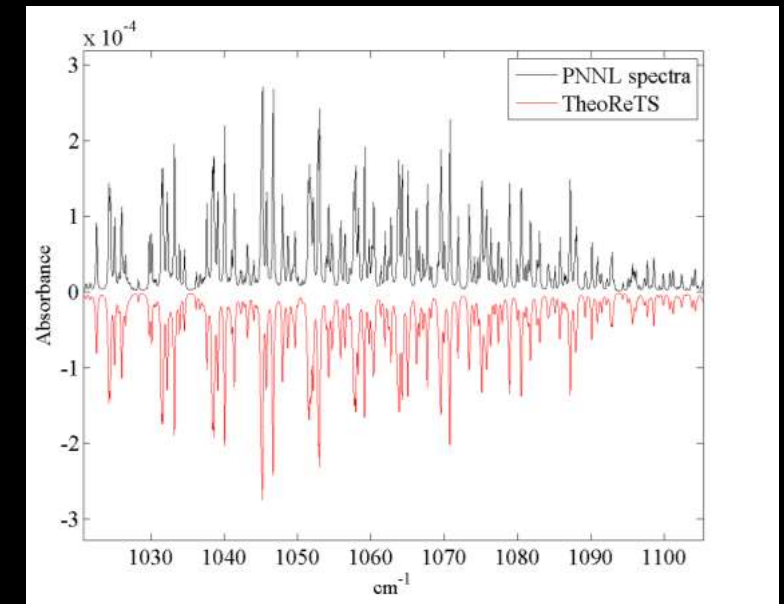
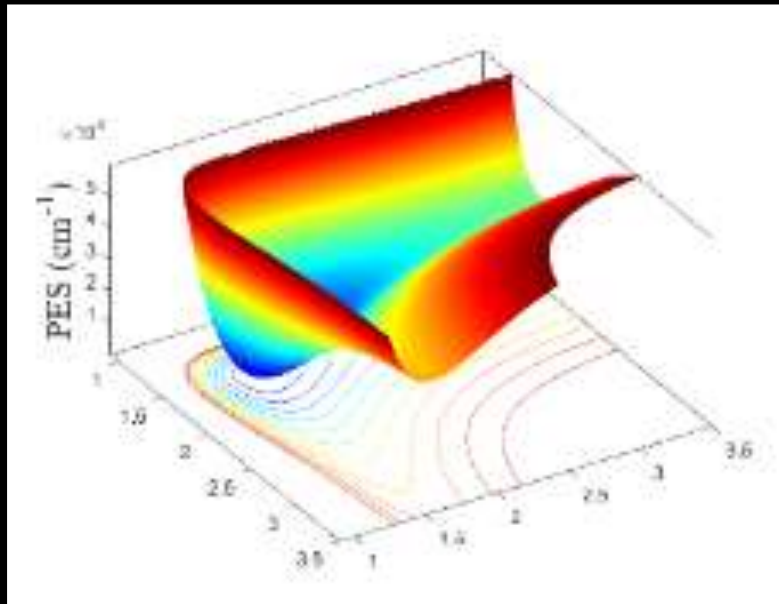


