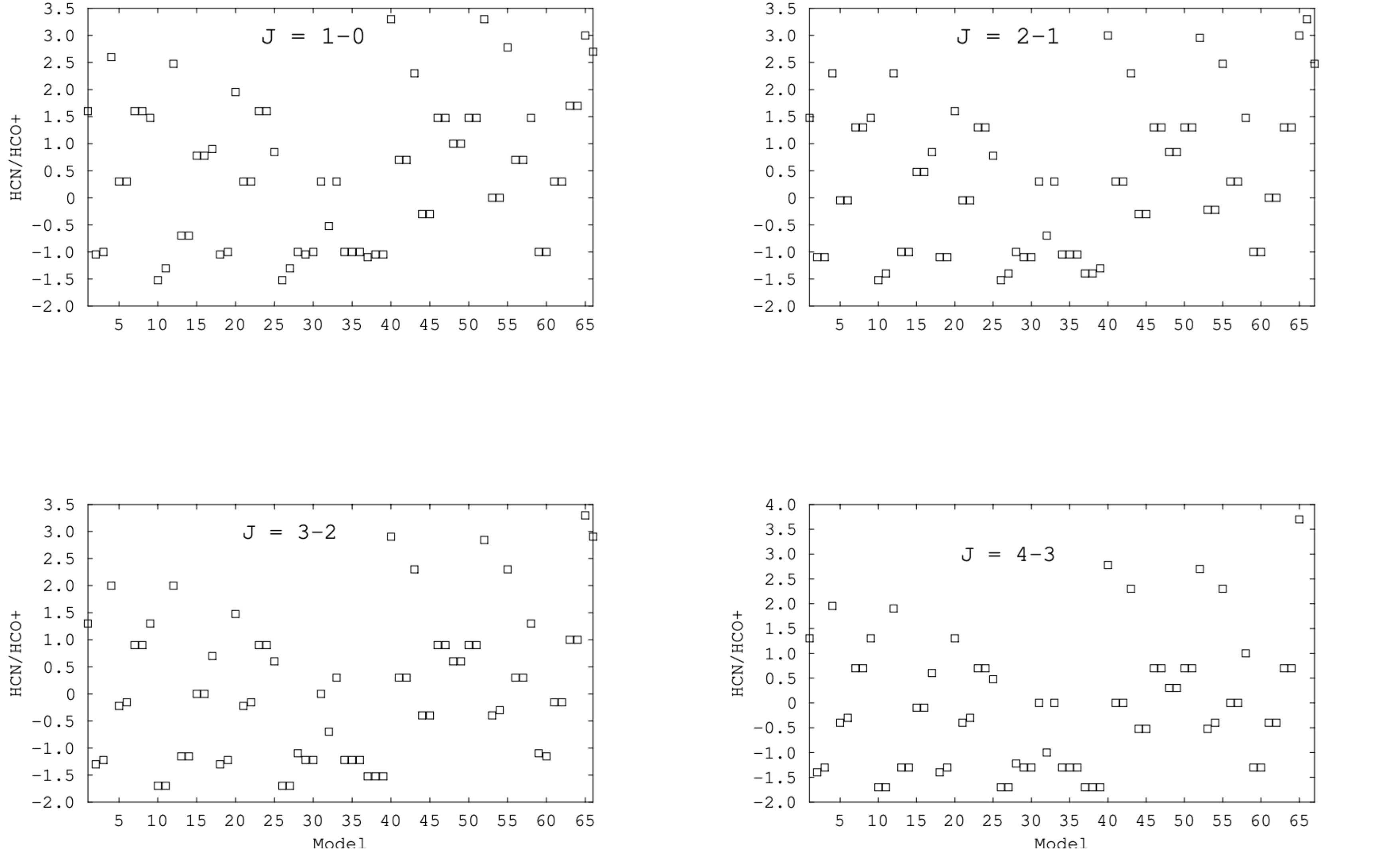
At high temperature there are some reactions that may increase the HCN abundance e.g.

$CN + H_2 \rightarrow HCN + H$ Energy barrier ~ 800K

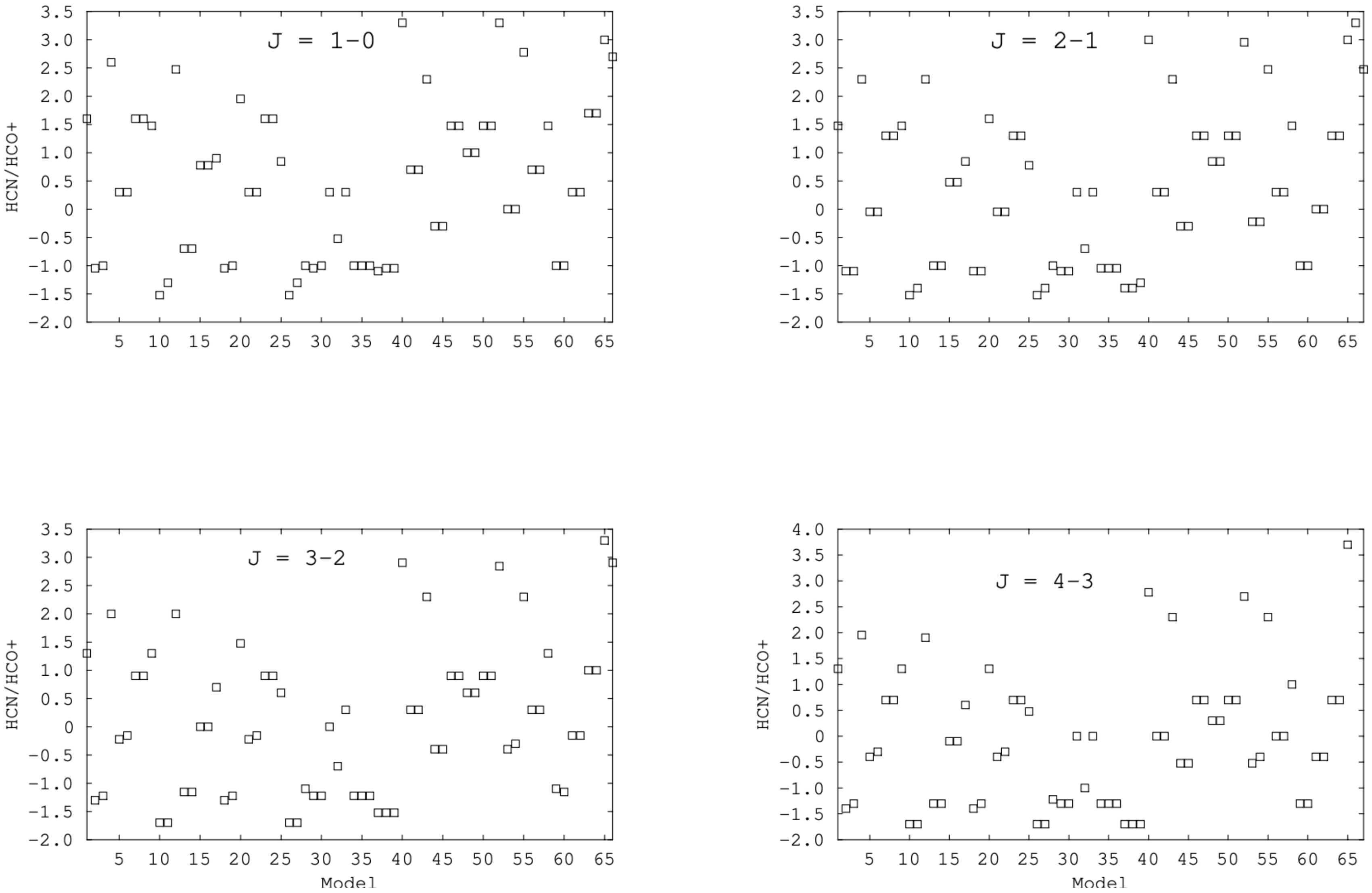
Also, while at 100 K HCO^+ makes up much of the positive charge, by 300 K its relative abundance is reduced.

Note: the energy barrier is *not* the kinetic temperature of the gas but obviously the two are related.
The energy barrier is the amount of energy the particles must have to react when they collide → for a chemical reaction to proceed at a sufficient rate, Tk has to be high enough so that there are enough molecules with an energy equal to or greater than the activation energy .

Let us consider the HCN/HCO^+ line ratios → below are the ratios as a function of different chemical models:



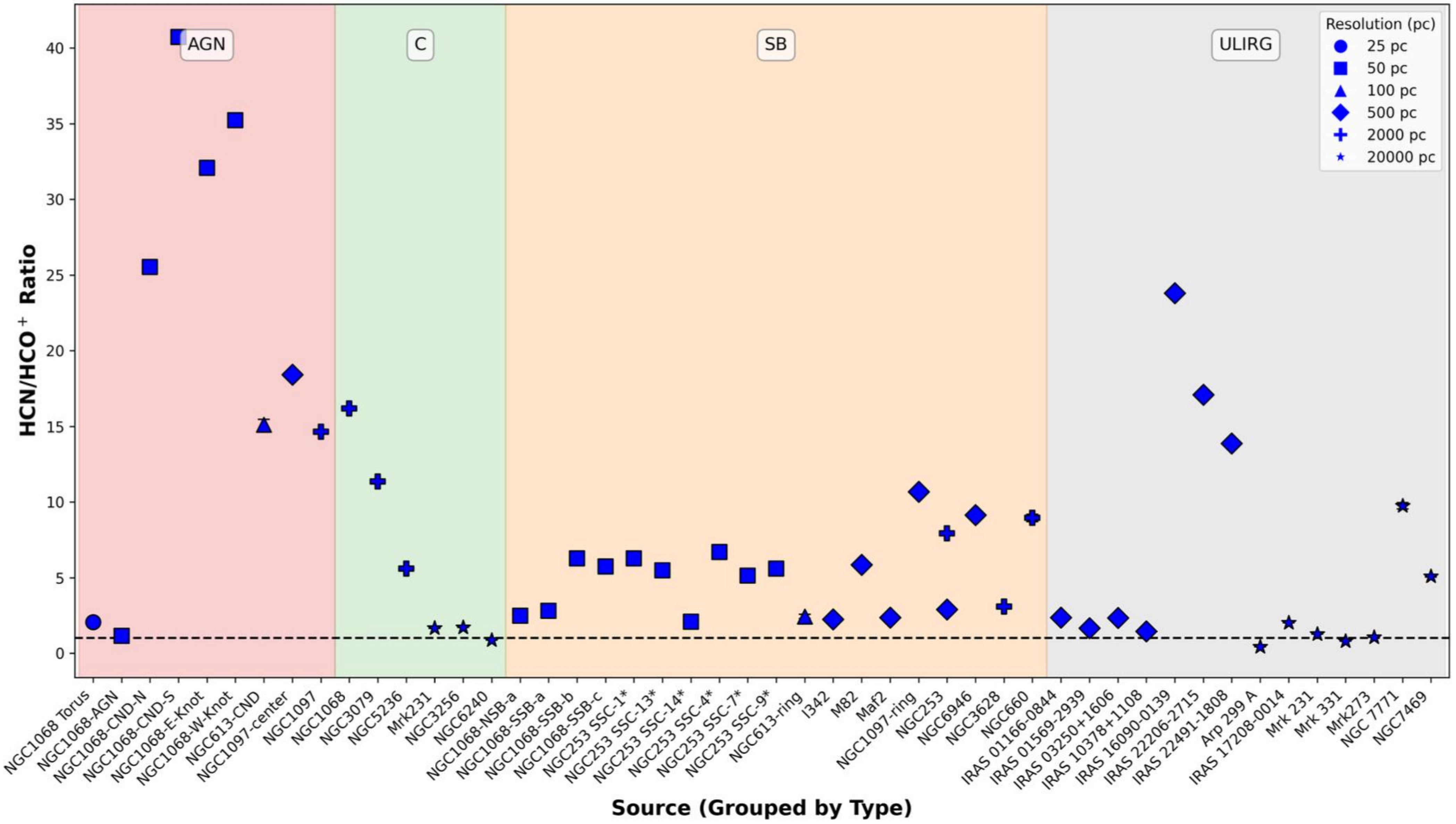
These plots show how a relatively standard grid of chemical models can lead to large ranges for the HCN(1–0)/HCO^+ ratio of key transitions.



