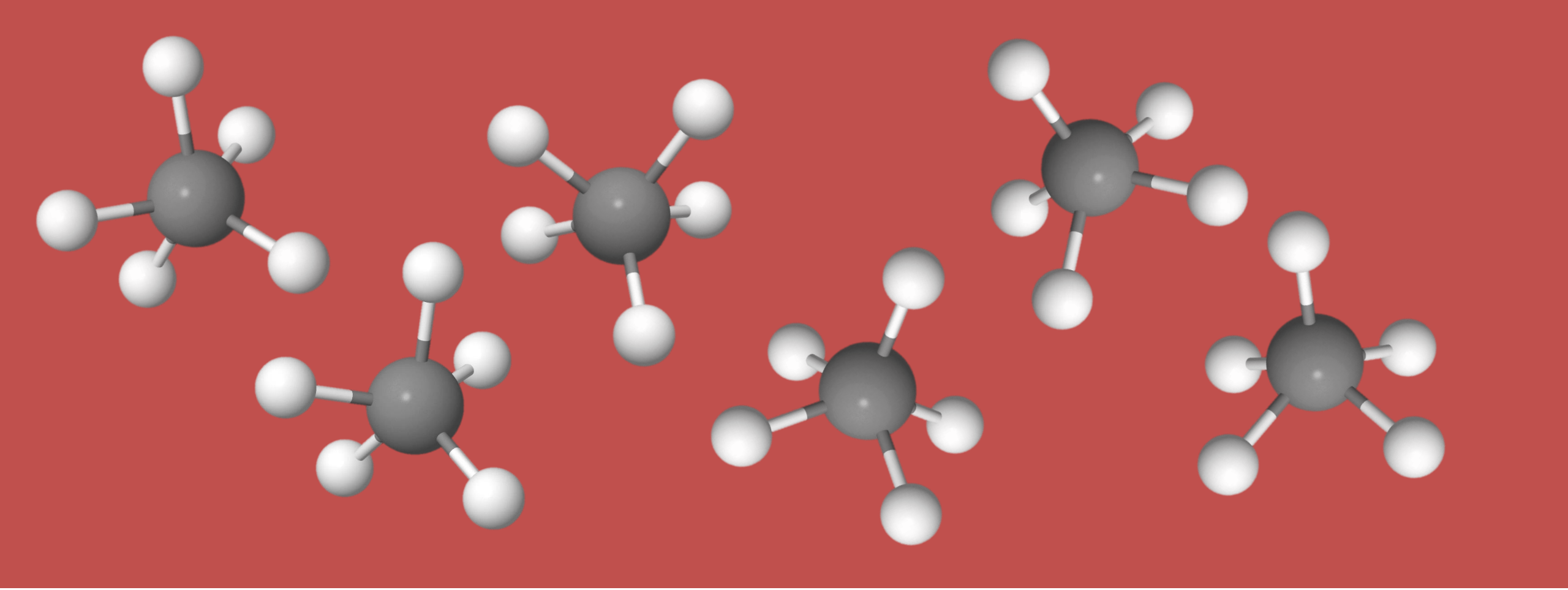


DIFFUSION MONTE CARLO

ROLLING THE DICE BUT THE DICE ARE MOLECULES

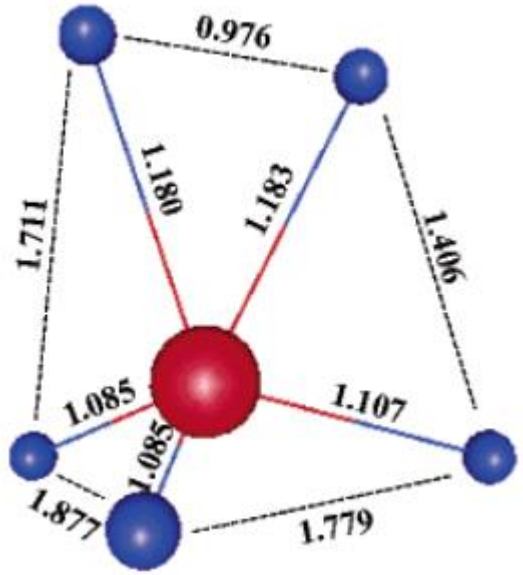
Meredith Fore
Physics PhD student @UW

CARBON WITH FIVE HYDROGEN ATOMS?

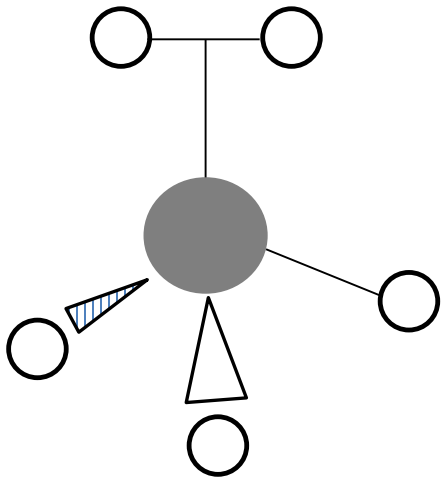
It can exist!

An H_2 bound to a CH_3^+

But that H_2 is not the same two hydrogen atoms all the time…
can we even say it has a structure?



Minimum energy configuration
McCoy et al., J. Phys. Chem. A, 2004.



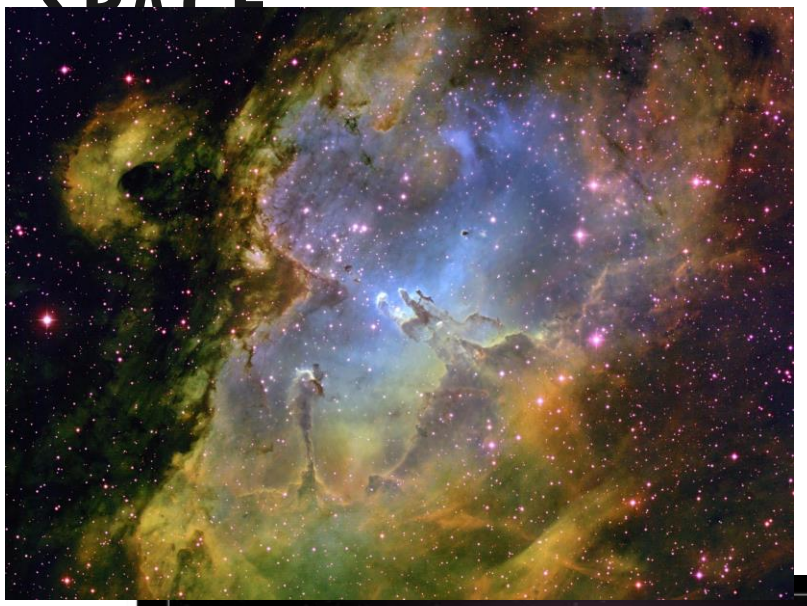
ASTROCHEMISTRY: CHEMICALS IN SPACE

Is the space between stars really empty?

What are stars/nebulae made of?

Do exoplanets have water/atmospheres?

Can we detect life on other planets?



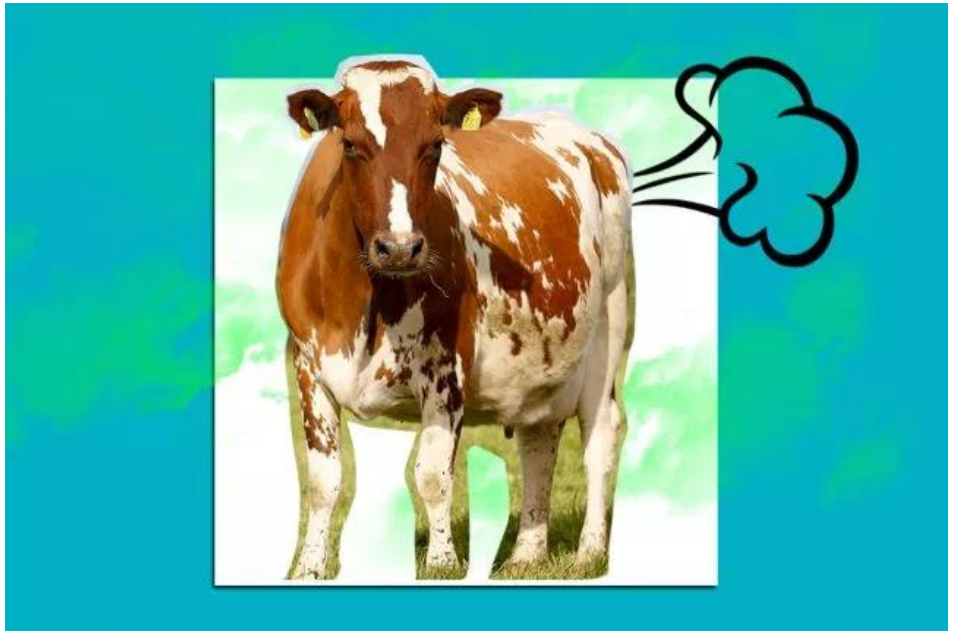
ASTROCHEMISTRY: CHEMICALS IN SPACE

Scientists Detect Abundant Methane in Space

By **Thomas O'Toole**
July 4, 1978

Methane, the major constituent of natural gas and a prominent product of biologic decay, has been a found to be even more abundant in distant space than on earth.

-Washington Post, 1978



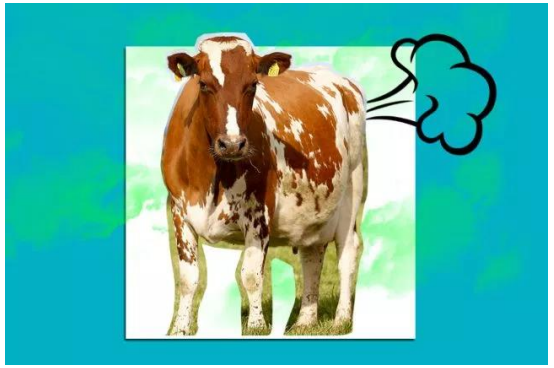
CH_4

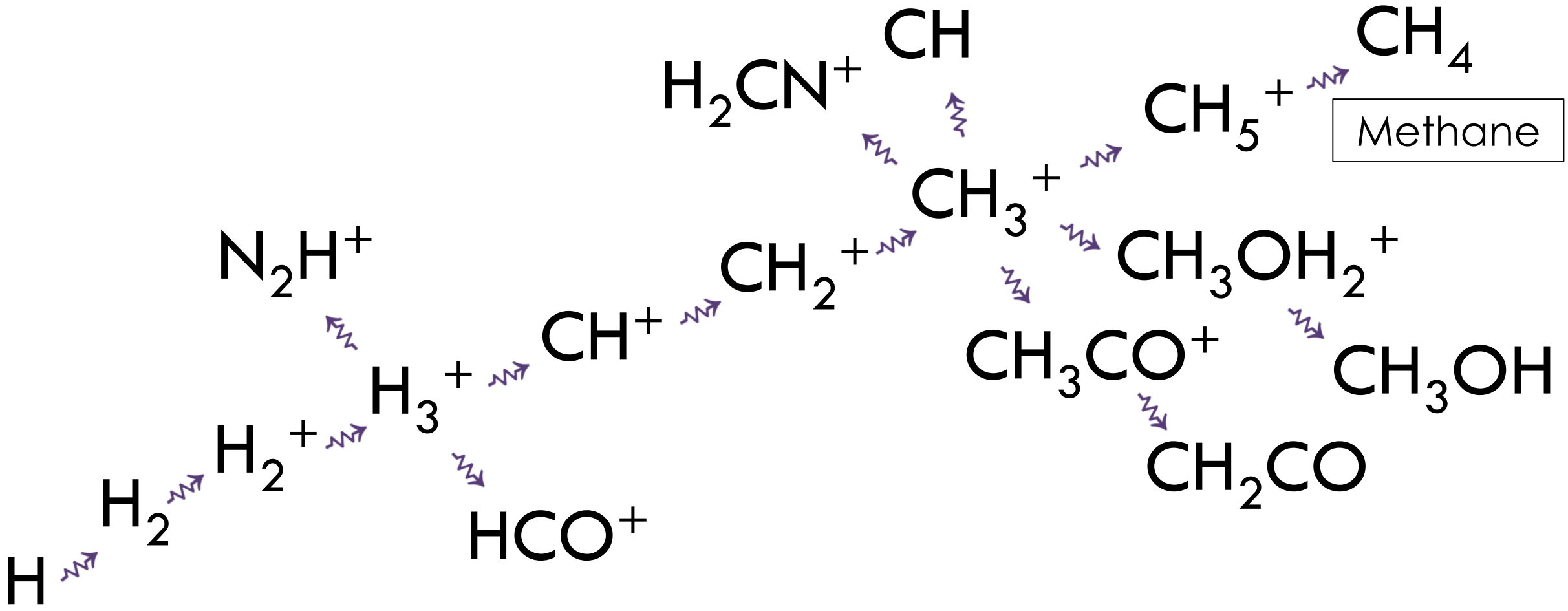
Methane

One of the "building blocks" of life

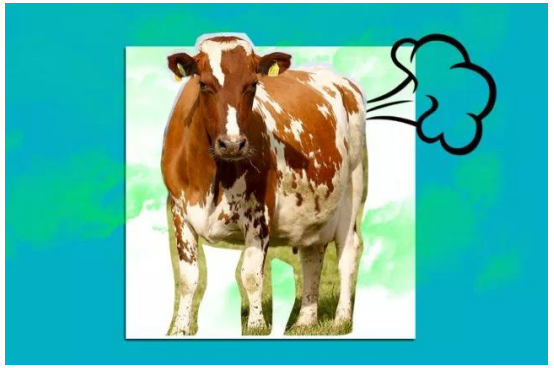
How did it get there?