# Building theoretical molecular spectra

## *Role of ab initio calculations & construction of line lists*

Michaël Rey - GSMA Reims



Ecole des Houches – 17/09/2022

# Motivations of this lecture

## An Overview of Molecular Opacities

Peter Bernath<sup>1,2</sup>

<sup>1</sup> *Old Dominion University, Norfolk, Virginia, USA; pbernath@odu.edu*

<sup>2</sup> *Also, University of Waterloo, Waterloo, Ontario, Canada*

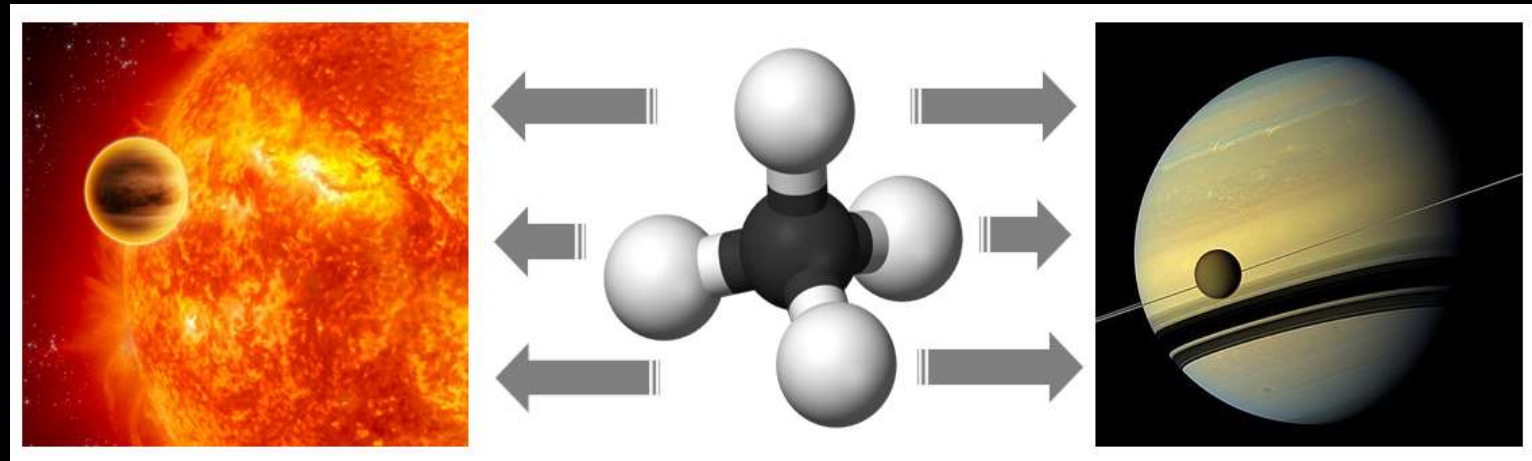
Molecules are ubiquitous in the Universe and are found in diverse sources including diffuse clouds, dark clouds, giant molecular clouds, planetary nebulae, circumstellar envelopes, stellar and brown dwarf atmospheres, protoplanetary disks, comets, supernovas, planetary and exoplanetary atmospheres, and galaxies (Bernath 2009). Except

### ✓ Construction of reliable & complete spectroscopic line lists

→ Earth atmosphere

→ Planetological (Titan,..)

→ Astrophysical (hot bodies,..)



# Aim of this lecture: *going inside the molecule*

Describe the construction of molecular databases, step-by-step

Show that quantum-mechanical calculations are very demanding, even for small molecules

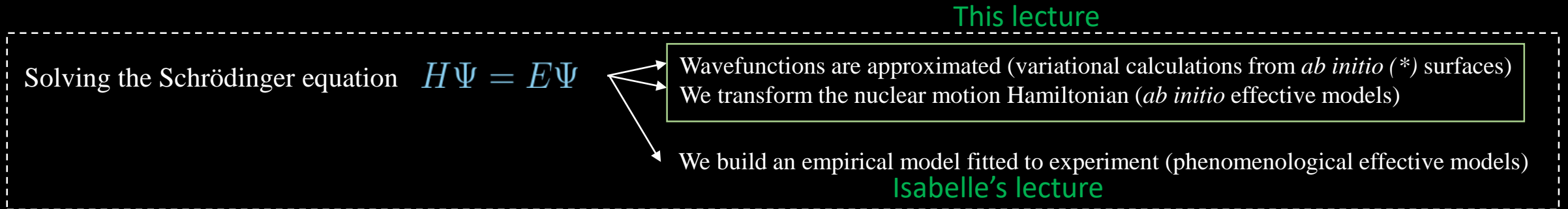
Not a black-box procedure, both for solving electron and nuclear motion equations

Show that building spectra requires highly-optimized computational methods

We will see that solving a quantum chemical or quantum mechanical problem will consist in making a series of approximations

-  
Find the good compromise between accuracy and feasibility

# A mandatory step before the line list...



(\*) Latin « *ab initio* » = « from the beginning » = *no prior experimental knowledge*

# Role of *ab initio* in modern spectroscopy

*ab initio* is strongly involved in spectroscopic databases for historical molecules