- Model 1 has the same HCN/HCO$^+$(1–0) and similar HCN/HCO$^+$(2–1) ratio to Model 7 but all the other ratios are very different.
- These two models differ substantially only in gas density, which is a physical characteristic that the lower transition ratios could not have traced.

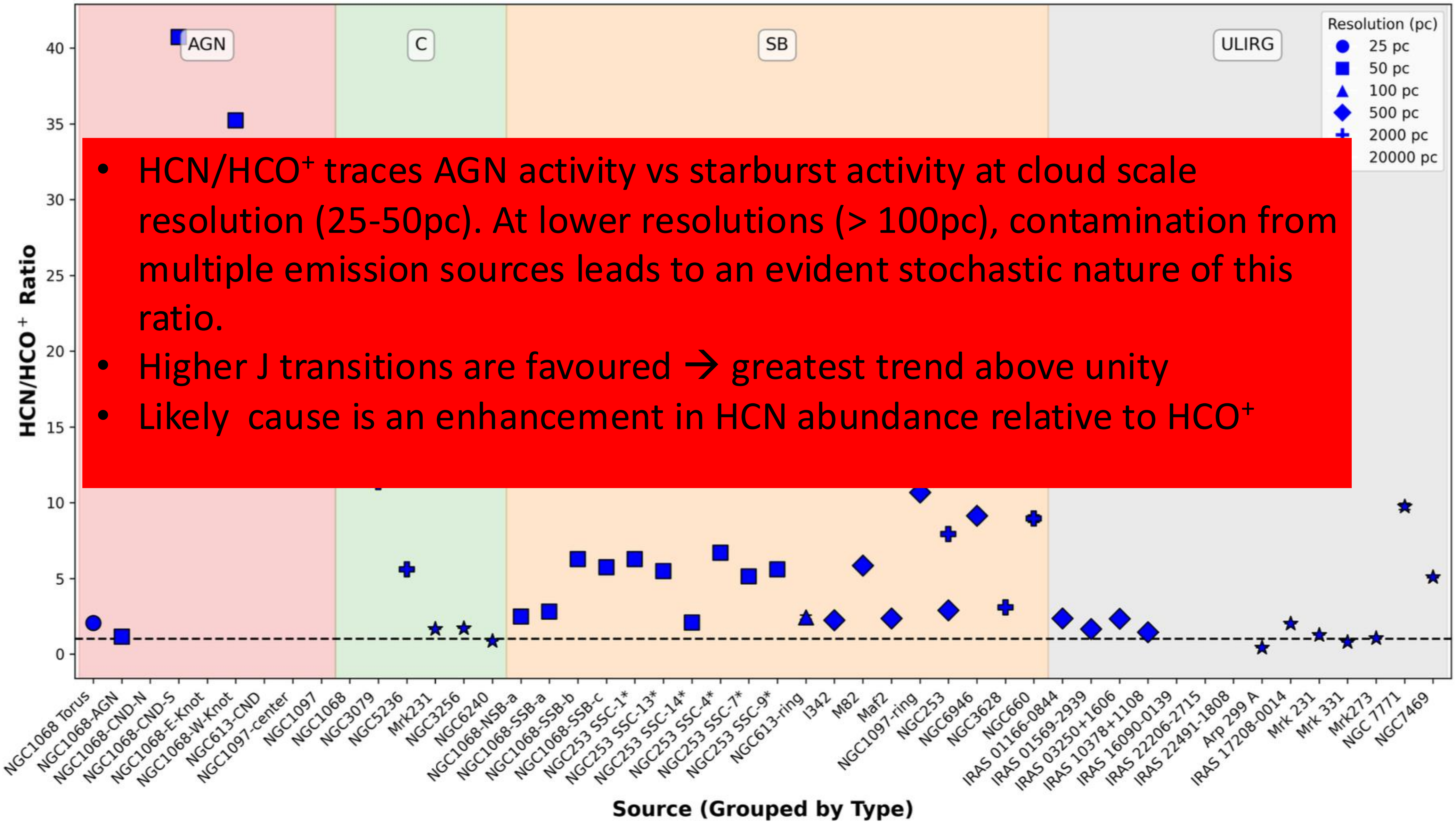
(Butterworth et al. 2025, A&A)

So does HCN/HCO⁺ trace AGN activity or not?



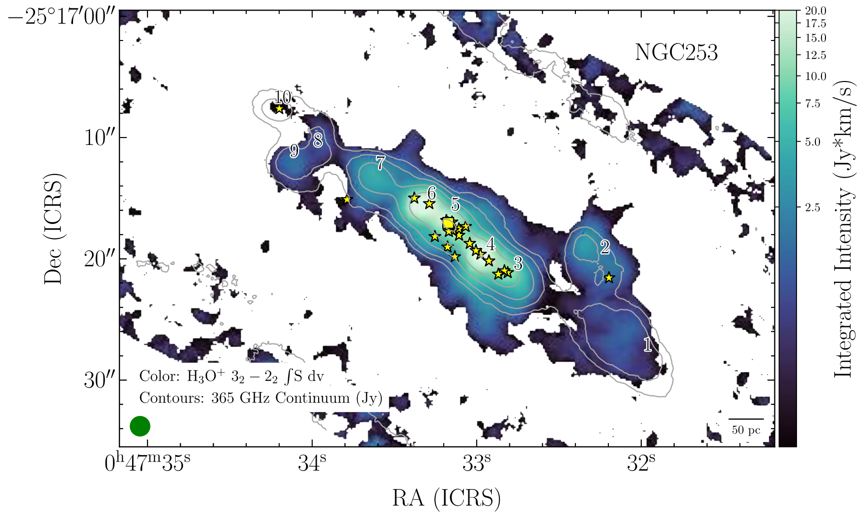
HCN/HCO⁺ as a tracer of AGN activity

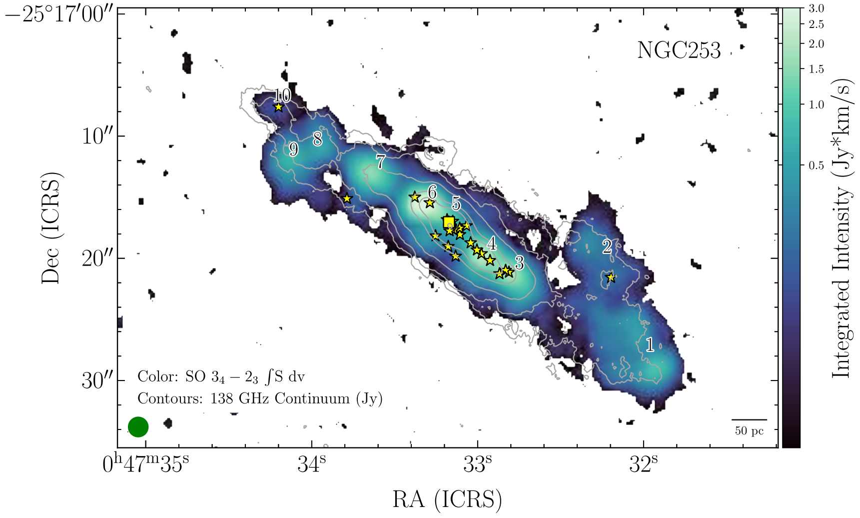
(Butterworth et al. 2025, A&A)



- HCN/HCO$^+$ traces AGN activity vs starburst activity at cloud scale resolution (25-50pc). At lower resolutions (> 100pc), contamination from multiple emission sources leads to an evident stochastic nature of this ratio.
- Higher J transitions are favoured → greatest trend above unity
- Likely cause is an enhancement in HCN abundance relative to HCO$^+$