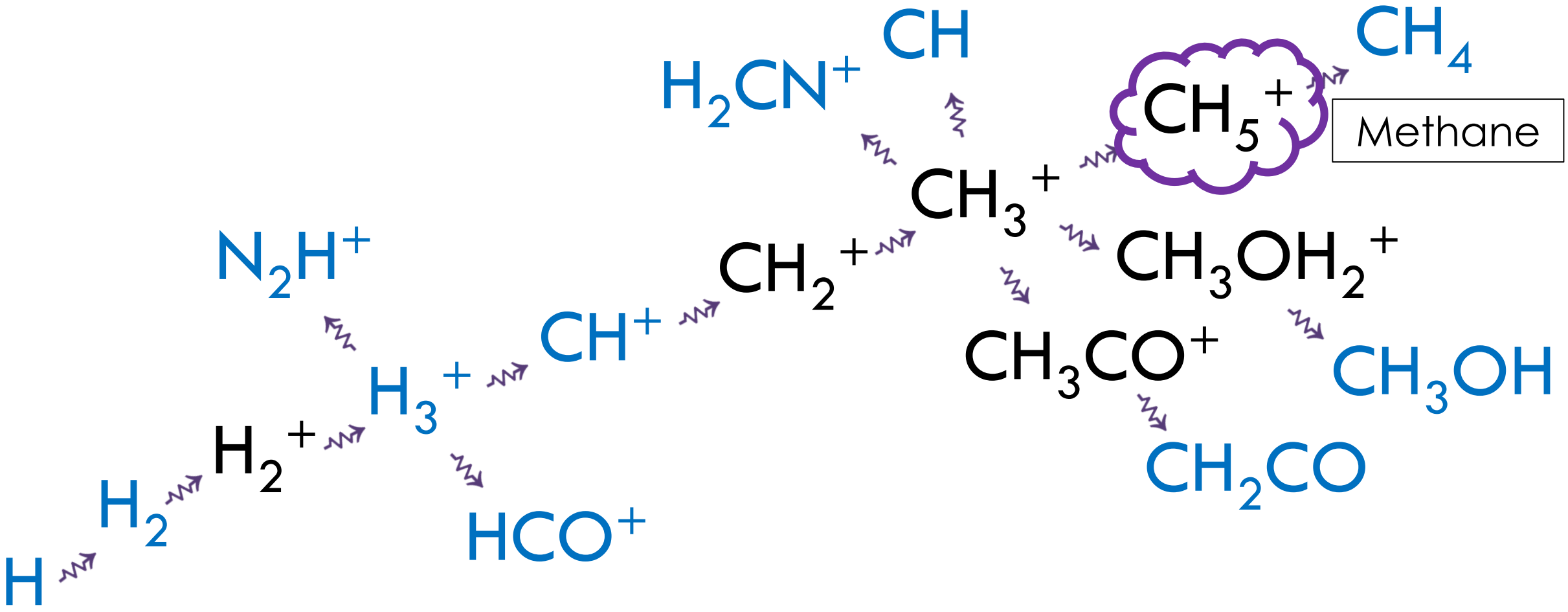
ASTROCHEMISTRY: CHEMICALS IN SPACE





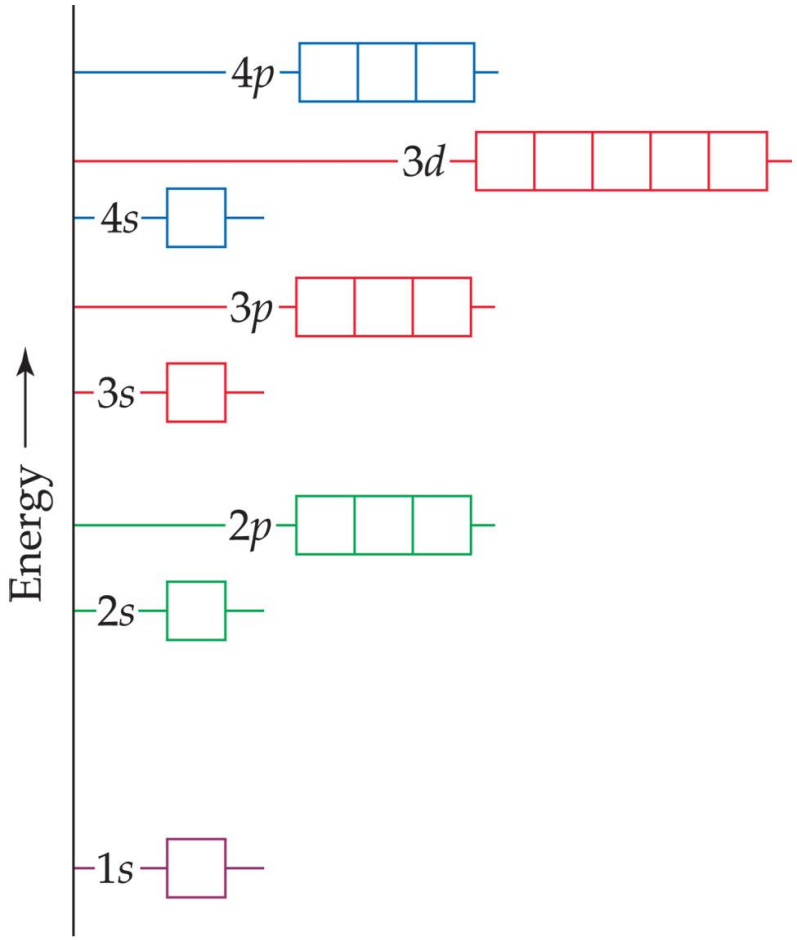
ASTROCHEMISTRY: CHEMICALS IN SPACE





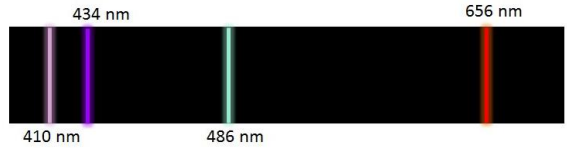
"quantized" = quantum mechanics!

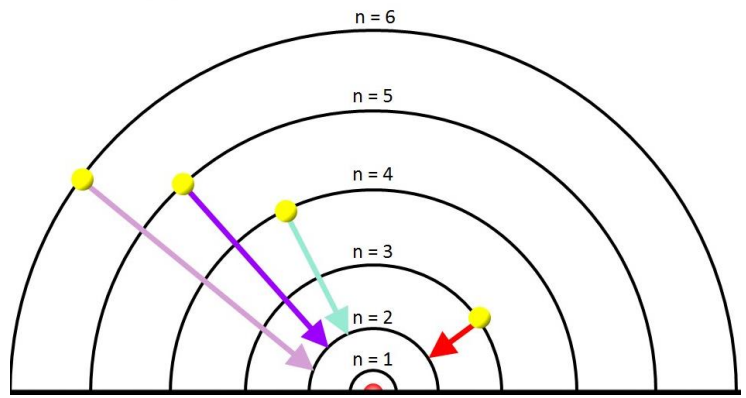
ELECTRONIC ENERGY



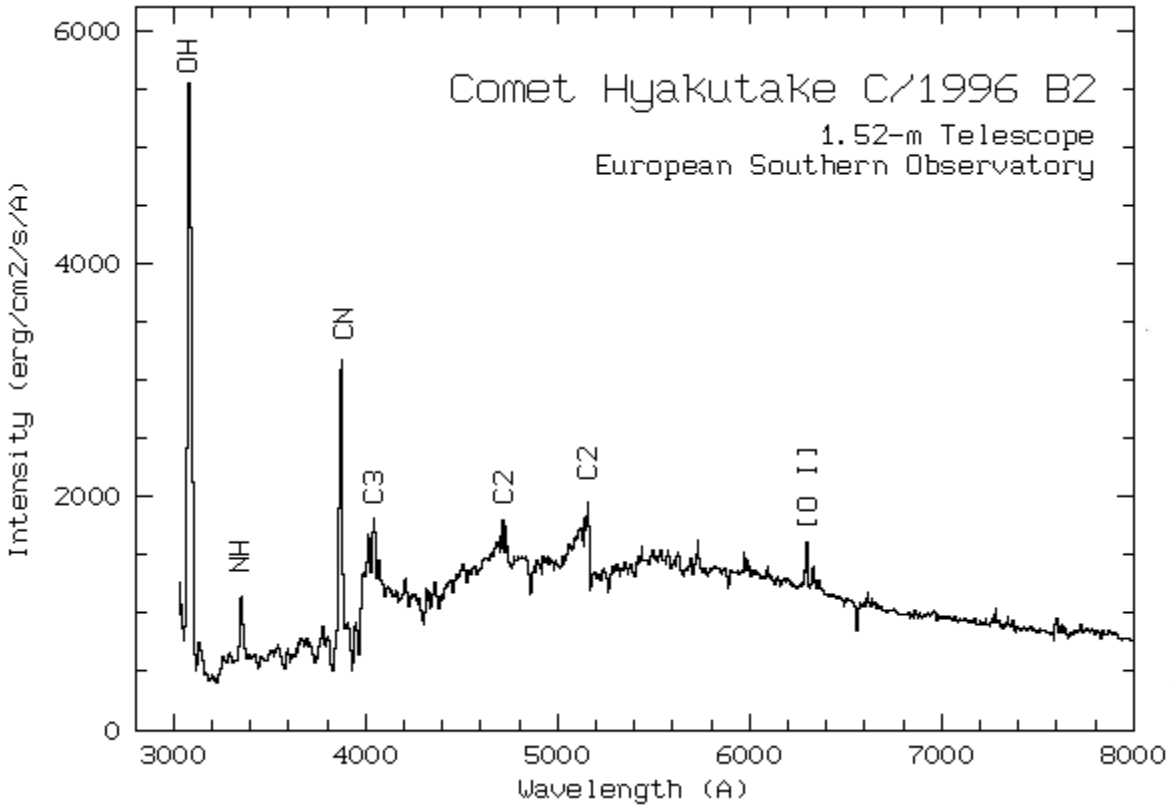
- Atoms/molecules are only allowed to have certain energies
- So they can only absorb or emit light (photons) of certain energies
- Electron(s) can absorb or emit the energy to change orbitals