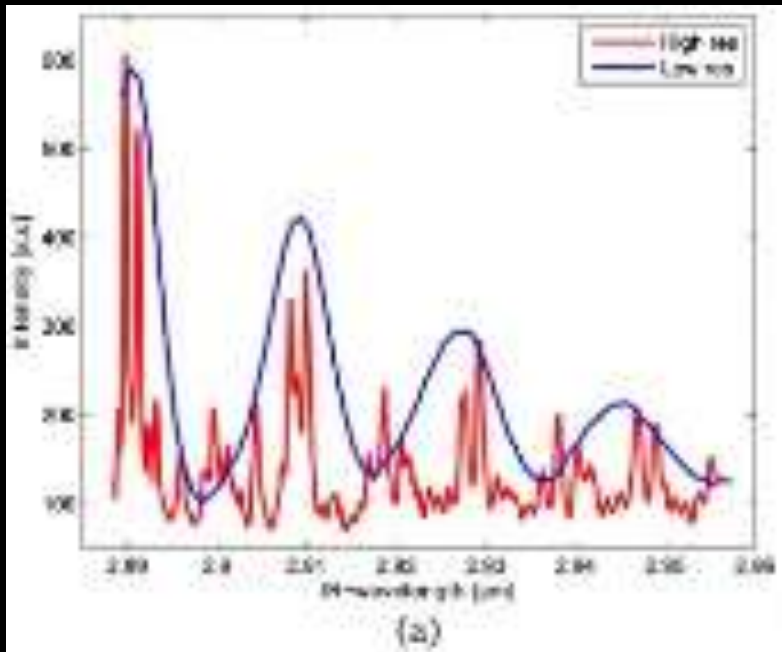
*Diatomics, H<sub>2</sub>O, NH<sub>3</sub> by UCL London*

*Ozone, methane, phosphine, etc. in HITRAN/GEISA*

*Future updates in databases (ethane, SF<sub>6</sub>, CF<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, formaldehyde, etc. ?)*

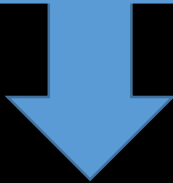
# Role of *ab initio* in modern spectroscopy

HR spectra analyses are completely revisited : *ab initio* intensities may replace the experimental measurements in some cases (better when many overlapped lines difficult to extract, for dense spectra like those of hot or heavy molecules)



“change of paradigm”  
in high-resolution infrared spectroscopy ?

# Available databases

(I) <i>Experimental, empirical or both</i>	(II) <i>From first-principles (ab initio + variational)</i>
HITRAN GEISA WKLMC PNNL VAMDC CDMS STDS SMPO ...	<div data-bbox="1192 445 2091 1015" style="border: 1px solid black; padding: 10px;"><p>ExoMol (UCL London)</p><p>NASA Aims</p><p>TheoReTS (Reims – Tomsk)</p><p>More recently, in Stuttgart (Rauhut et al.)</p></div>  <p data-bbox="1243 1225 1989 1278">How to build such line lists??</p>

Designed for Room T  
Limited for high T & Wnb  
Few HBs  
Accurate in position

Way more complete  
Designed for low & high T  
Lower accuracy in position

« Numerical recipe » for building a

vibration-rotation spectrum

from *ab initio* surfaces

(not unique – there exists other ones)





# Ingredients

- (1) *ab initio* PES & DMS ..... Commercial codes (Molpro, etc.)  
(resolution of the electronic SE: domain of quantum chemistry)
- (2) Resolution of the Schrödinger equation for the nuclear motions..... Home-made computer codes

# The molecular Hamiltonian

For a molecules composed of  $N$  nuclei &  $n$  electrons

$$H = - \sum_{i=1}^n \frac{\hbar^2}{2m_e} \nabla_{e_i}^2 - \sum_{I=1}^N \frac{\hbar^2}{2m_{N_I}} \nabla_{N_I}^2 + \sum_{i < j}^n \frac{e^2}{4\pi\epsilon_0 r_{ij}} + \sum_{I < J}^N \frac{Z_I Z_J e^2}{4\pi\epsilon_0 r_{IJ}} - \sum_i^n \sum_I^N \frac{Z_I e^2}{4\pi\epsilon_0 r_{Ii}}$$

Kinetic  
(*electron*) Kinetic  
(*nuclei*) Coulomb  
(*e-e*) Coulomb  
(*n-n*) Coulomb  
(*e-n*)

No chance to solve the Schrödinger equation exactly!

Approximations are thus required

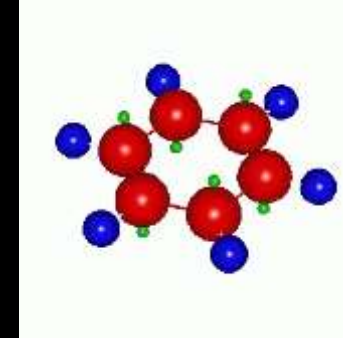
# The Born-Oppenheimer approximation

In the Schrödinger equation, nuclear coordinates are **parameters** and the nuclei are held fixed

- Nuclei are 1800 times heavier than an electron
- Separation of the wavefunctions
- The Schrödinger equation is solved in sequence

$$\Psi_e(\mathbf{r}; \mathbf{R}) \Psi_n(\mathbf{R})$$

↑ Electronic coord.    ↑ Nuclear coord.