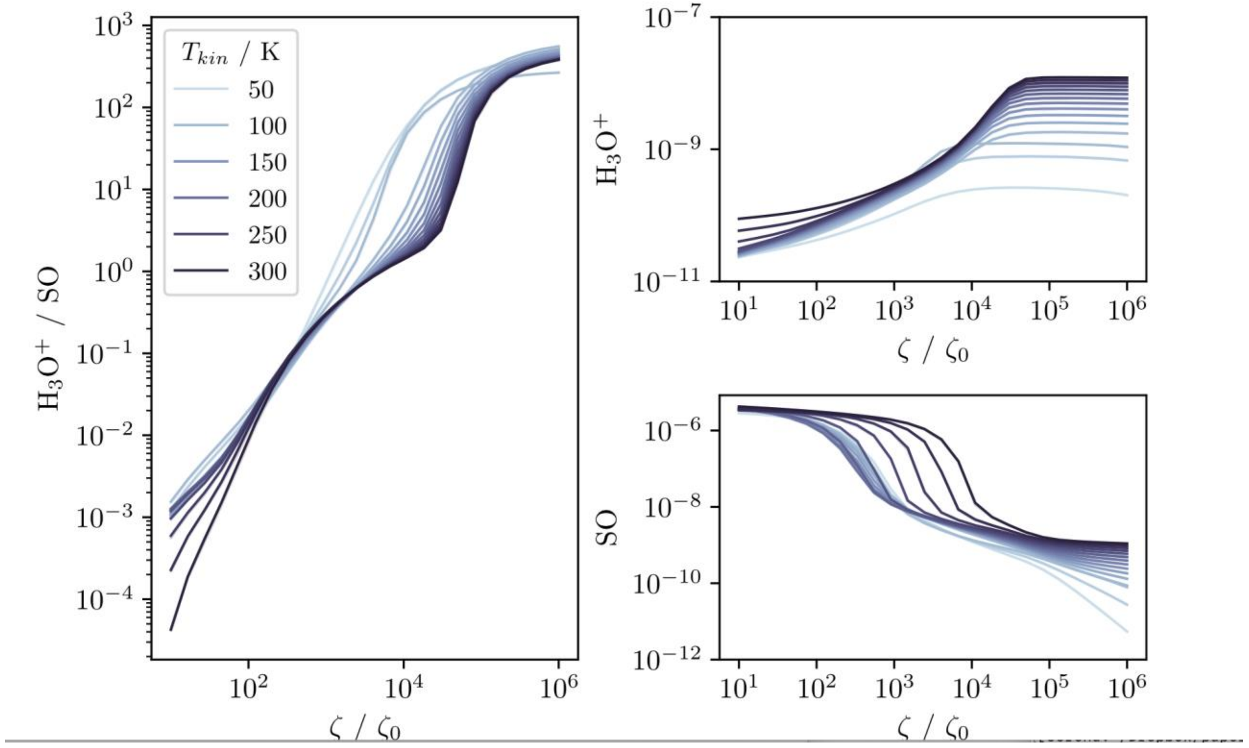
Let's have a quick look at other ratios: H_3O^+/SO



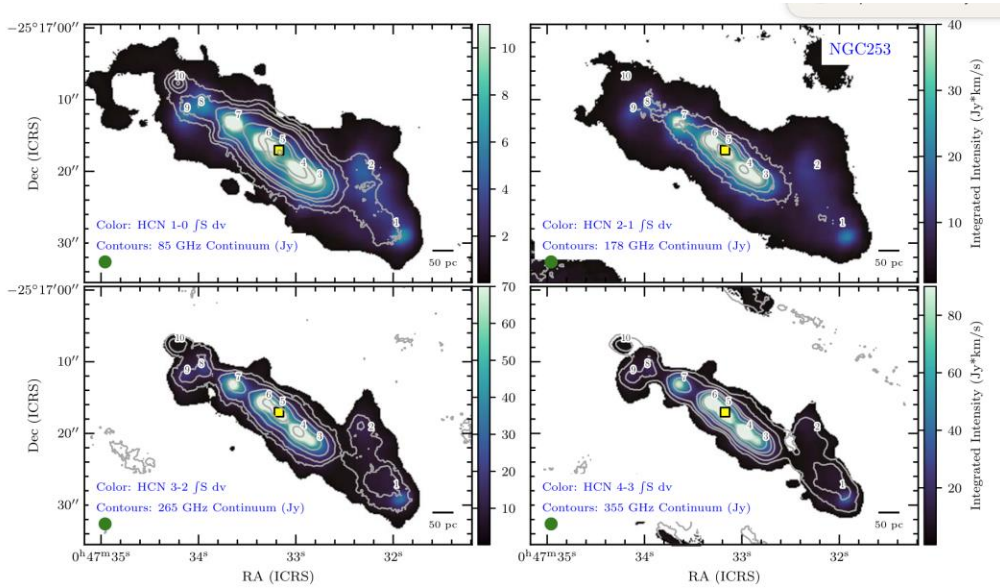


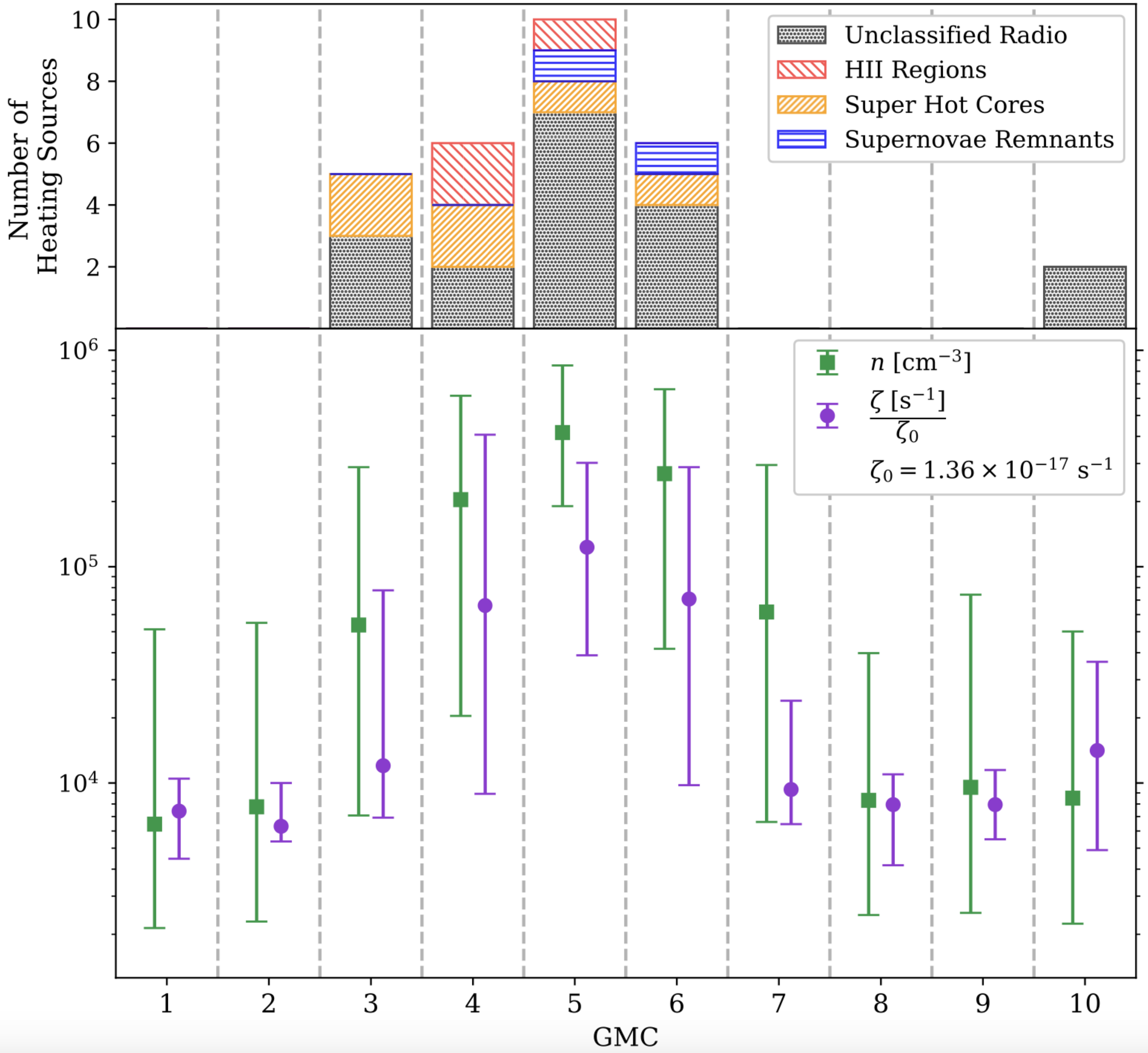
Holdship et al. (2022)

- SO and H_3O^+ are tightly coupled to the cosmic ray ionization rate → in NGC 253 it was found that this rate is 10^{-14} to 10^{-12} s^{-1} (10^2 to 10^4 times the CRIR in the Milky Way)



Let's have a quick look at other ratios: HCN/HNC





Behrens et al. (2022)

So molecular ratios can be powerful tools

However there are two more problems with ratios that we need to be aware of: when we use a ratio we make the implicit assumptions <u>that (i) the two transitions arise from the same gas and (ii) the individual column densities are both correct</u>

And a final word of caution: in general, when using ratios be aware that:

(i) time dependent effects on chemical abundances could be important (e.g. in starbursts)
(ii) Line intensities ratios, such as HCN(1–0)/HCO+(1–0), are not unique tracers of one energetic process
(iii) Individual species *can* be unique tracers of a particular energetic process, but only within specific physical conditions.

<u>To sum up</u>: changing the physical conditions (UV flux, cosmic ray ionization rate, etc.) that determine the chemical *drivers* will also change the *chemistry* and the *abundances* of the molecules produced by those *drivers* → <u>*molecules have an active role in controlling some important aspects of the gas, in particular, its heating and cooling and its level of ionization*</u>.

Let's take as an example - low mass star formation: Timescales

Timescale	Equation
Free-fall Collapse	$t_{\rm ff} = \sqrt{\frac{3\pi}{32G\rho}} = 0.75\times10^8/(n_H)^{\frac{1}{2}}$ yr,
Cooling	$t_{\rm cool} = \frac{\frac{5}{2}n_{\rm H}kT}{\xi\Lambda_{\rm tot}}$ yr,
Freeze-out	$t_{fo} = \frac{0.9\times10^6(m_X/28)^{\frac{1}{2}}}{(T/10)^{\frac{1}{2}}(n_{\rm H}/10^4)D}$ yr,
Desorption	$t_{\rm des} = \frac{1\times10^9}{[n_{\rm H}n({\rm H})(T/100)^{\frac{1}{2}}\gamma\xi]}$ yr,
Ambipolar diffusion	$t_{\rm amb} = 4\times10^5(x_i/10^{-8})$ yr.
Ion-molecule chemistry	$t_{\rm chem} \simeq \frac{3\xi(n_{\rm C}^{\rm tot}+n_{\rm O}^{\rm tot})}{n({\rm H_2})\zeta} = \frac{5\times10^6\xi}{\zeta/1\times10^{-17}}$ yr.

Free-fall collapse: Gravity determines the free-fall timescale → does not depend on the chemistry.