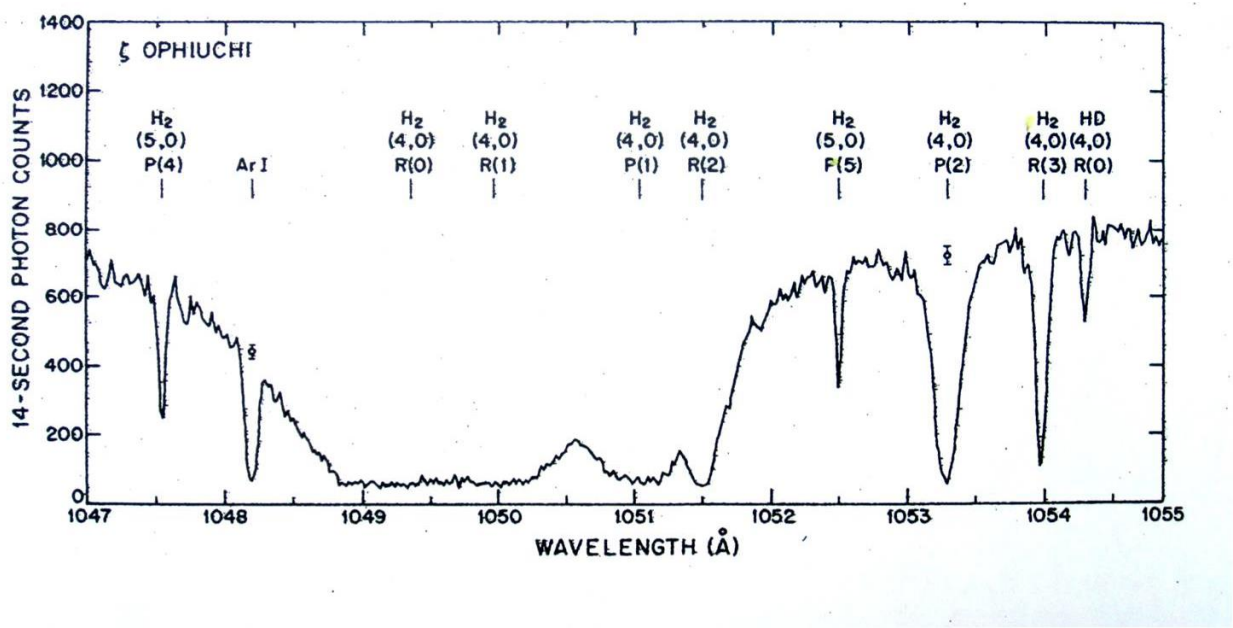
This pattern of energies is a **unique fingerprint**





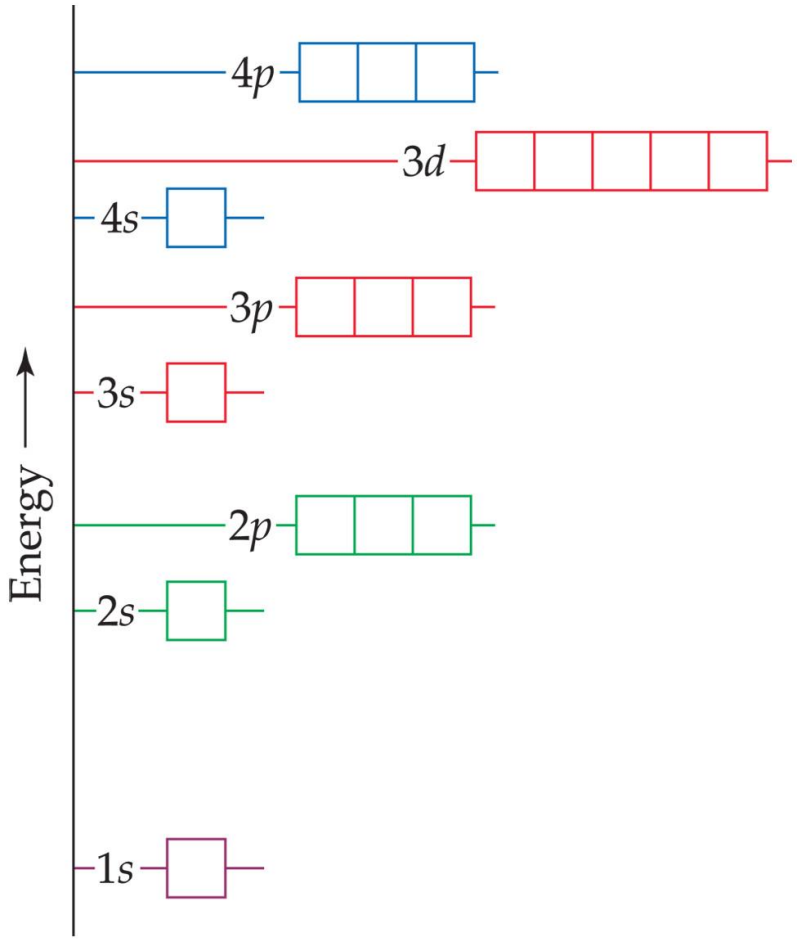
RECOGNIZE CHEMICALS IN SPACE!





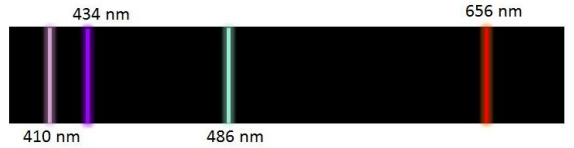
"quantized" = quantum mechanics!

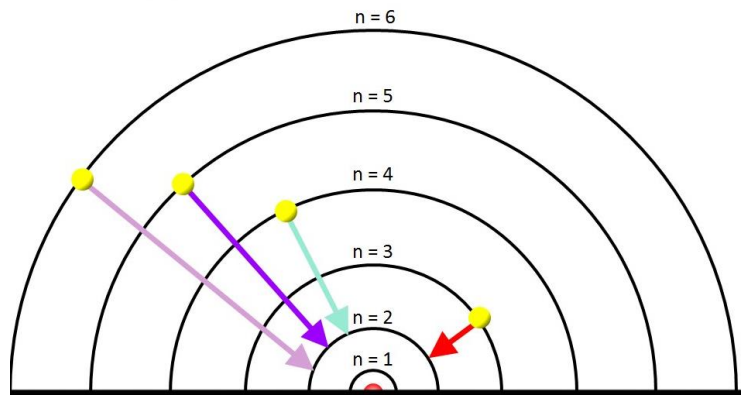
ELECTRONIC ENERGY



- Atoms/molecules are only allowed to have certain energies
- So they can only absorb or emit light (photons) of certain energies
- Electron(s) can absorb or emit the energy to change orbitals

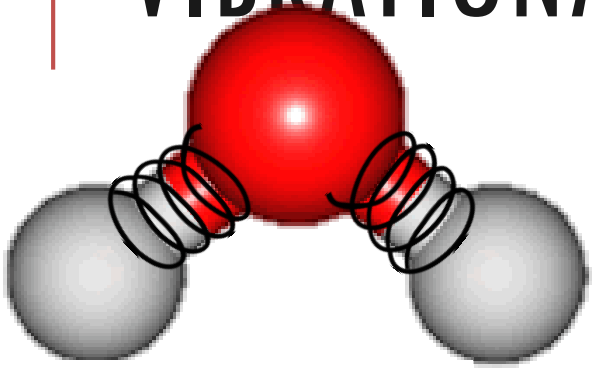
This pattern of energies is a **unique fingerprint**

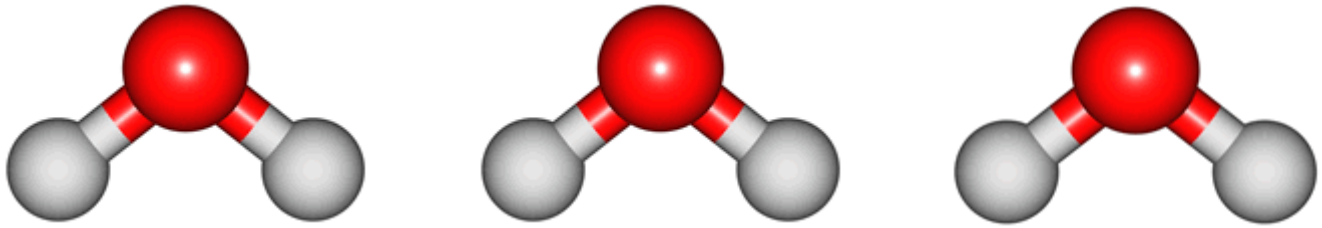




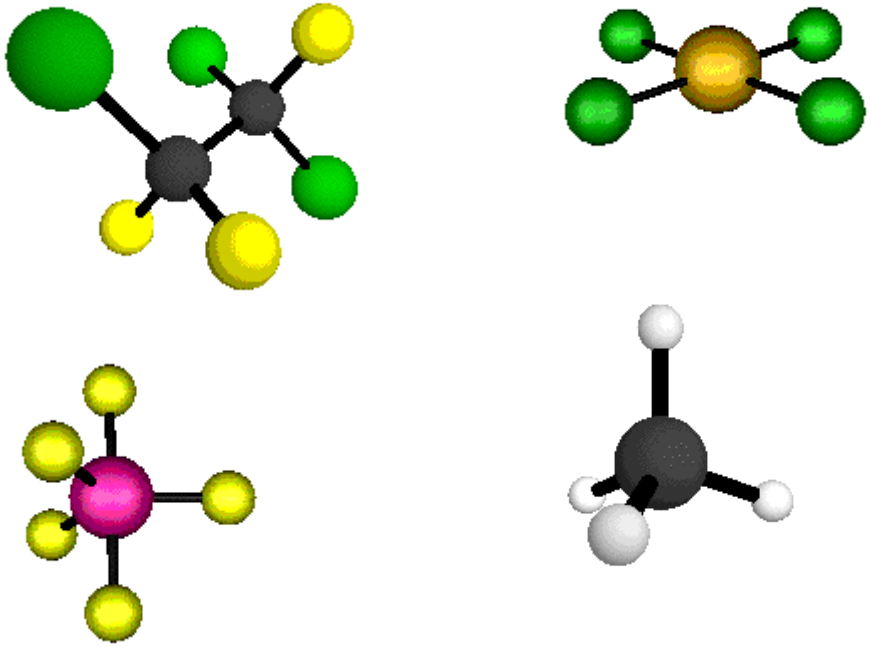
VIBRATIONAL ENERGY

also quantized!