Step 1. Electronic structure calculation (*ab initio* methods = developed by quantum chemists = not detailed here)

$$\left\{ -\sum_{i=1}^n \frac{\hbar^2}{2m_e} \nabla_{e_i}^2 + \sum_{i<j} \frac{e^2}{4\pi\epsilon_0 r_{ij}} - \sum_i \sum_I \frac{Z_I e^2}{4\pi\epsilon_0 r_{Ii}} \right\} \Psi_e(\mathbf{r}; \mathbf{R}) = E_e(\mathbf{R}) \Psi_e(\mathbf{r}; \mathbf{R})$$

Step 2. Nuclear dynamics

$$\left\{ -\sum_{I=1}^N \frac{\hbar^2}{2m_{N_I}} \nabla_{N_I}^2 + \sum_{I<J} \frac{Z_I Z_J e^2}{4\pi\epsilon_0 r_{IJ}} + E_e(\mathbf{R}) \right\} \Psi_n(\mathbf{R}) = E \Psi_n(\mathbf{R})$$

$\mathbf{R}$  : grid of points  $\sim 10^4 - 10^5$   
Polyatomic molecule

Plays the role of an “effective” potential for the nuclei =  
POTENTIAL ENERGY SURFACE

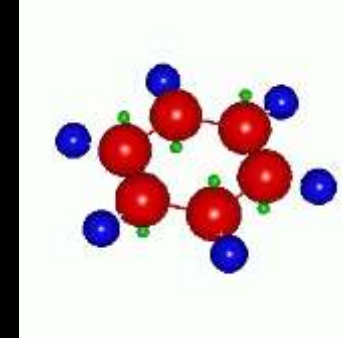
# The Born-Oppenheimer approximation

In the Schrödinger equation, nuclear coordinates are **parameters** and the nuclei are held fixed

- Nuclei are 1800 times heavier than an electron
- Separation of the wavefunctions
- The Schrödinger equation is solved in sequence

$$\Psi_e(\mathbf{r}; \mathbf{R}) \Psi_n(\mathbf{R})$$

Electronic coord.      Nuclear coord.



Step 1. Electronic structure calculation (*ab initio* methods = developed by quantum chemists = not detailed here)

Use of commercial computer codes like MOLPRO, GAUSSIAN

Different levels of calculation

Quality will strongly depend on the number of electrons (degrees of freedom) - few days up to several months of calculation

Step 2. Nuclear dynamics

Use of home-made computer codes (depending on the type of coordinates)