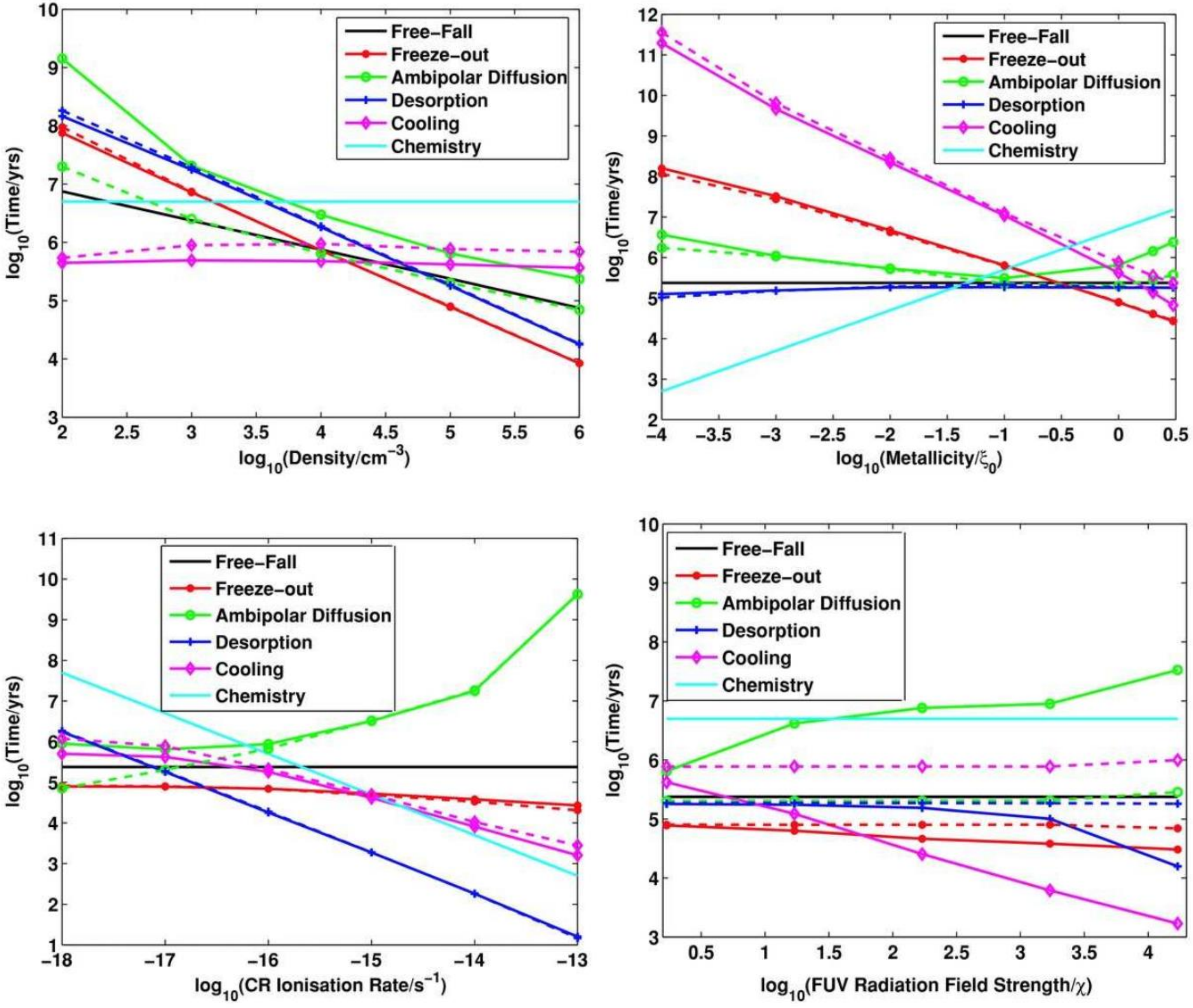
Cooling: Determines how quickly the gravitational potential energy of the cloud can be radiated away by molecules

Freeze-out: Determines when gas-phase molecular abundances are significantly reduced by "freezing" on grain surfaces.

Desorption: Determines how quickly molecules may be desorbed from ices to the gas phase.

Ambipolar diffusion: Determines how quickly magnetic support for a cloud can be removed.

Ion-molecule chemistry: Determines how soon an atomic gas becomes molecular



Banerji et al. (2009)

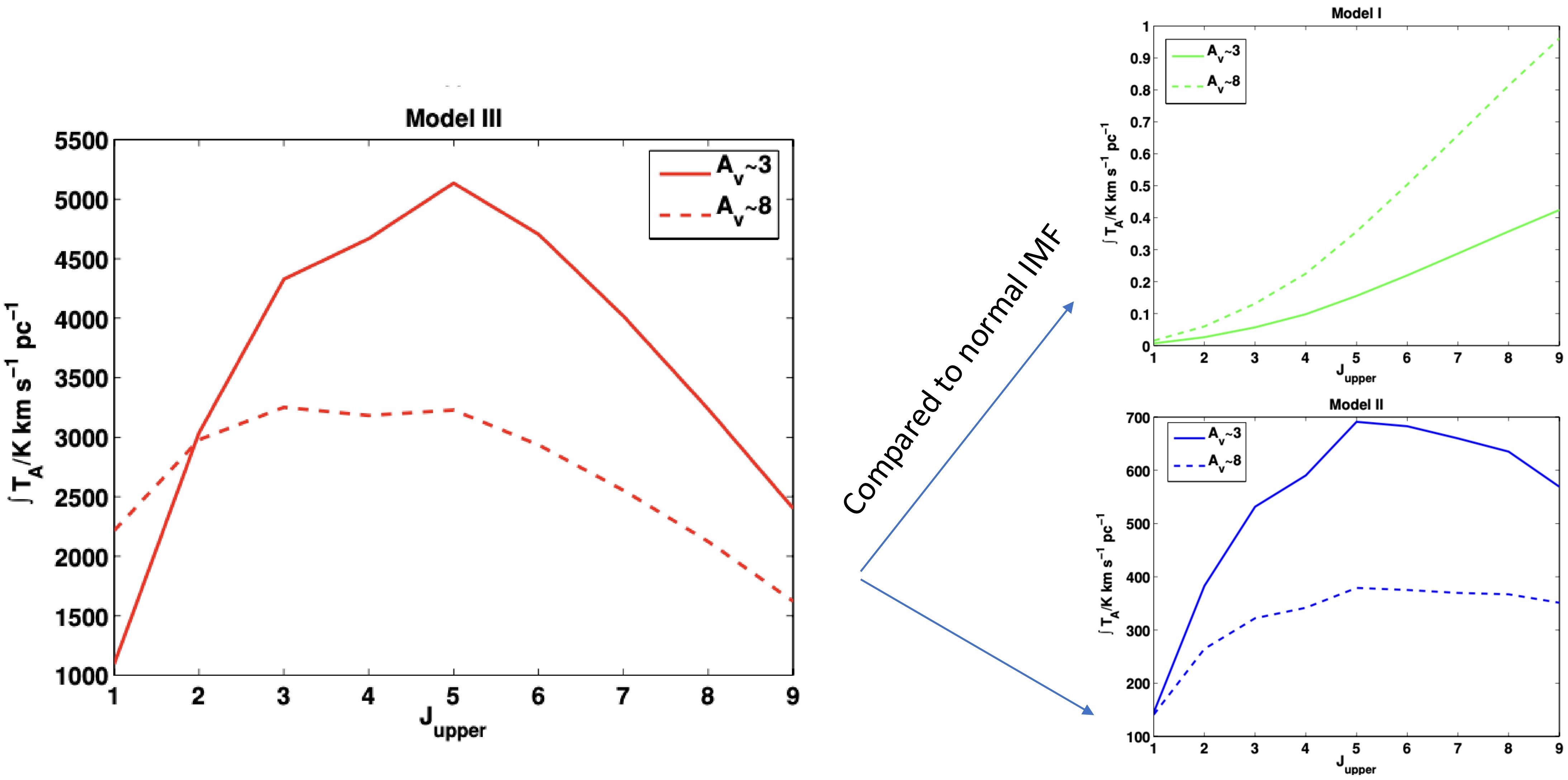
- when the timescales do not differ too much → low mass star formation can occur.
- If, e.g., the cooling time is long compared with the free-fall time → the gravitational potential energy of a collapsing core cannot be radiated away sufficiently quickly and therefore star formation will not occur.
- Or if the ambipolar diffusion timescale is too long → magnetic support will remain significant and will impede the gravitational collapse.

The initial Mass function

- Assuming formation of high mass stars is unrelated to the formation of low mass stars → some physical conditions may generate a conventional IMF (like that in the Milky Way Galaxy; with large numbers of low mass stars for each high mass star) while other conditions may lead to a ‘top heavy’ Initial Mass Function (IMF), i.e. having a relative lack of low mass stars compared to the number of high mass stars.
- Conditions likely to suppress low mass star formation (”top heavy” IMF):
  - Solar metallicity + intense UV fields + high cosmic ray fluxes
  - These conditions may be found in active galaxies at high red-shift.
  - Another galaxy type that may show a ”top heavy” IMF is one similar to the Milky Way but with sub-solar metallicities.
- *Can we then use molecules to determine the type of IMF?*
- The CO rotational emission integrated antenna temperatures seems to be dependent on the metallicity of the galaxy and on the activity of the galaxy

Banerji et al. (2009)

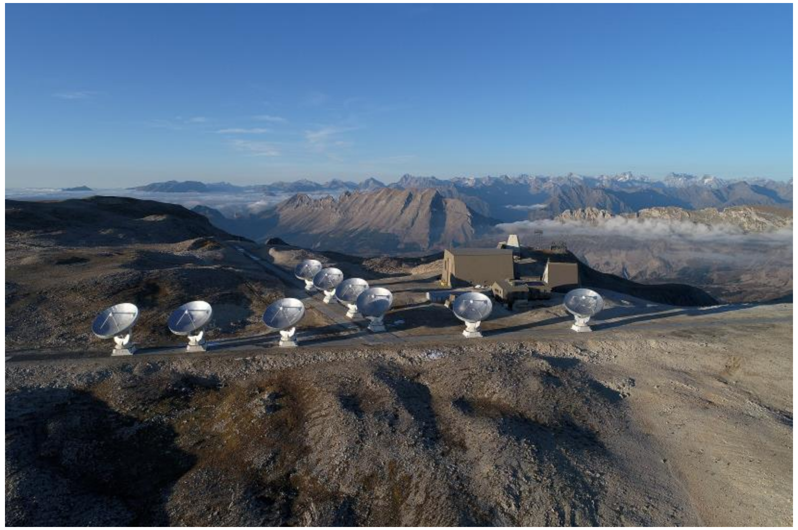
Top-heavy IMF: Variation of theoretical velocity-integrated CO antenna temperatures for high-redshift models