This also gives us a unique fingerprint of energies



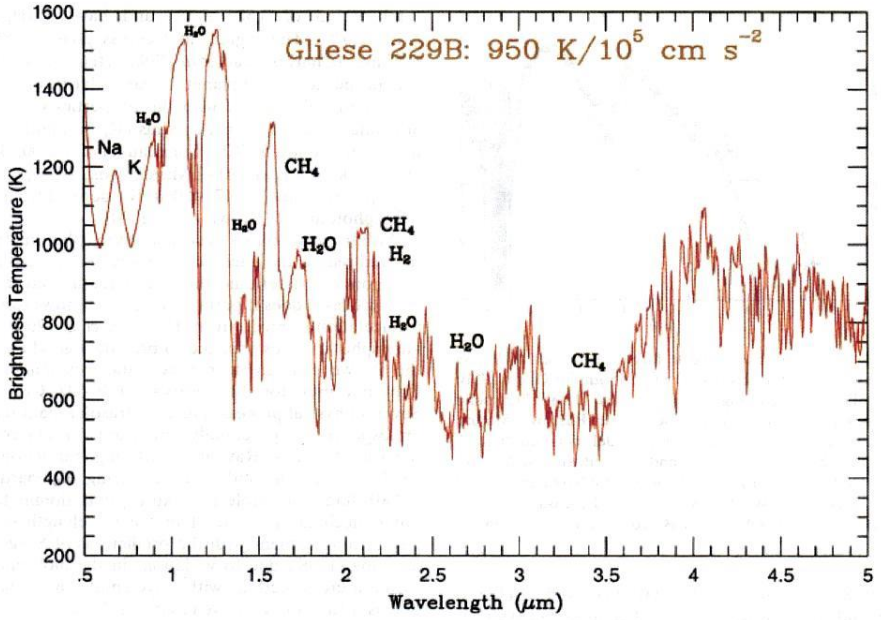
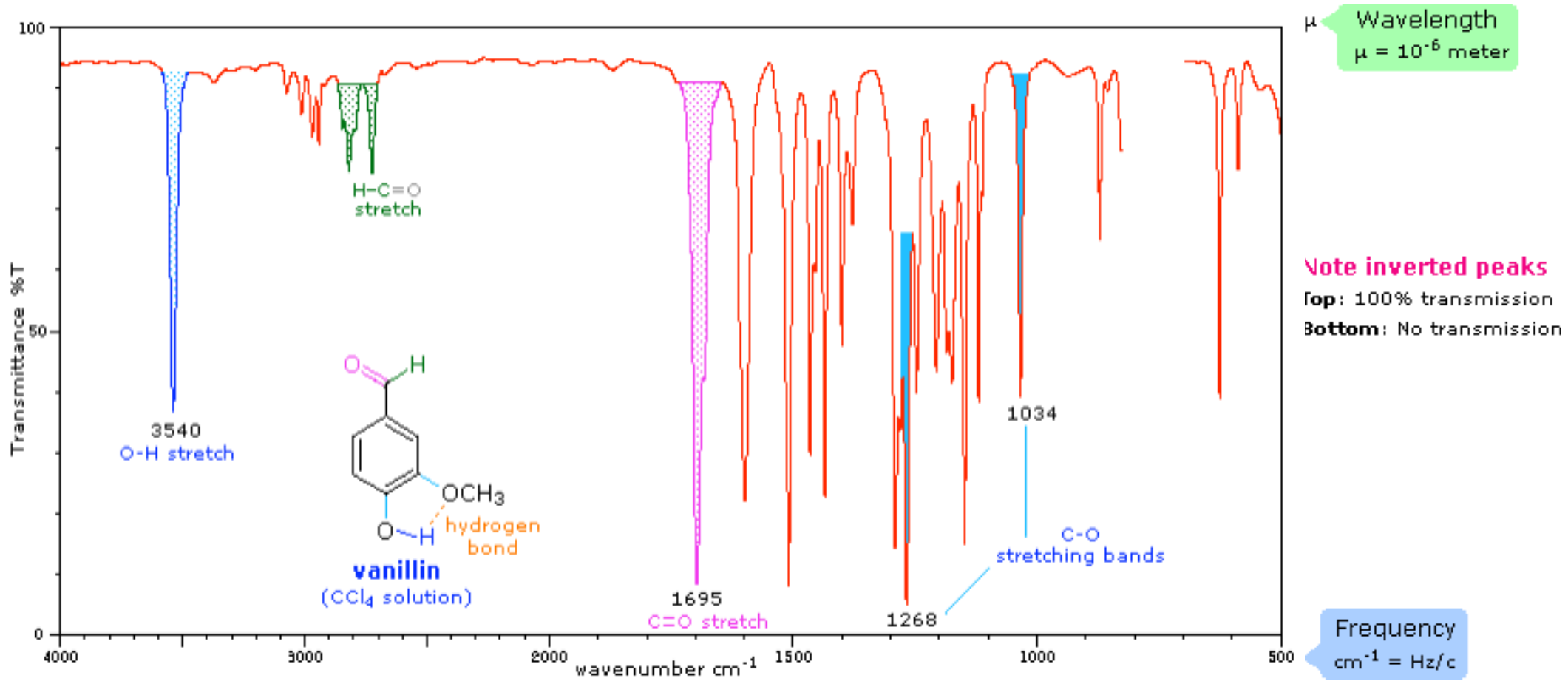
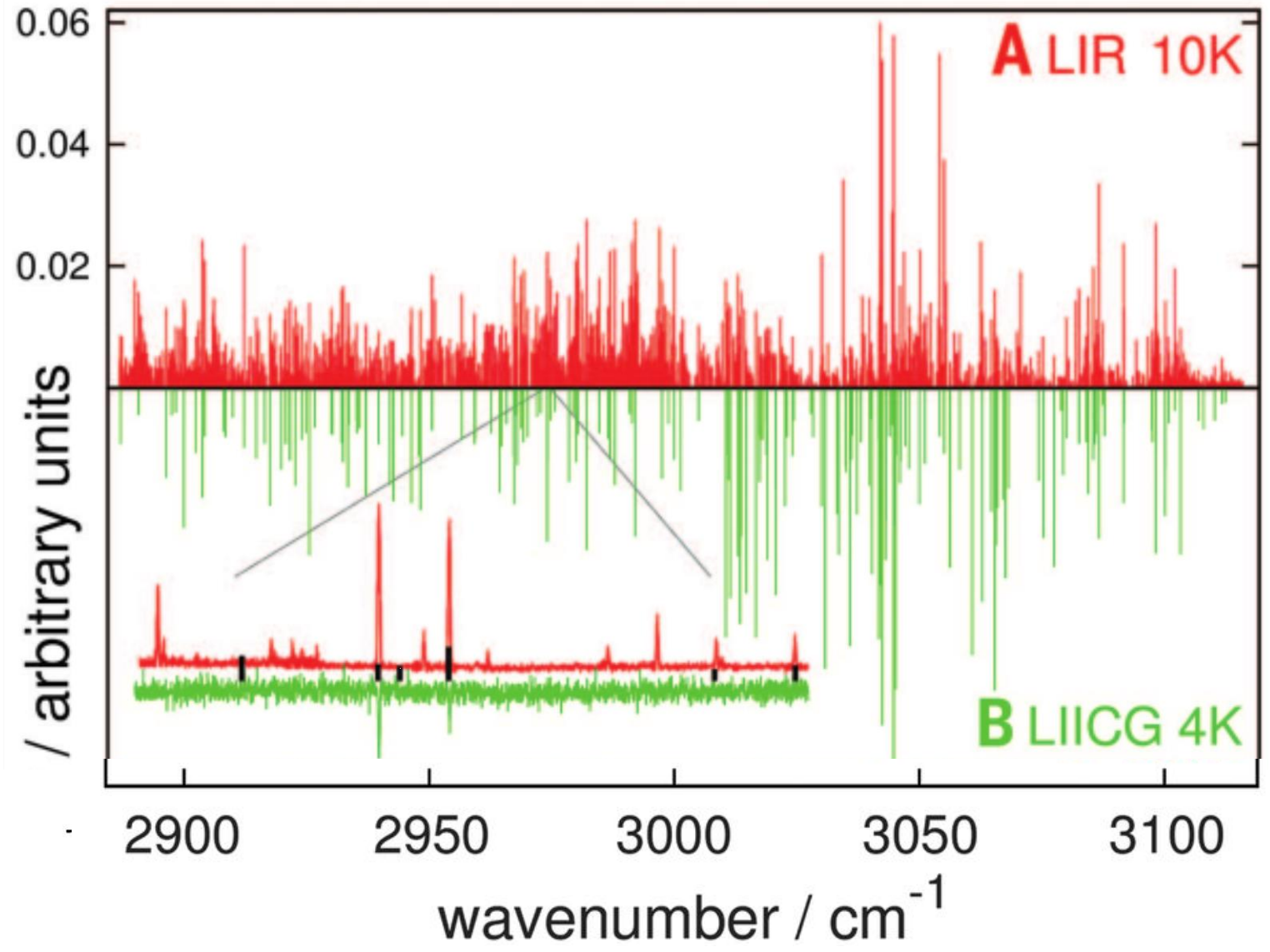


FIG. 28. The "brightness" temperature (in K) vs wavelength (in microns) from 0.5 to 5.0 μm for a representative model of Gliese

VIBRATIONAL ENERGY





Asvany, Yamada, Brunken, Potapov, Schlemmer, *Science* (2015)

2897 lines

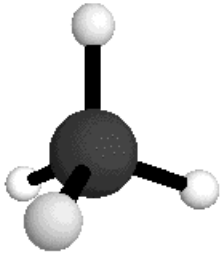
"enfant terrible"

It isn't enough to have this spectrum; we must understand it

White, Tang and Oka, *Science* (1999)

CH_5^+ : WEIRD AND WIGGLY

*Based on the surfaces of A. Brown, J. Zhong, B. J. Braams and J. M. Bowman



Molecule can access all 120 permutations of five hydrogen atoms in its ground state.

No well-defined structure!

What if we had a theoretical tool that didn't need one?

MONTE CARLO

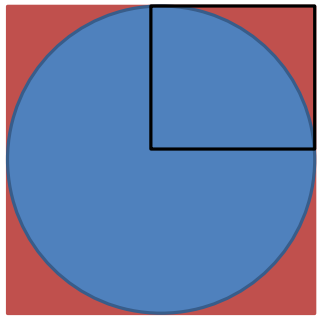
Monte Carlo refers to a class of computational algorithms that use random sampling to achieve numerical results

To implement Monte Carlo, you will need:

1. A range or domain from which to pull sample points (optional: a probability distribution within that domain)
2. A deterministic calculation to perform on your points
3. To collect all of your results

MONTE CARLO

$$A_C = \pi r^2$$
$$A_S = 4r^2$$
$$\pi = 4\,\frac{A_C}{A_S}$$



What is my domain?

[0,1] in x and y.

What is my deterministic calculation?

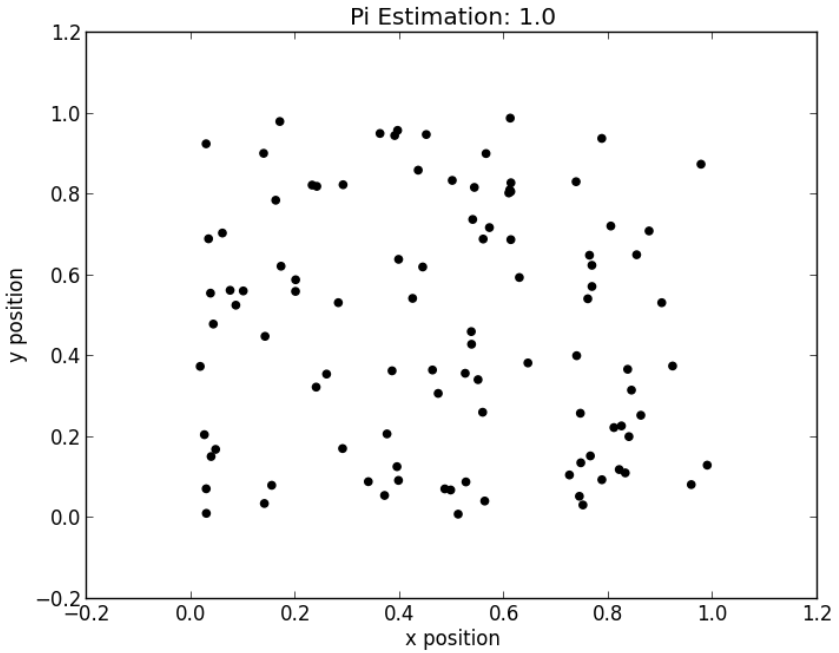
Whether my point is in the area of the circle or not.

Mathematically:

$$x^2 + y^2 > 1$$
$$x^2 + y^2 < 1$$

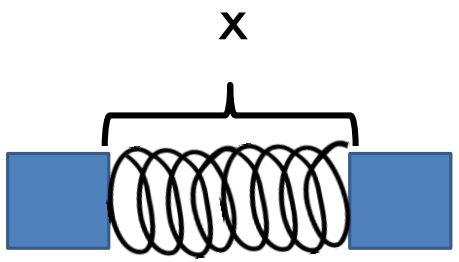
Collect my results:

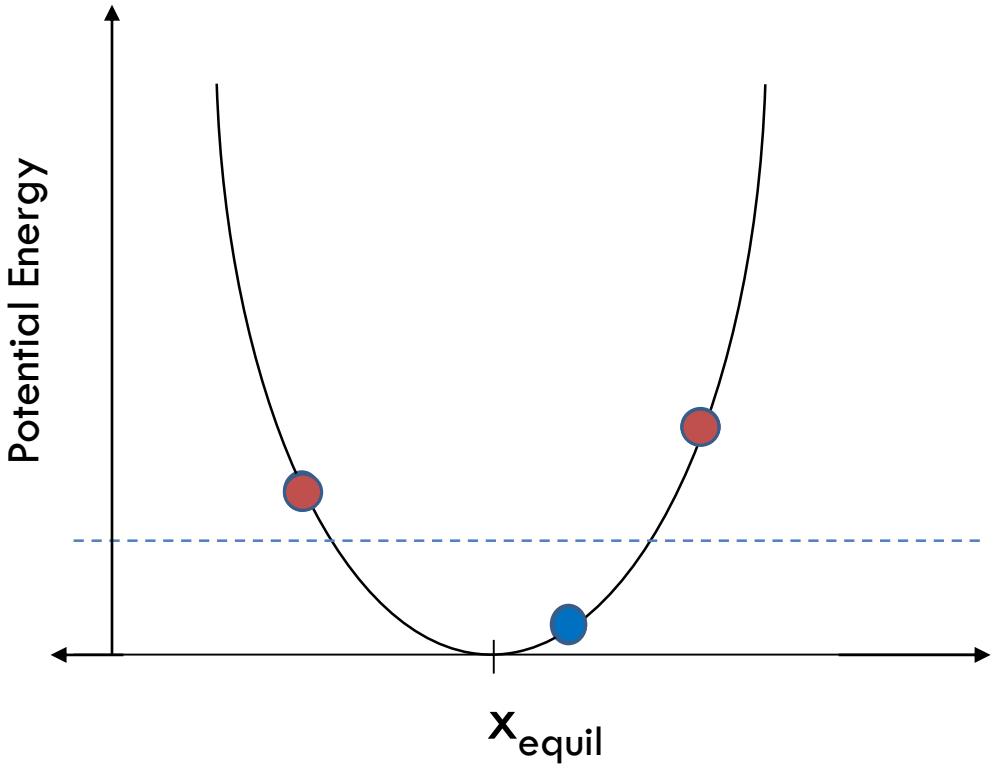
$$\pi = 4\,\frac{N_{in\ circle}}{N_{total}}$$