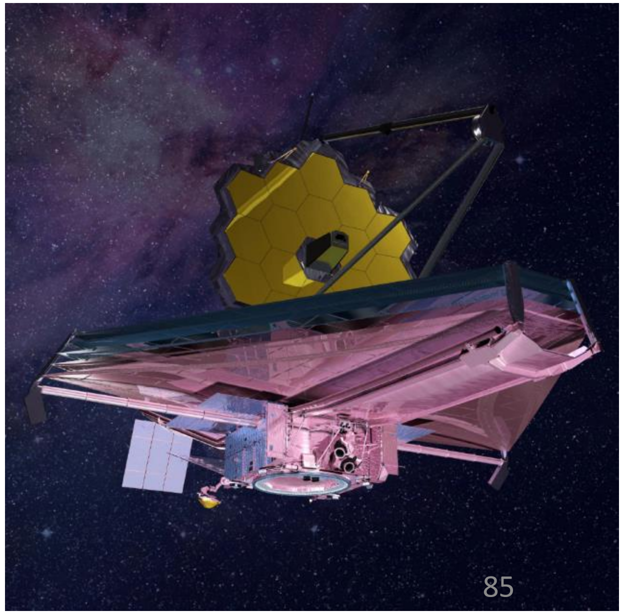


Model I: n_H = 10^4 cm^{-3}; Z=0.05; CR=1e^{-13}s^{-1}; FUV=1e^4 – Model II: n_H = 10^5 cm^{-3}; Z=0.05; CR=1e^{-14}s^{-1}; FUV=1e^3 – Model II: n_H = 10^5 cm^{-3}; Z=1; CR=1e^{-14}s^{-1}; FUV=1e^3

In summary

- It is clear that molecules play a key role in the formation and evolution of galaxies.
- Recent years have witnessed a boom of extragalactic molecular surveys which have brought detailed information about the amount and distribution of the molecular gas in different types of galaxies.
- Especially with ALMA, NOEMA, and JWST, the intermediate to high redshift Universe is/will be revealed in molecular emission at unprecedented spatial resolution.
- It is now possible to use molecular emissions from distant galaxies to explore the physical conditions in them and their likely evolutionary status, as we routinely now do for the Milky Way.

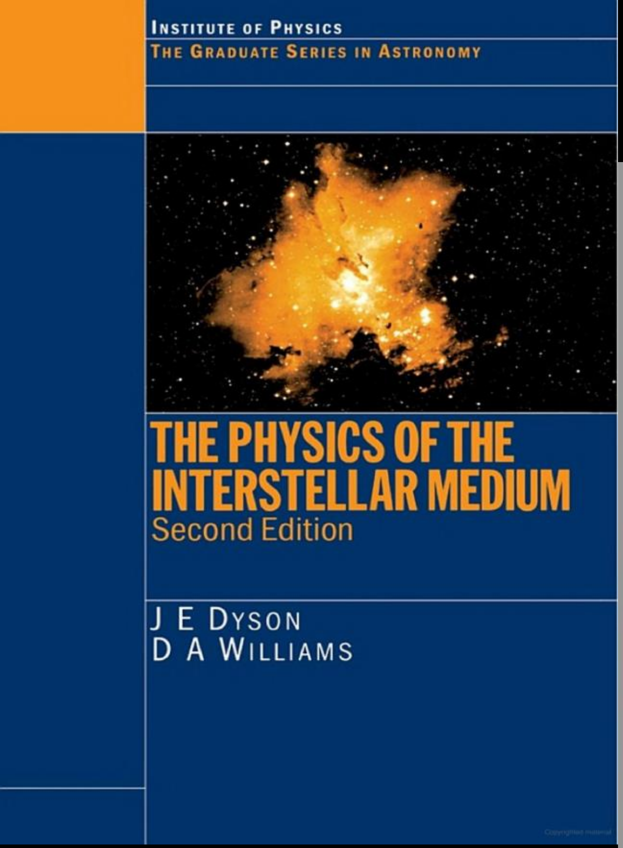


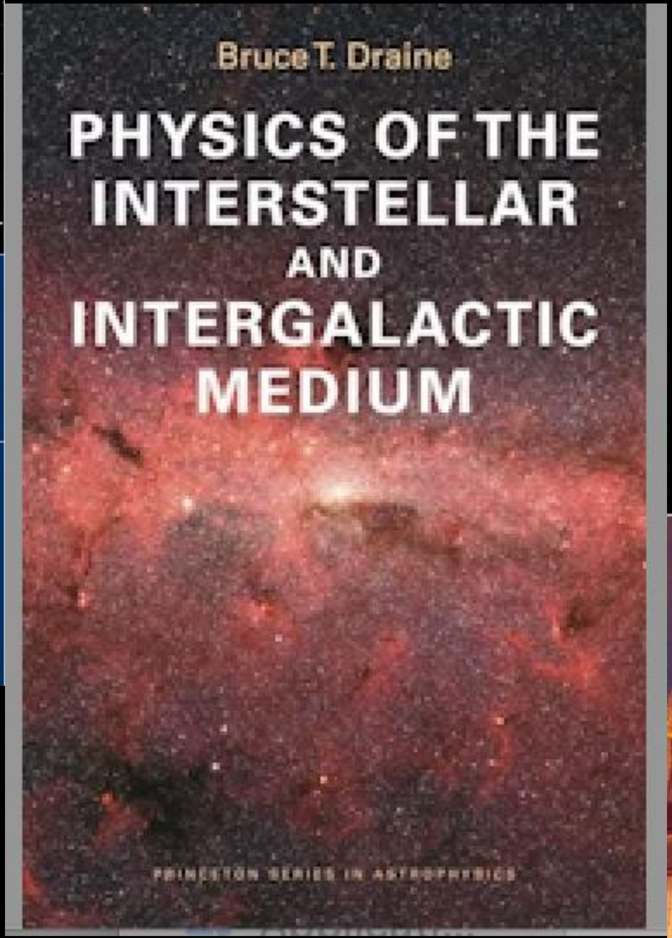


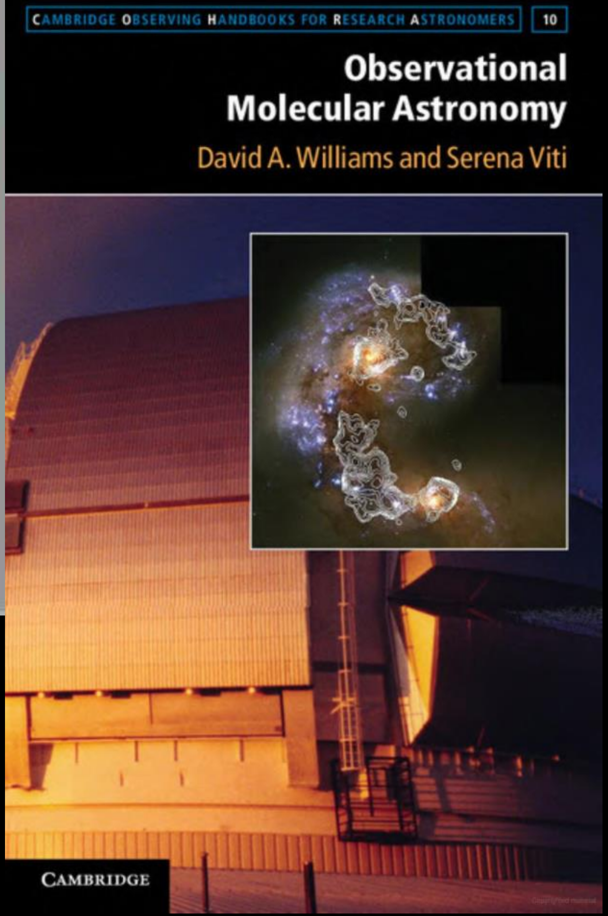
Concluding remarks

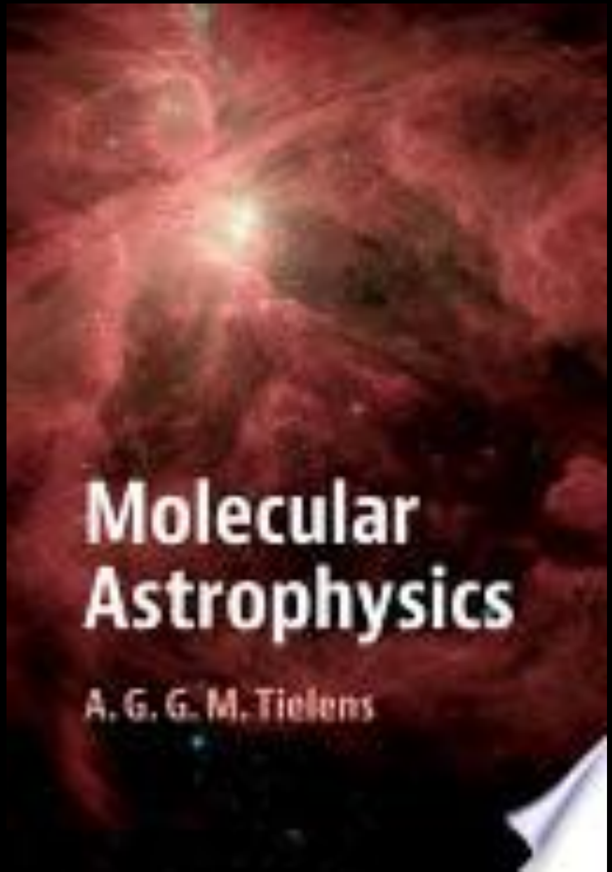
- Molecules are abundant everywhere as long as densities are high (> 1000 cm^{-3}) and temperature are low (< 500 K).
- Every molecule has a tale to tell → molecules are excellent tools of the dense gas in galaxies
- It is important to know the basics of the spectroscopy and chemistry in order to *robustly* interpret molecular spectra.
- In the Milky Way molecules have allowed us to study and characterize the million-year cycle of star formation, from clouds to planets.
- The interaction between the different processes ("drivers") associated to different gas is very complex → particularly important when interpreting extragalactic observations.
- There are challenges we face when observing external galaxies → (i) unresolved or only partially resolved observations (ii) very different physical conditions → can not use the Milky Way as a template blindly.

There are many books on the molecular universe









If time allows, we finish the course with a parenthesis on the use of isotopologues of the main molecules we have considered so far

Definitions:

- *Isotopes* are atoms with the same number of protons but different numbers of neutrons
- An *isotopologue* is a molecule where one of the atoms is replaced by its isotope.

- Many isotopologues, in which, for example, D replaces H, or ^{13}C replaces ^{12}C, or ^{17}O or ^{18}O replaces ^{16}O are found in the ISM.

- As examples, we shall look at deuterium, carbon, and nitrogen isotopologues in external galaxies and what their role is (both as a tools and in terms of chemistry)

Deuterium-bearing molecules

- Deuterium is present in the Milky Way Galaxy at an abundance, on average, of 1.4×10^{-5} relative to hydrogen.
- Deuterated molecules are important probes of the gas in embedded environments (where CO is depleted for example)
- Interestingly, in our own Galaxy at least, the ratio of deuterium-containing molecules to their hydrogen-containing version is often much higher!
- Two possible mechanisms: a) gas phase chemistry and ion–molecule deuterium exchange reactions taking place at low temperatures; b) grain chemistry
- In dark interstellar clouds, deuterium is largely locked in deuterium hydride, HD, by the reaction

$$D^+ + H_2 \rightarrow H^+ + HD$$

Formed by charge exchange with H+: $D + H^+ \rightarrow D^+ + H$

Reactions of HD with molecular ions containing hydrogen can exchange deuterium for hydrogen (note that D is slightly more strongly bound to X than H)

$$XH^+ + HD \rightarrow XD^+ + H$$

Although the potential well is the same for both XH+ and XD+, the ground vibrational level of the heavier isotope sits lower in the the potential well than that of the lighter isotope. The energy difference is ~few hundred degrees Kelvin → at temperatures below that level the reaction preferentially goes forward

However, at temperatures above that level the reaction can proceed easily forward and backwards, so fractionation is not enhanced → *high level of D trace cold gas!*

Several reactions can then happen that spread the deuterium e.g.

$$H_3^+ + D \rightarrow H_2D^+ + H$$

$$H_3^+ + HD \rightarrow H_2D^+ + H_2$$

- The latter is the most efficient reaction.
- H_2D^+ can be particularly enhanced when CO is highly depleted as CO is one of the major destroyer of H_2D^+ → *i.e could be an ideal tracer of CO-dark gas!*

HD can be observed in absorption towards quasars

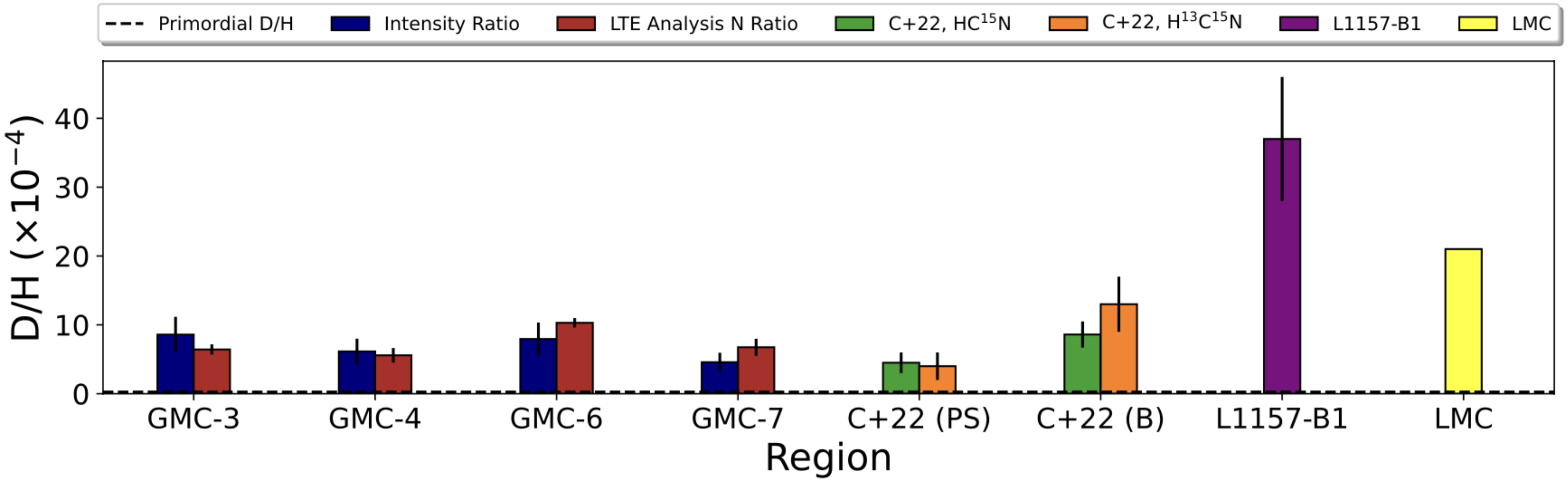
Table 3. Results from different experiments on D/H ratio determination.

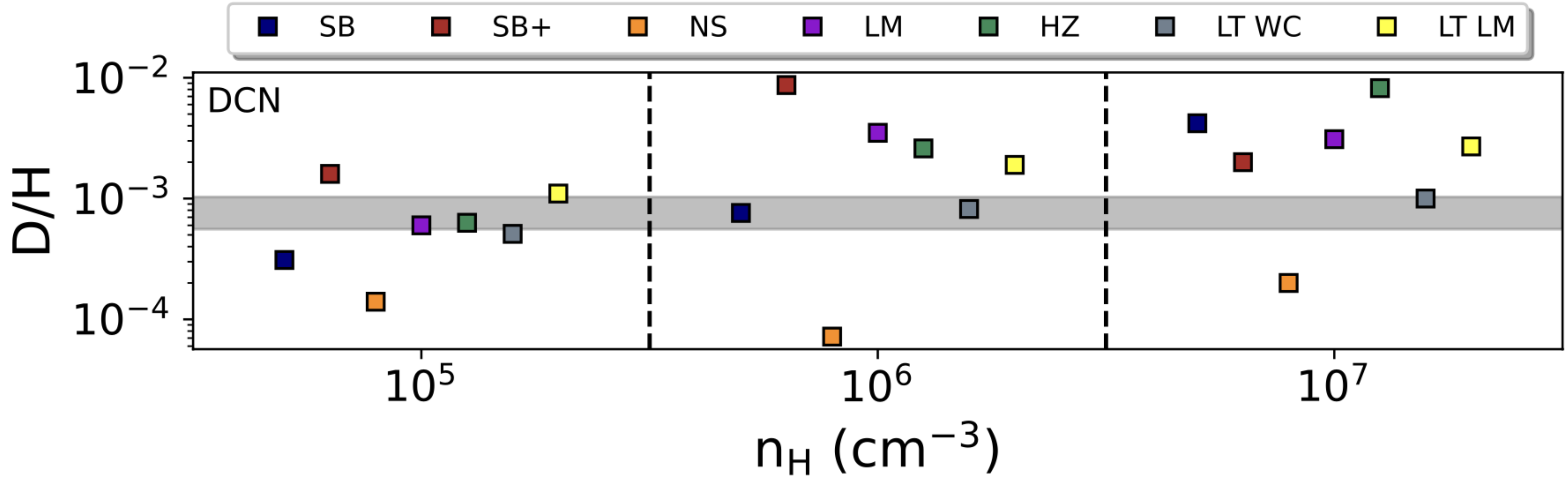
	Redshift	D/H	$\Omega_b h^2$	Reference[a]
Local Galactic disk	**0**	$>\mathbf{2.31 \times 10^{-5}}$		1
$HD/2H_2$	**0**	$>\mathbf{3.7 \times 10^{-7}}$ to $\mathbf{4.3 \times 10^{-6}}$		2
Q2206 − 199	2.08	$(1.65^{+0.35}_{-0.35}) \times 10^{-5}$		3
Q1009 + 2956[b]	2.50	$(3.98^{+0.59}_{-0.67}) \times 10^{-5}$		4
Q1243 + 3047[b]	2.53	$(2.42^{+0.35}_{-0.25}) \times 10^{-5}$		5
HS0105 + 1619[b]	2.54	$(2.54^{+0.23}_{-0.23}) \times 10^{-5}$		6
Q0913 + 072[b]	2.62	$(2.75^{+0.27}_{-0.24}) \times 10^{-5}$		7
SDSS 1558 − 0031[b]	2.70	$(3.31^{+0.49}_{-0.43}) \times 10^{-5}$		8
Q0347 − 3819	3.03	$(3.75^{+0.25}_{-0.25}) \times 10^{-5}$		9
Q1937 − 1009	3.26	$(1.60^{+0.25}_{-0.30}) \times 10^{-5}$		10
Q1937 − 1009[b]	3.57	$(3.30^{+0.30}_{-0.30}) \times 10^{-5}$		11
Average[b]	**2–3.6**	$\mathbf{(2.82 \pm 0.20) \times 10^{-5}}$	$\mathbf{0.0213 \pm 0.0010}$	7
CMBR	**1500**		$\mathbf{0.022\,67^{+0.000\,58}_{-0.000\,59}}$	12
$HD/2H_2$	**2.3377**	$\mathbf{(3.6^{+1.9}_{-1.1}) \times 10^{-5}}$	$\mathbf{0.0182^{+0.0047}_{-0.0042}}$	This paper

There are very few detections of deuterated species in external galaxies:

In **NGC 253** only recently a firm detection of a deuterated species has been published (Butterworth et al. 2024)

Region	DCN/HCN ($\times10^{-4}$)	DCO^+/HCO^+ ($\times10^{-4}$)	N_2D^+/N_2H^+ ($\times10^{-3}$)	T_{ex} (K)	FWHM (km s^{-1})	$^{12}C/^{13}C$
GMC-3	6.43 ± 0.74	(< 1.51)	(< 4.47)	50 ± 5	74	48 ± 4
GMC-4	5.58 ± 1.06	(< 0.8)	(< 2.51)	60 ± 7	74	57 ± 10
GMC-6	10.3 ± 0.1	(< 1.08)	(< 3.02)	98 ± 4	74	41 ± 2
GMC-7	6.75 ± 1.23	(< 5.49)	(< 4.17)	61 ± 11	79	44 ± 5





The models from Roueff et al. (2007) [LT models above] were run using more comparable temperatures (50-70 K) and as can be seen in Figure 5 the warm core model at a density of 106cm−3 and temperature of 70 K fits very well with our observations,