Animation credit to Dr. Lindsey Madison

DIFFUSION MONTE CARLO





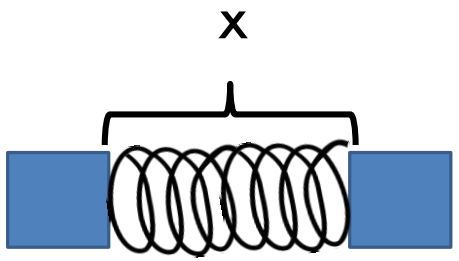
Avg Energy of
all my points

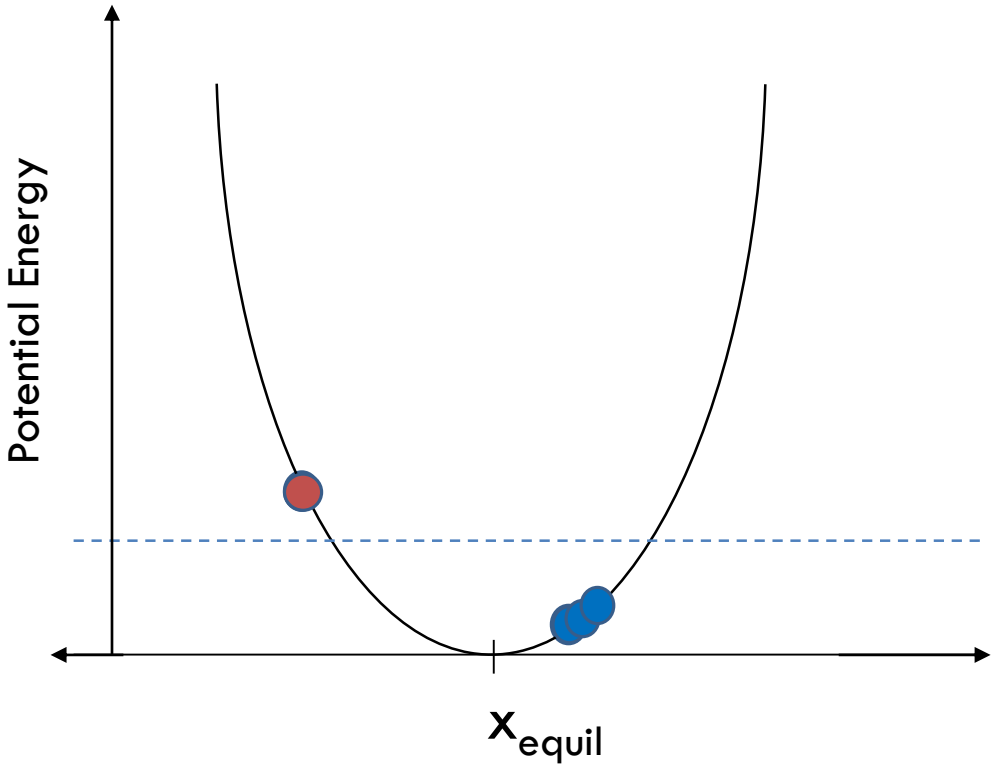
Represent our wavefunction with points that we call “walkers”

Tag them: below or above average?
(Classically-allowed or classically-forbidden?)

Roll the dice! Do they survive?
Do they get to replicate?

DIFFUSION MONTE CARLO





Avg Energy of
all my points

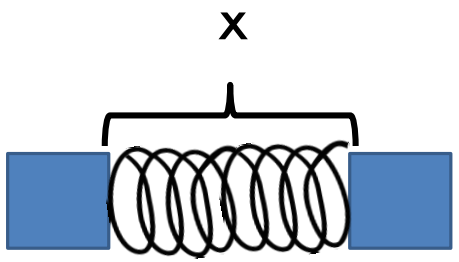
Represent our wavefunction with points that we call "walkers"

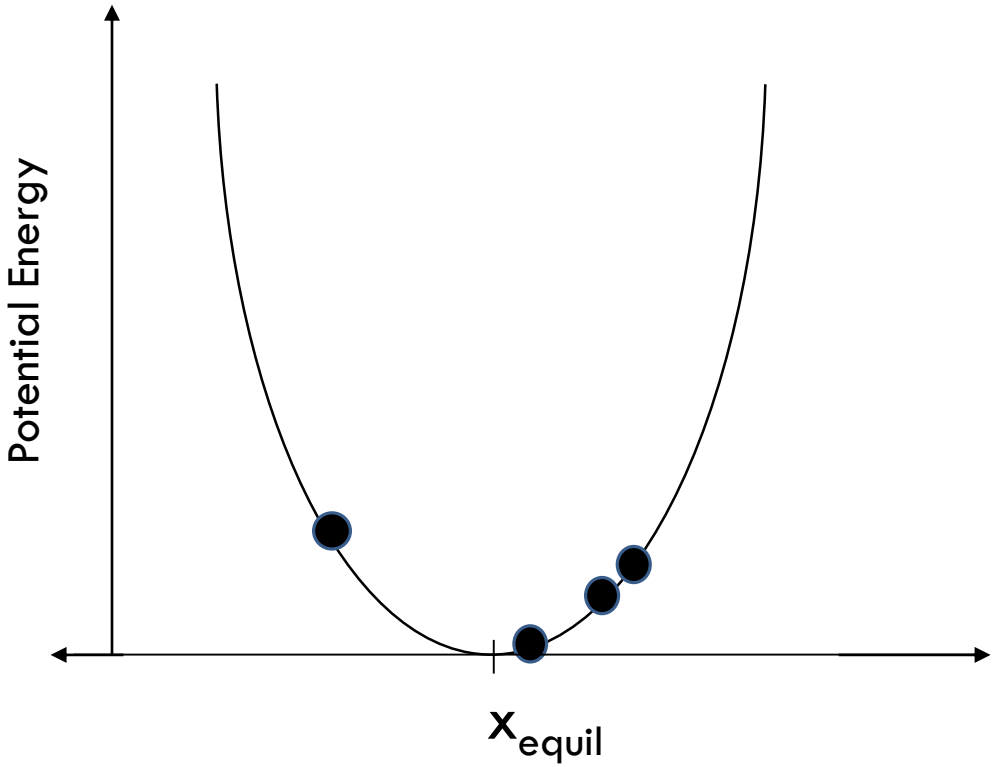
Tag them: below or above average?
(Classically-allowed or classically-forbidden?)

Roll the dice! Do they survive?
Do they get to replicate?

Diffuse your new set of points

DIFFUSION MONTE CARLO





Represent our wavefunction with points that we call “walkers”

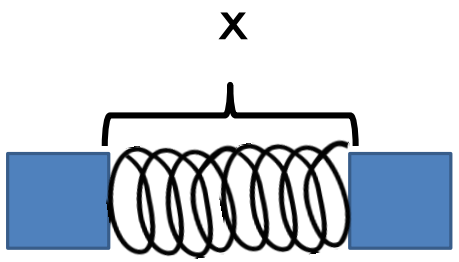
Tag them: below or above average?
(Classically-allowed or classically-forbidden?)

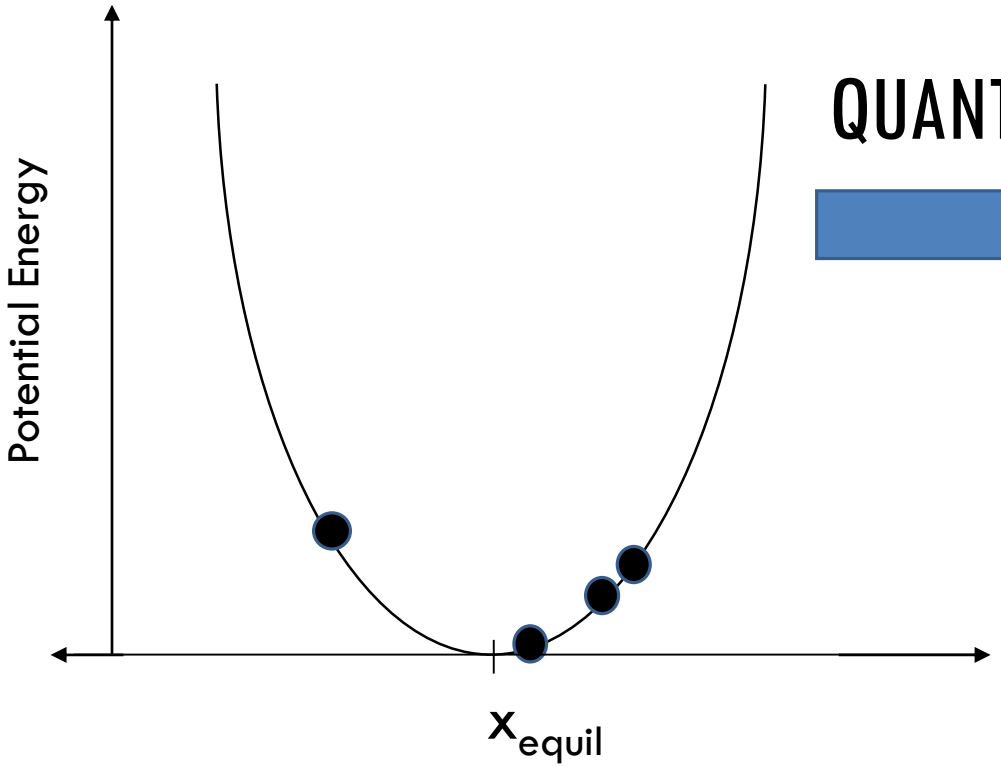
Roll the dice! Do they survive?
Do they get to replicate?

Diffuse your new set of points

Take your new average energy, start over!

DIFFUSION MONTE CARLO





QUANTUM

Represent our wavefunction with points that we call “walkers”

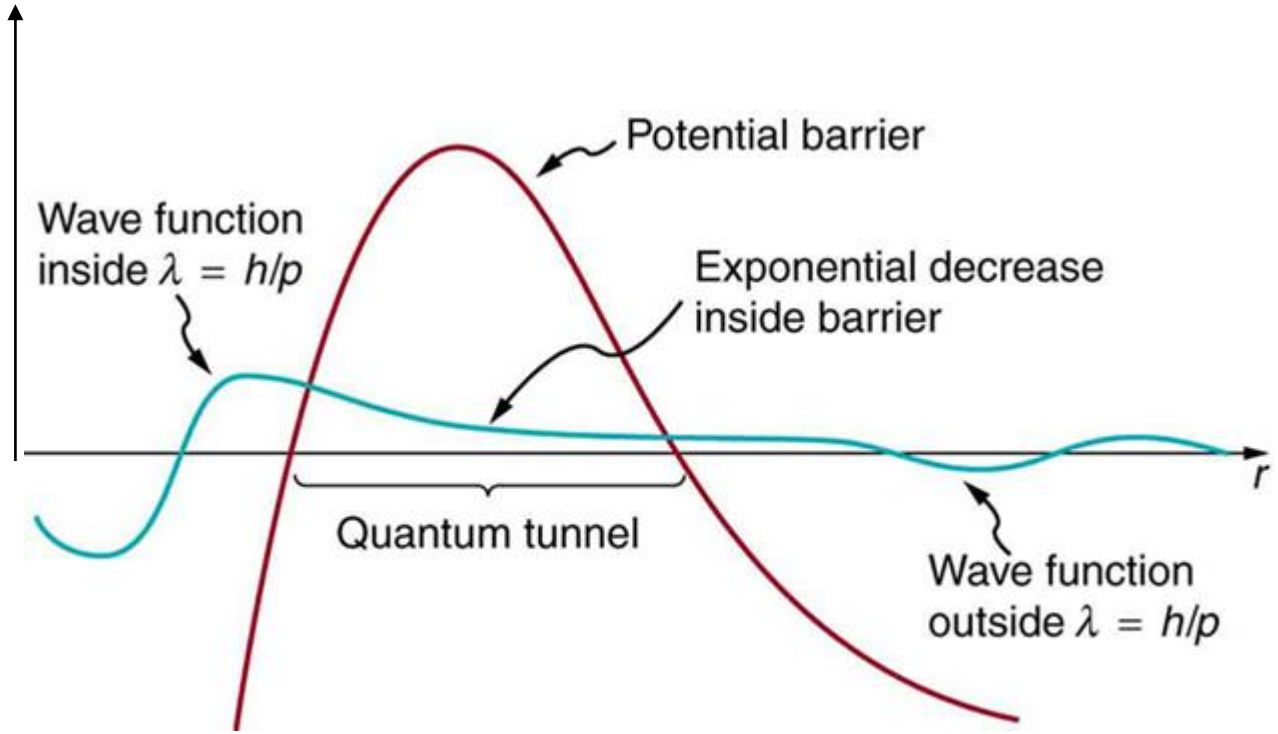
Tag them: below or above average?
(Classically-allowed or classically-forbidden?)