The Isotopologues of carbon

- Carbon is one of the most abundant and important elements in the Universe, and exists in the form of two stable isotopes, ^{12}C and ^{13}C.
- Its isotopic composition is believed to be a good indicator of nucleosynthesis in Galaxies: ^{12}C is synthesised rapidly via Helium burning in both low-mass and massive stars) while ^{13}C is synthesised through the CNO cycle in asymptotic giant branch (AGB) stars through slower processes → the ratio is on average ~ 69 (in our own galaxy)
- *ISM fractionation: Various chemical mechanisms may introduce deviations from the carbon isotopic elemental ratio*

$$^{13}C^+ + CO \rightleftharpoons {}^{12}C^+ + {}^{13}CO$$

$$^{13}CO + HCO^+ \rightleftharpoons CO + H^{13}CO^+$$

$$^{13}C^+ + CN \rightleftharpoons {}^{12}C^+ + {}^{13}CN$$

$$^{13}C + CN \rightleftharpoons {}^{12}C + {}^{13}CN$$

$$^{13}C + HCN \rightleftharpoons {}^{12}C + H^{13}CN$$

$$^{13}C + C_2 \rightleftharpoons {}^{12}C + {}^{13}CC$$

$$^{13}CH + CO \rightleftharpoons {}^{13}CO + CH$$

Galaxy	type	$^{12}C/^{13}C$	Molecule
NGC 253	starburst	~ 40; 30 – 67	CN
NGC 253	starburst	~ 27 – 70	CS
M82	starburst	> 40	CN
NGC 253	starburst nucleus	~ 21	$C^{18}O^{a}$
NGC 4945	starburst nucleus	6–44	CN
	starburst	~ 10 – 70	
VV 114	LIRG	~ 230	CO
NGC 1614	LIRG	~ 130	CO
Mrk 231	ULIRG	~ 100	CO, CN
Arp 220	ULIRG	~ 100	CO
Arp 193	ULIRG	~ 150	CO
Cloverleaf	ULIRG $z = 2.5$	100 – 200	CO
Eyelash	ULIRG $z = 2.3$	~ 100	CO
	LIRG/ULIRG	~ 100 – 230	
LMC	0.5 metal	~ 49	H_2CO
NGC 1068	AGN+starburst	~ 50 ;24–62	CN
NGC 4258	AGN	~ 46	HCO^+
NGC 3690	AGN+starburst	~ 40	HCO^+
NGC 6240	AGN+starburst	~ 41	HCN
NGC 6240	AGN+starburst	300 – 500	CO
	AGN/composite	~ 20 – 60 (except NGC 6240 in CO)	
IC 342	spiral local	> 30	CN
MA0.89	spiral $z = 0.89$	~ 27	HCN, HCO^+, HNC
MA0.68	spiral $z = 0.68$	~ 40	HCN, HCO^+, HNC
	spiral	~ 30 – 40	

Isotopologoues of nitrogen

- Nitrogen is the fifth most abundant element in the Universe that can exist in the form of two stable isotopes, ^{14}N and ^{15}N
- In star-forming regions, there is a large spread in the measured $^{14}N/^{15}N$ ratio, ranging from $\sim$100 for meteorites, comets, and protoplanetary discs to $\sim$1000 in pre-stellar and star-forming cores.
- While both are thought to be actively produced in the CNO cycles of massive stars and in asymptotic giant branch (AGB) stars, differences in their nucleosynthesis is needed to explain their observational behaviour
- *As for carbon, various chemical mechanisms may introduce deviations from the carbon isotopic elemental ratio (~440), including ISM fractionation*

$N^{15}N + N_2H^+$	$\rightleftharpoons$	$N^{15}NH^+ + N_2$
$N^{15}N + N_2H^+$	$\rightleftharpoons$	$^{15}NNH^+ + N_2$
$N^{15}N + {}^{15}NNH^+$	$\rightleftharpoons$	$N^{15}NH^+ + N^{15}N$
$^{15}N^+ + N_2$	$\rightleftharpoons$	$^{14}N^+ + N^{15}N$
$^{15}N + CNC^+$	$\rightleftharpoons$	$C^{15}NC^+ + {}^{14}N$
$^{15}N^+ + {}^{14}NO$	$\rightleftharpoons$	$^{14}N^+ + {}^{15}NO$
$^{15}N + N_2H^+$	$\rightleftharpoons$	$^{14}N + N^{15}NH^+$
$^{15}N + N_2H^+$	$\rightleftharpoons$	$^{14}N + {}^{15}NNH^+$
$^{15}NNH^+ + H$	$\rightleftharpoons$	$H + N^{15}NH^+$
$^{15}N + HCNH^+$	$\rightleftharpoons$	$^{14}N + HC^{15}NH^+$
$^{15}N + CN$	$\rightleftharpoons$	$^{14}N + C^{15}N$
$^{15}N + C_2N$	$\rightleftharpoons$	$^{14}N + C_2{}^{15}N$
$^{15}N + {}^{14}NO$	$\rightleftharpoons$	$^{14}N + {}^{15}NO$

Observed ratios in external galaxies

Galaxy	Type	$^{14}N/^{15}N$	Molecule
NGC 4945	Starburst	200–500	HCN
LMC	0.5 metal	111(±17)	HCN
Arp 220	ULIRG	440 (+140, −82)	HCN, HNC
NGC 1068	AGN + starburst	>419	HCN
IC 694	Starburst	200–400(?)	HCN
LMC	0.5 metal	91(±21)	HCN
M82	Starburst	>100	HCN
Galactic Centre	Standard with high ζ	≥164	HNC

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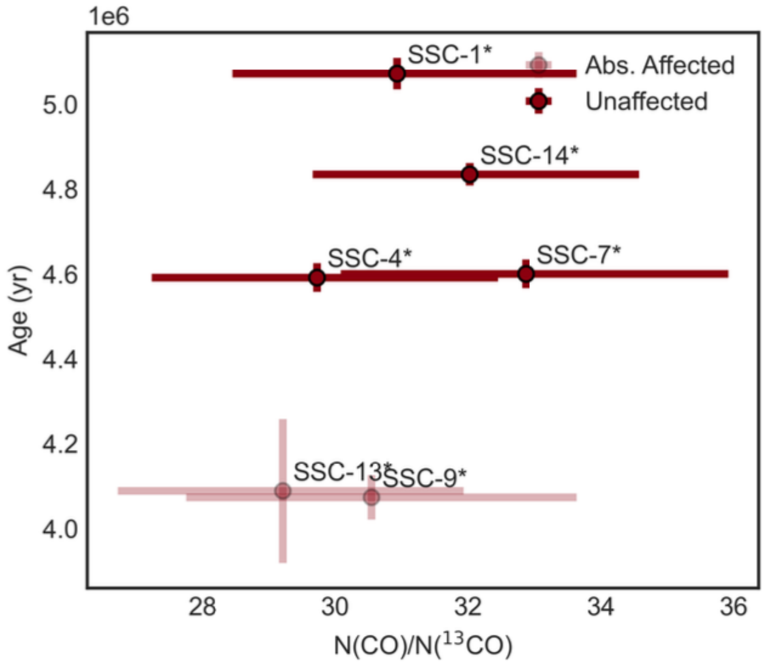
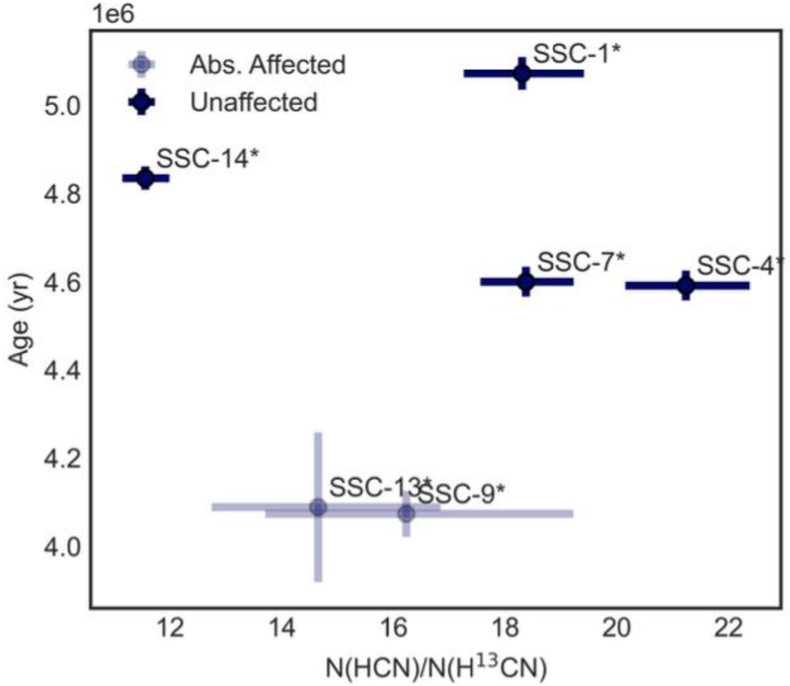
In general, isotopologues are observed because they give us clues about the nucleosynthesis process as well as being good indicators of "age" – Nuclear regions of starburst galaxies undergo heavy processing of matter → ideal targets to investigate elemental and isotopic abundances.

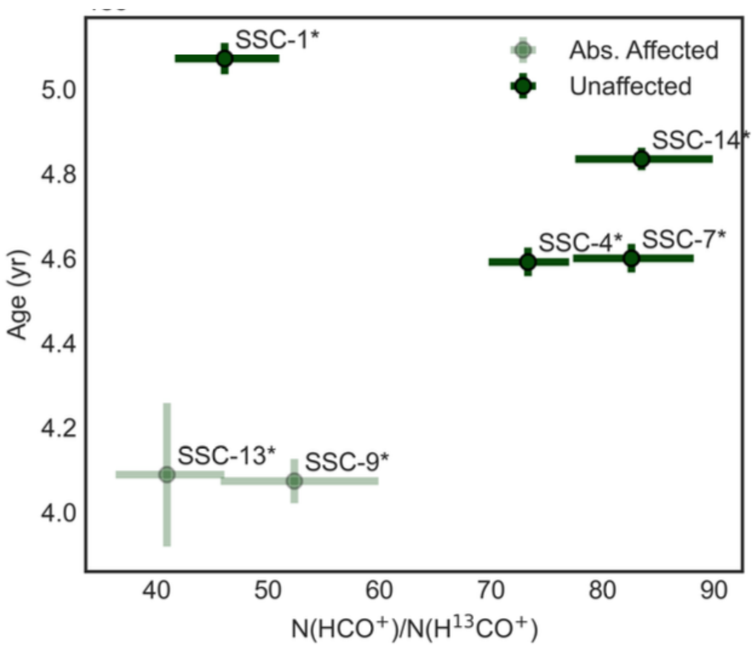
In NGC 253: no correlation found

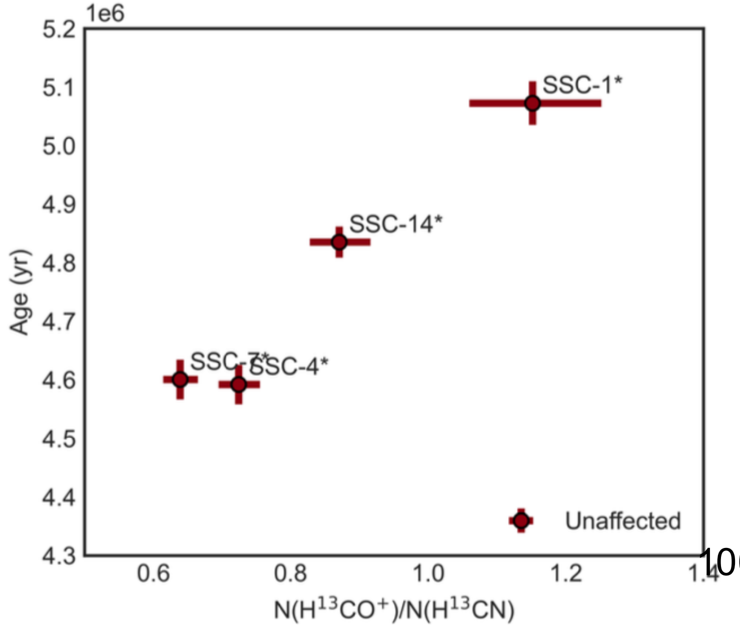


No correlation!

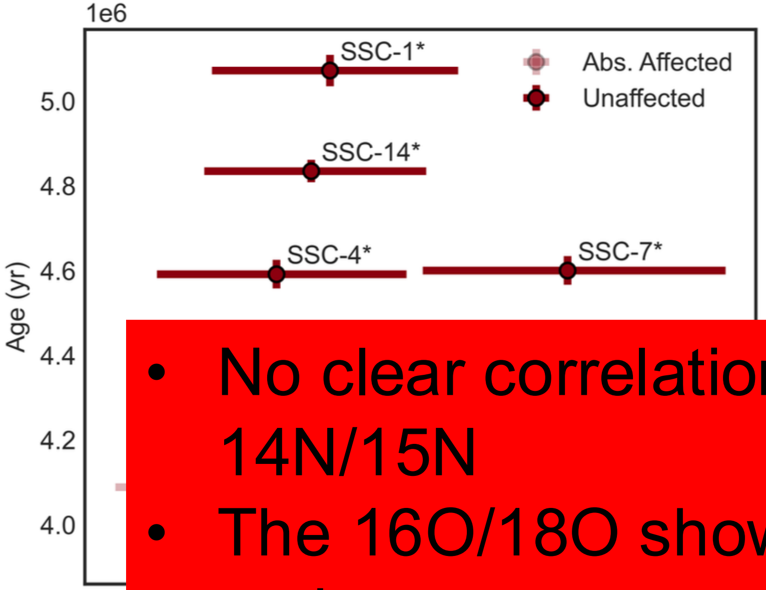


Positive correlation

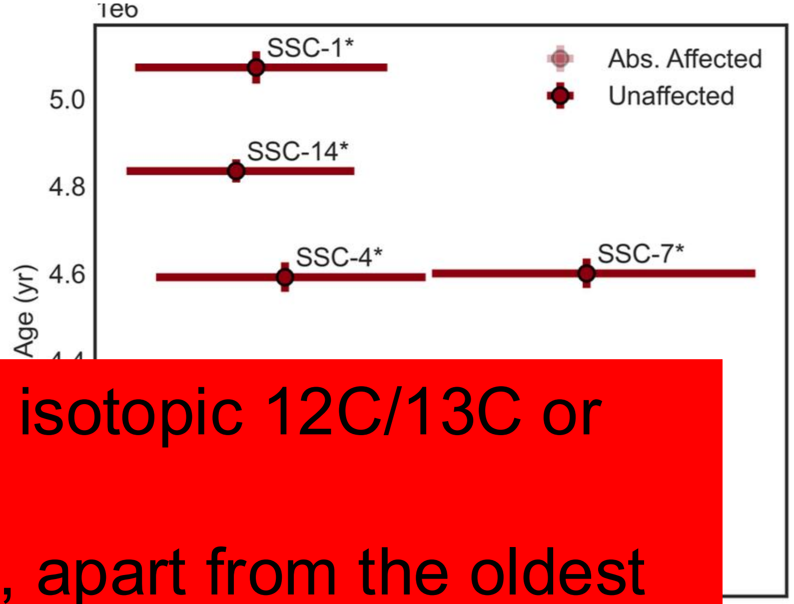




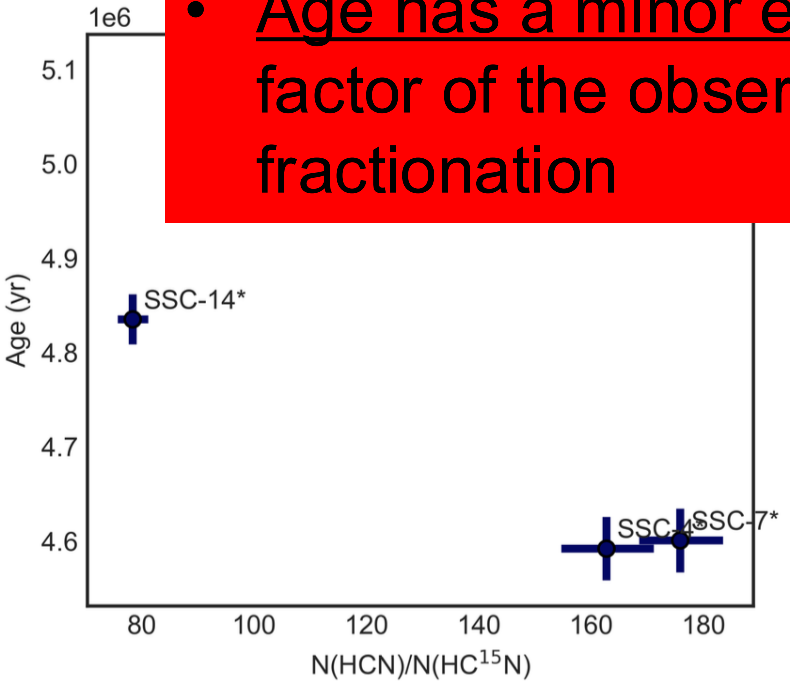
Butterworth et al. (2024)

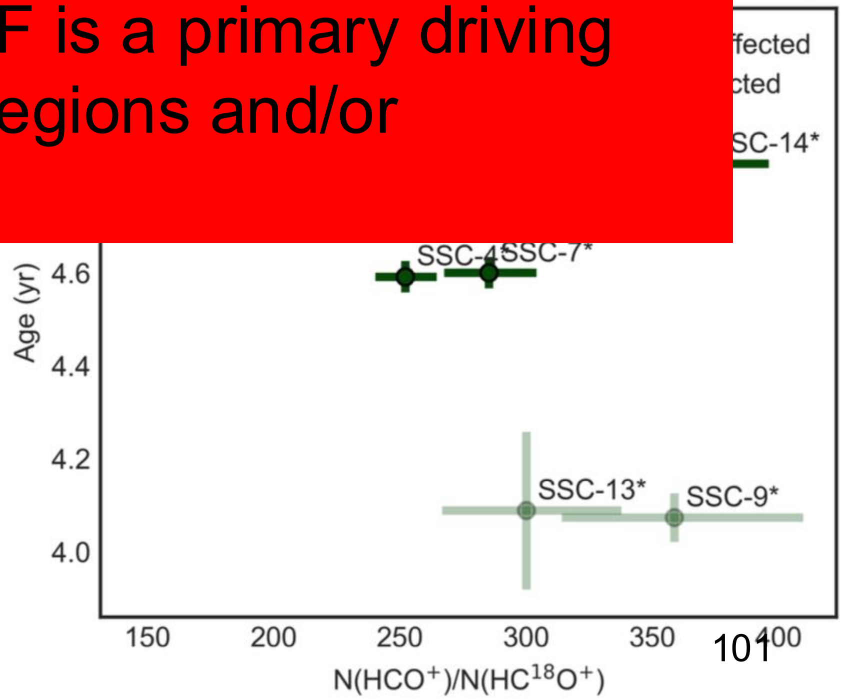


No correlation



- No clear correlation between ages of stars and isotopic 12C/13C or 14N/15N
- The 16O/18O shows little correlation with ages, apart from the oldest regions.
- Age has a minor effect on isotopic ratios → IMF is a primary driving factor of the observed isotopic ratios in these regions and/or fractionation





No correlation (but note oldest SSC)

Observed ratios in external galaxies

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In general, isotopologues are observed because they give us clues about the nucleosynthesis process as well as being good indicators of "age" – Nuclear regions of starburst galaxies undergo heavy processing of matter → ideal targets to investigate elemental and isotopic abundances.

But there is another reason why it is important to observe isotopologues…

The power of isotopologues: determination of the optical depth

- Abundant molecules can be optically thick → this means that when you derive the column density you do not have a measure of the *true* amount of that molecule
- On the other hand, the less abundant isotopologues of a molecule will tend to be more optically thin.
- Hence – *provided the abundance ratio between the more abundant and less abundant isotopologue is known* – one can use the *less* abundant line to constrain the optical depth of the *more* abundant line.

E.g.:

- The widely used tracer of molecular hydrogen, CO, is so abundant that, in the cold dark clouds in which stars are forming, it has a large optical depth and thus cannot trace the densest material (at least for the low J transitions)
- Very rare CO isotopologues are therefore used, and in order of decreasing abundance these are ^{13}CO, $C^{18}O$, $C^{17}O$, $^{13}C^{18}O$ and $^{13}C^{17}O$,
- By using several different isotopologues of CO, the optical depths could be cross-checked and the *true* column densities measured.