Roll the dice! Do they survive?
Do they get to replicate?

Diffuse your new set of points

Take your new average energy, start over!

QUANTUM TUNNELING



Non-zero probability of being in a region where the potential energy is greater than the energy of the system

Quantum mechanics and Monte Carlo: both inherently probabilistic!

QUANTUM MONTE CARLO

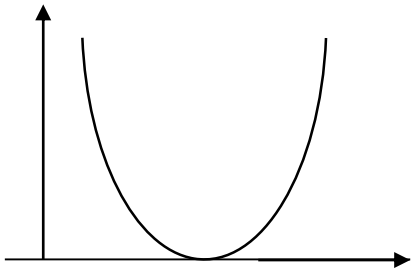
There are **many** different flavors of quantum Monte Carlo.
They all have essentially one goal: solve the Schrödinger equation.

$$i\hbar\frac{d\psi}{dt} = -\frac{\hbar^2}{2m}\nabla^2\psi + V\psi$$

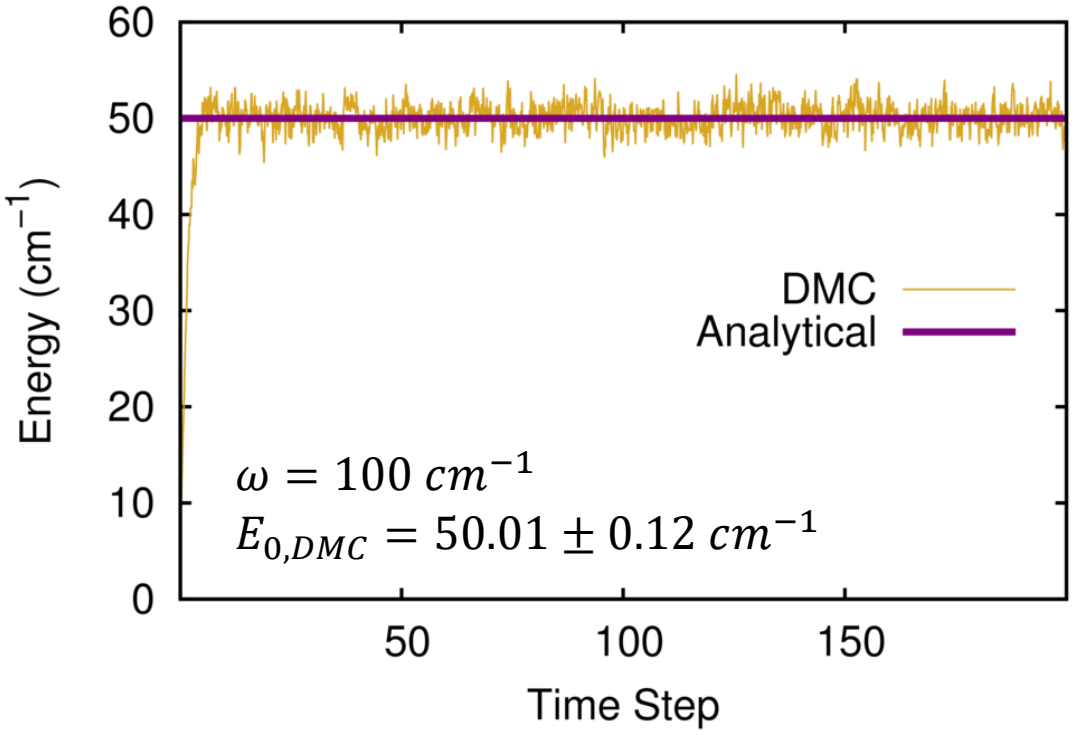
Get the wavefunction: ψ

Usual data run:
25,000 walkers
10,000 timesteps
x10 simulations
Time: ~10 hours

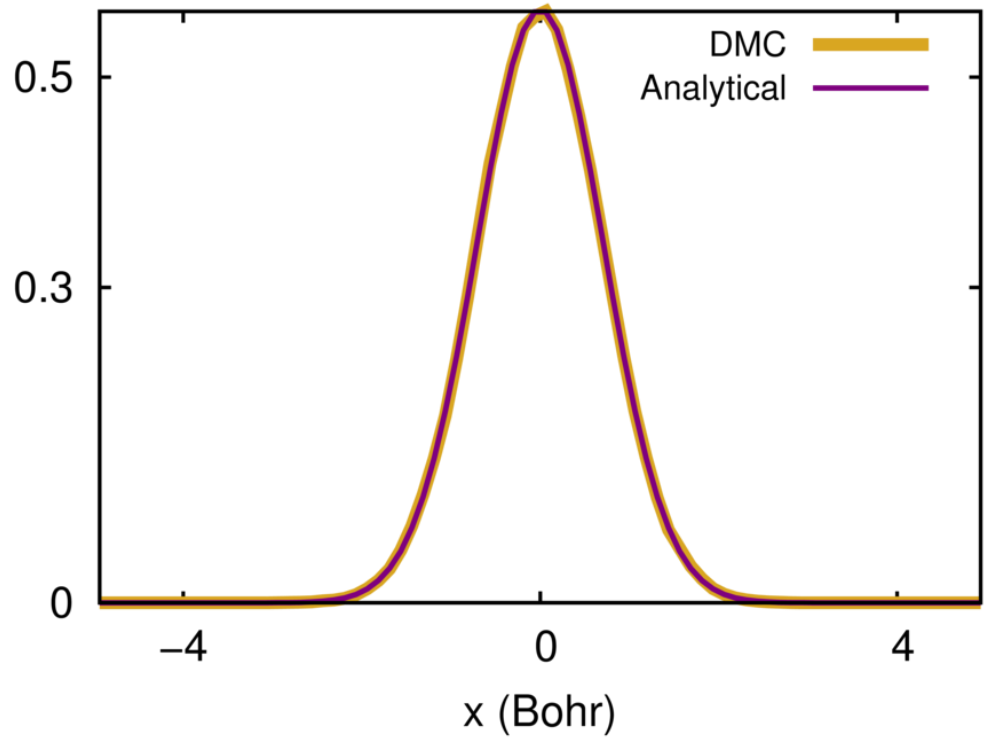
DMC CAN CALCULATE:



Zero-point energy



Wavefunction as a density of walkers

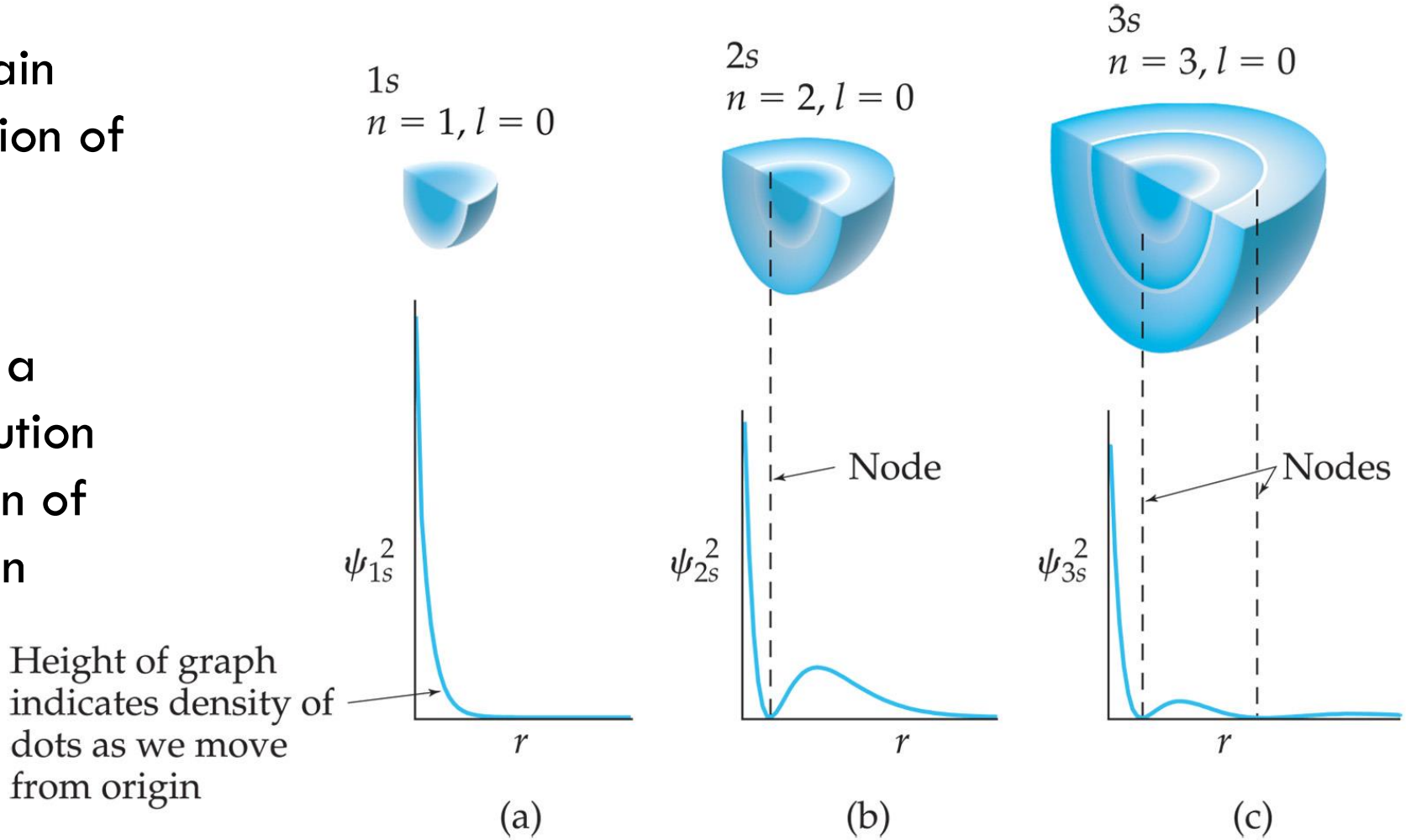


But how do I look at a multi-dimensional density?

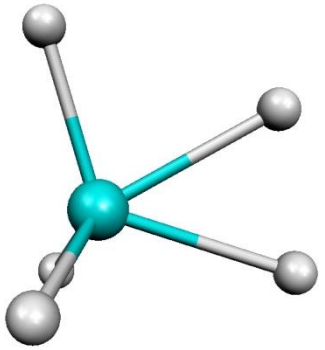
PROBABILITY DISTRIBUTION: $|\psi|^2$

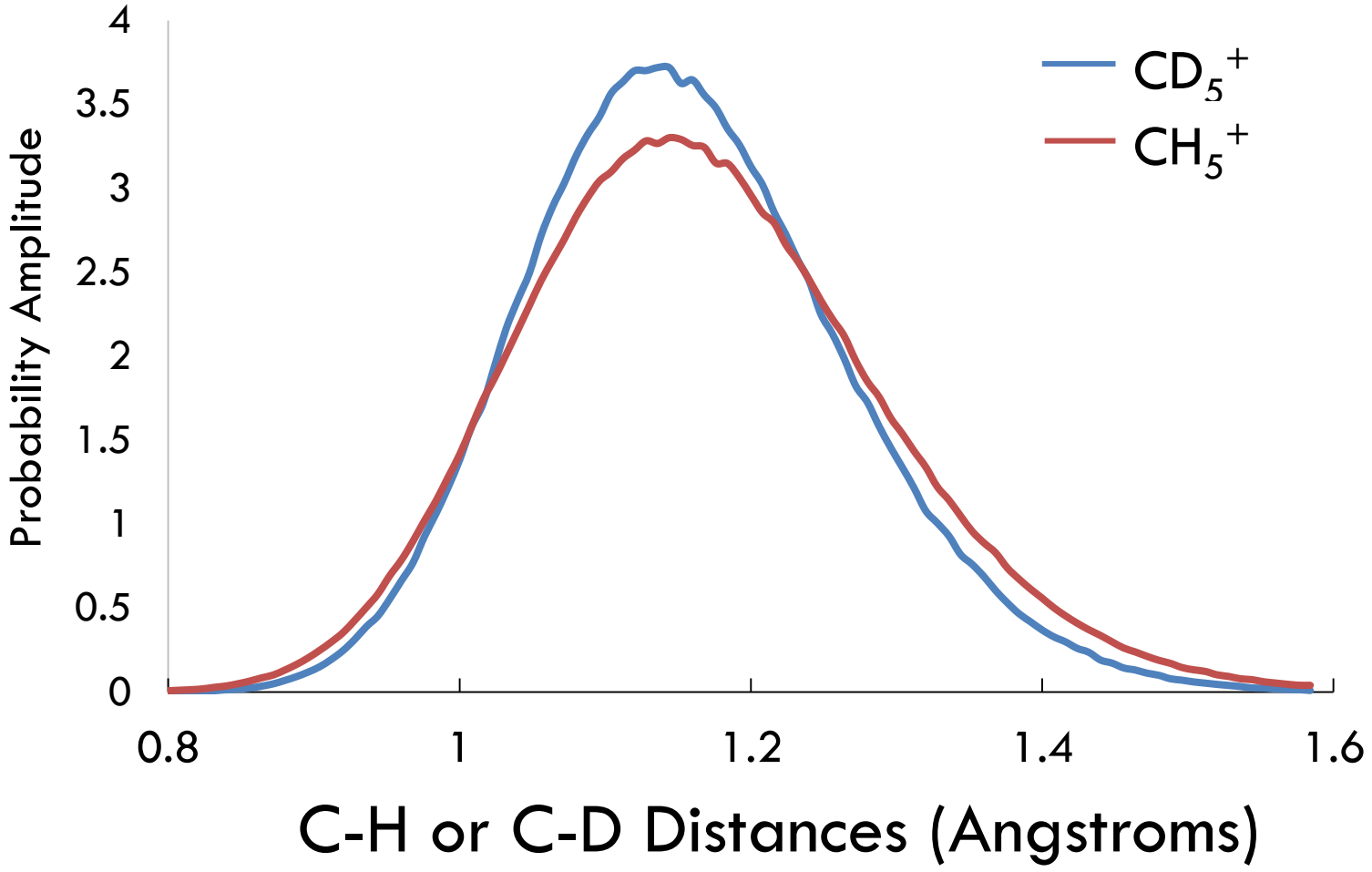
We have ψ, obtain another representation of it to get $|\psi|^2$

Use $|\psi|^2$ to get a probability distribution over **one** dimension of the wavefunction

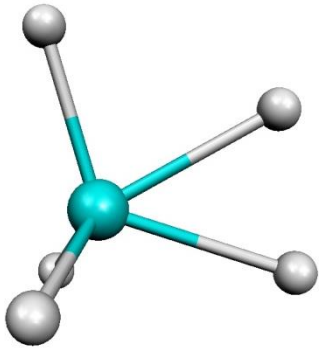


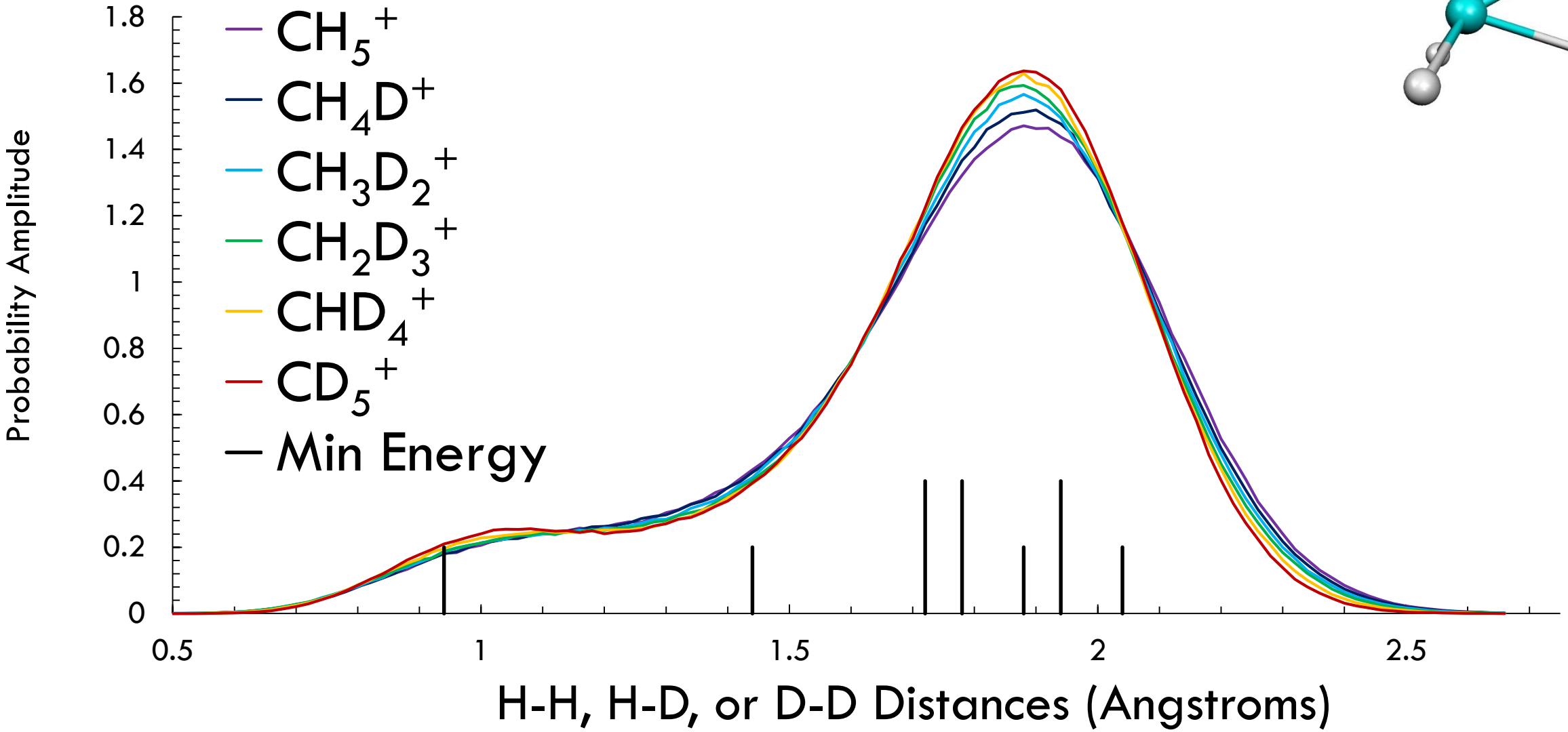
C-H, C-D DISTRIBUTIONS



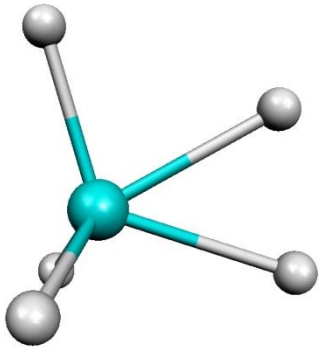


Internuclear 1D Probability Distributions

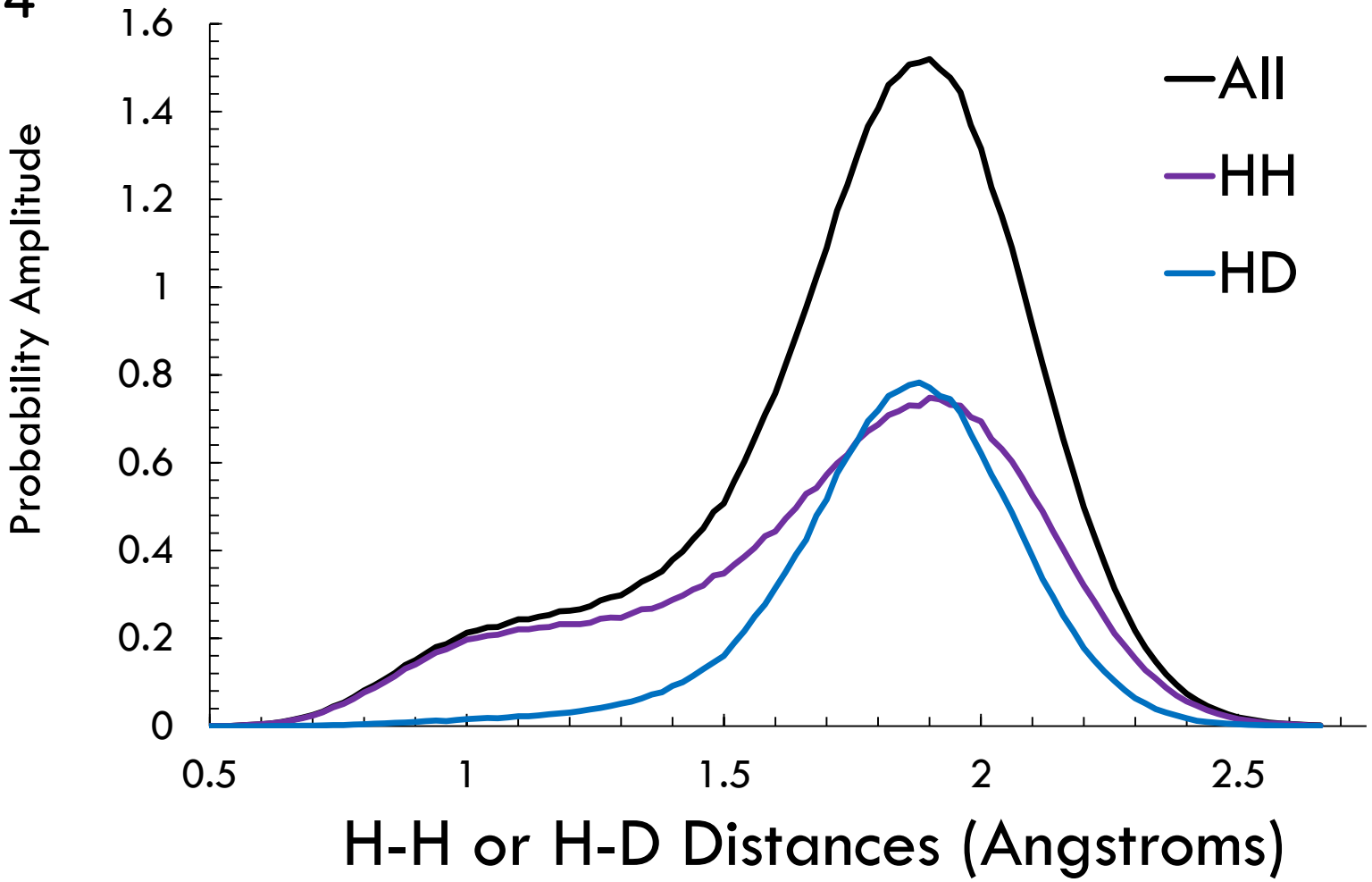




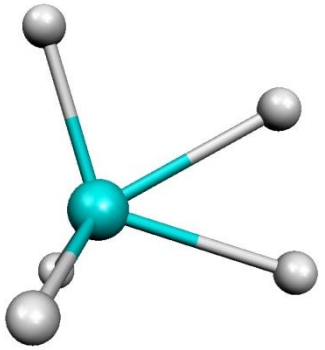
Internuclear 1D Probability Distributions

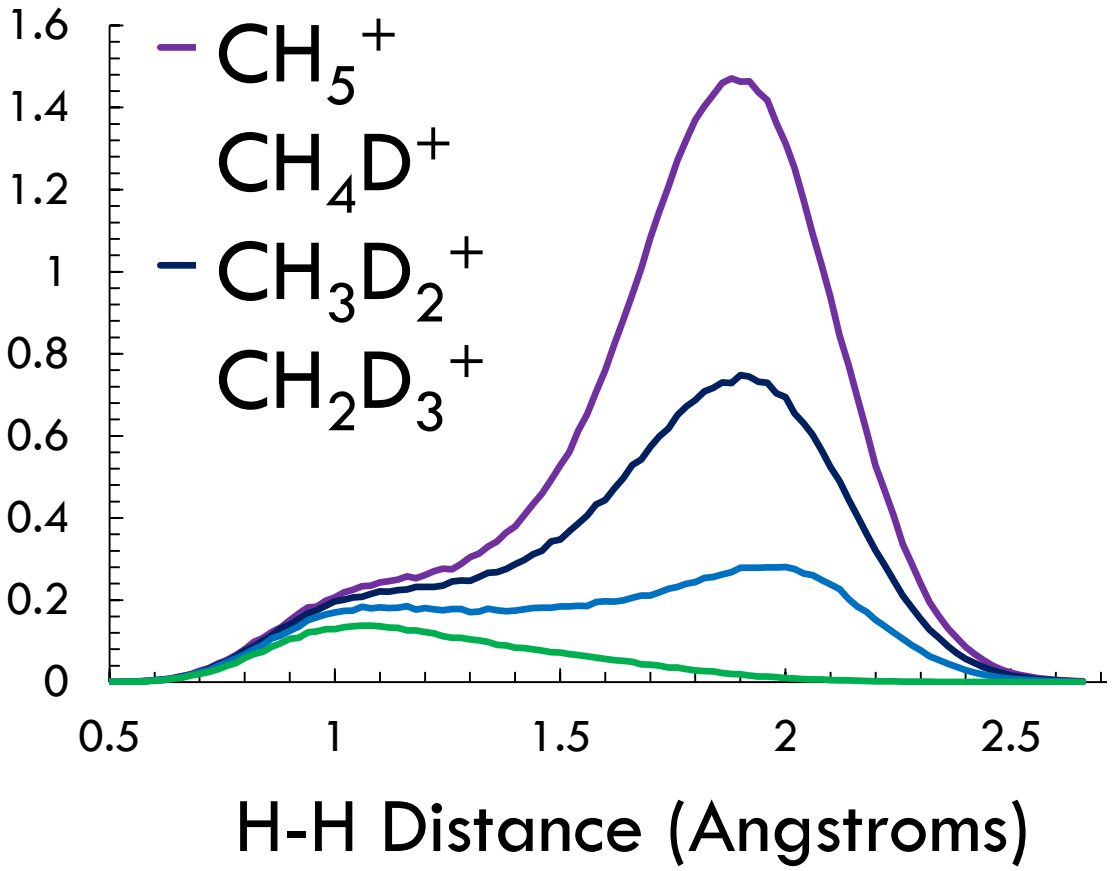


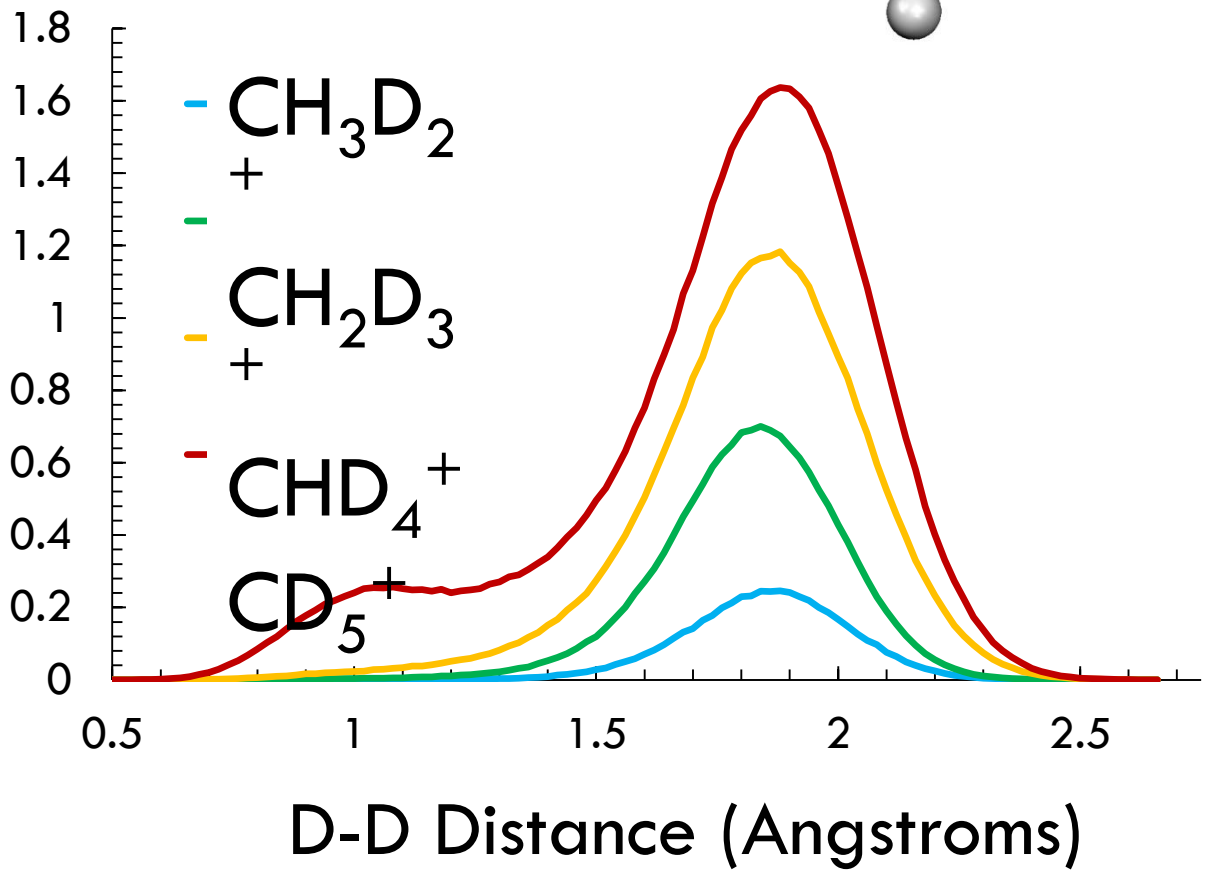
CH_4D^+



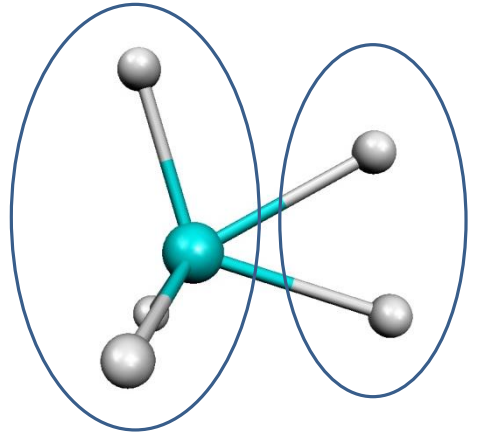
Internuclear 1D Projections: H-H and D-D







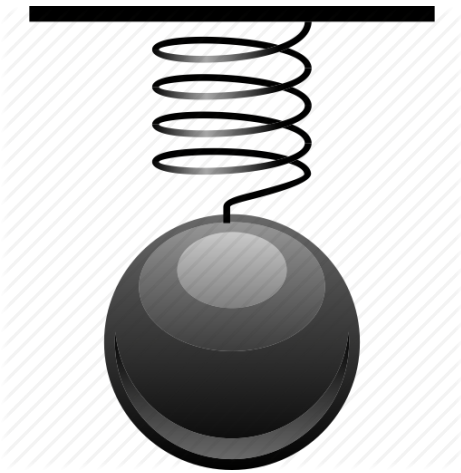
NOT ALL FIVE POSITIONS ARE EQUAL!



The C-H bonds in the CH_3^+ are stronger (higher energy, frequency) than the C-H bonds in the H_2

The molecule's zero point energy is lowered more if we place a higher-mass atom in a position with a stronger C-H bond

Can we quantify how the distributions are changing as we add mass?



$$\omega = \sqrt{\frac{k}{\mu}}$$

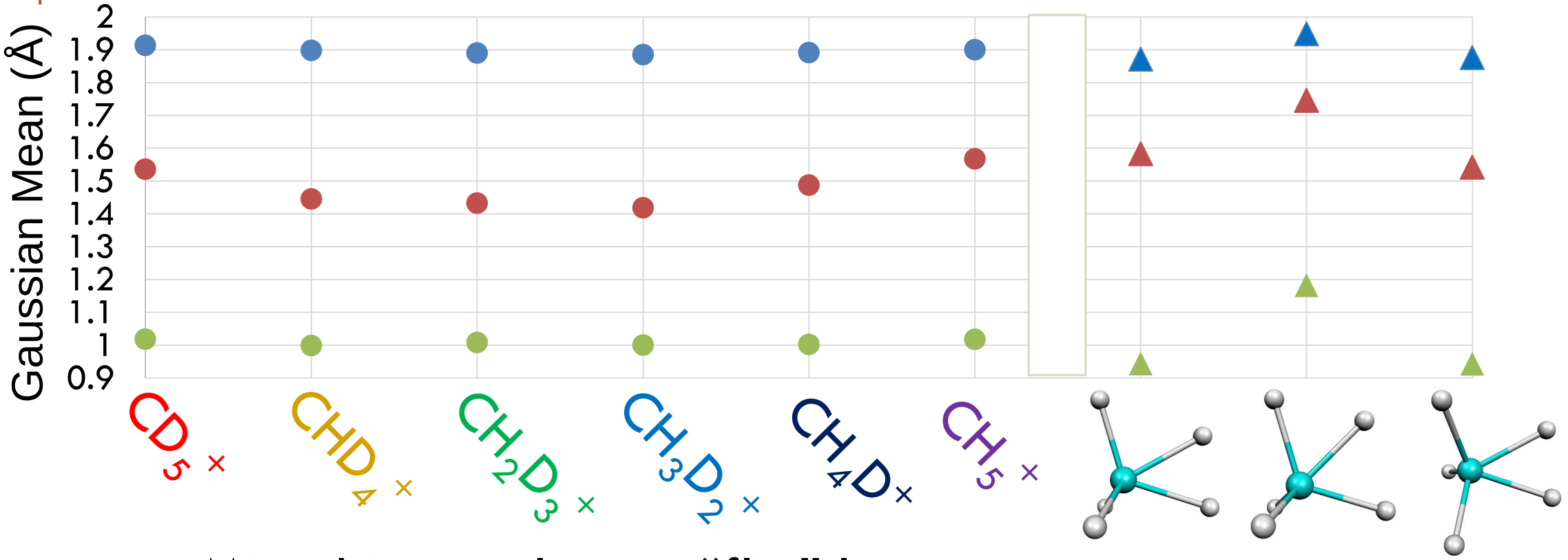
$$\frac{1}{\sqrt{2}}\omega = \sqrt{\frac{k}{2\mu}}$$

CAN WE GET TO UNDERLYING PHYSICS BY FITTING?

$$f(x) = \sum_{i=1}^{N} A_i e^{\frac{-(x-c_i)^2}{2\sigma_i^2}}$$

But how many Gaussians do I need?

TRENDS IN SUMMED DISTRIBUTIONS



Mixed isotopologues “flip” less

Reinforces localization we’ve seen

CURRENT/FUTURE WORK

Implementing DMC with 5-dimensional angular momentum

Theorized by Schmiedt, Schlemmer, and Jensen

$$\hat{H}_{rot} = \frac{B}{2} \sum_{a<b} \hat{J}_{ab}^2$$
$$a, b = 1 \ldots 5$$

Key Future Goal: What do these states mean *physically?*

Use this new perspective to shed light on the physics behind the spectrum

Preliminary Results

Exp. CDs (cm^{-1})	DMC (cm^{-1})	Corresponding 5D transitions
26.472	25.869	[3,0]-[1,0]
30.270	30.689	[3,1]-[1,0]
36.353	38.581	[3,2]-[1,0]

Thank you!

Prof. Anne McCoy
Prof. Lindsey Madison
Dr. Meng Huang
Victor Lee
Ryan DiRisio
Mark Boyer
Mathew Joyner

DEPARTMENT OF PHYSICS
UNIVERSITY of WASHINGTON

NSF

GRFP
NSF GRADUATE RESEARCH FELLOWSHIP PROGRAM