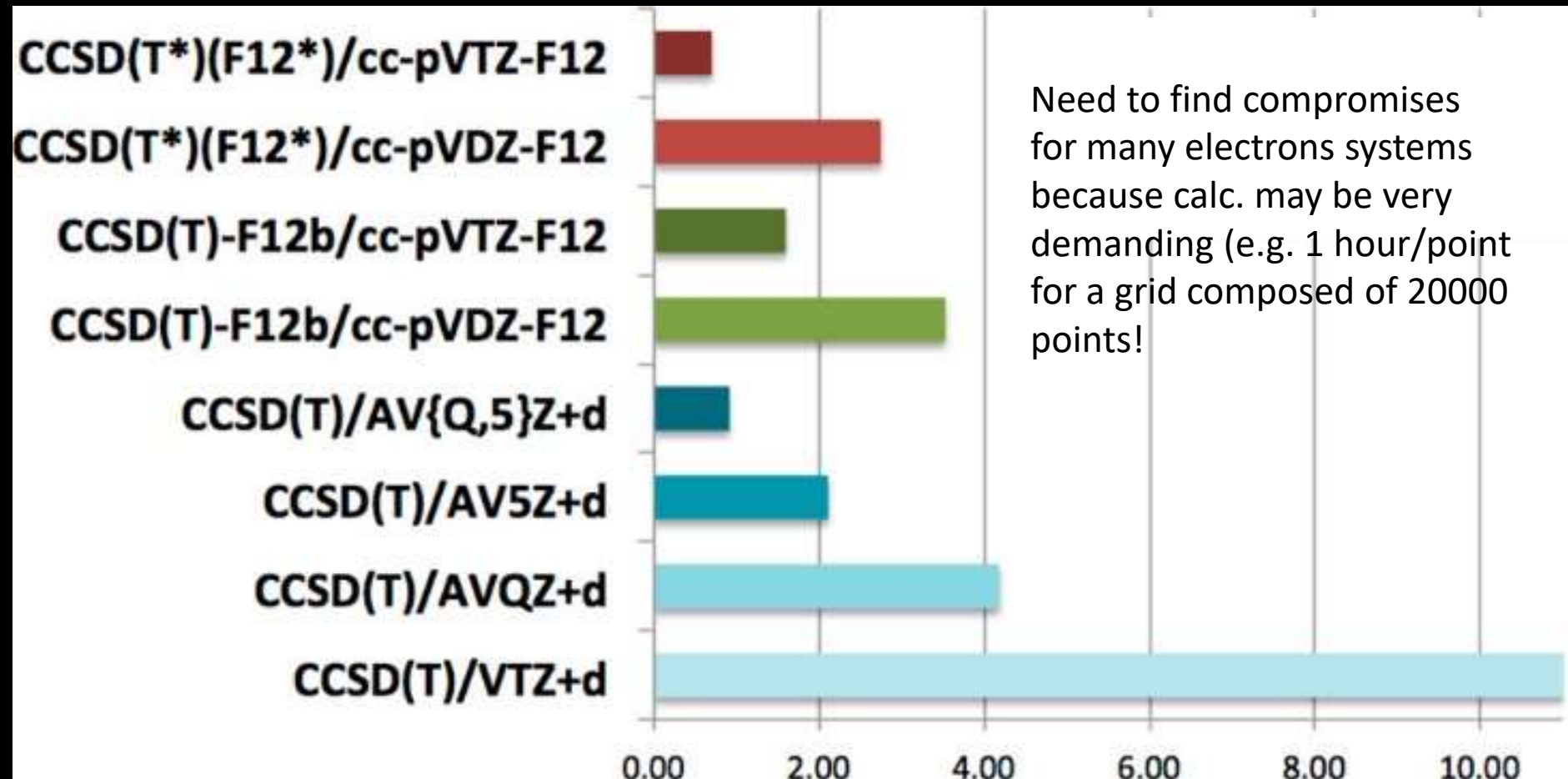
Different levels of calculation

(Slow or fast) convergence of calculation will strongly depend on the number of atoms (degrees of freedom) - few hours up to few weeks of calculation

# Electronic structure calculations

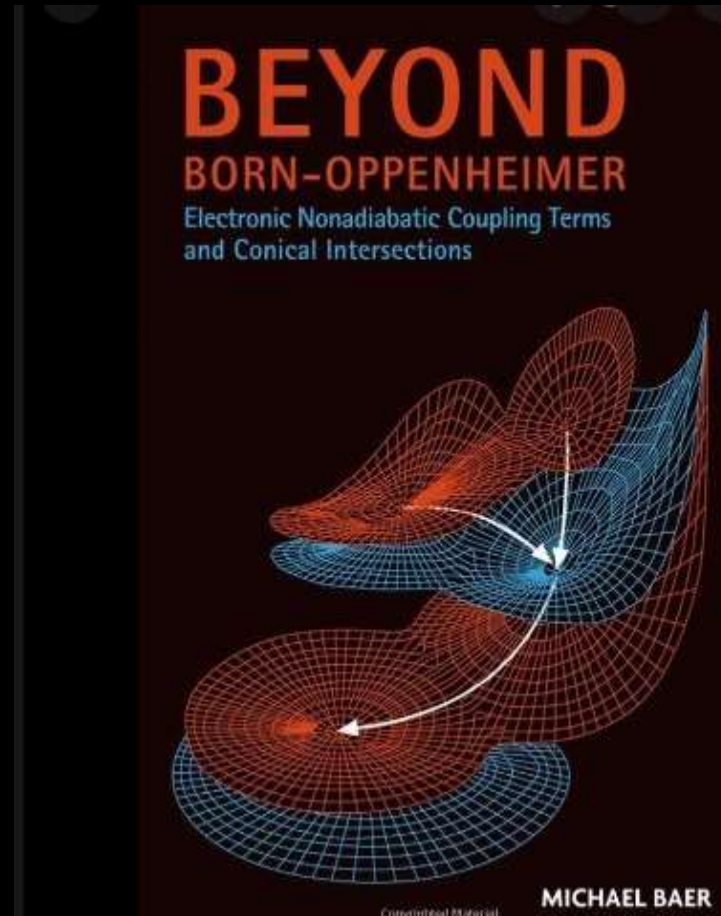
MOLPRO, COLUMBUS, GAUSSIAN, etc.

Type of method / Type of orbital basis → for electron correlation, QED, DBOC, rel., etc



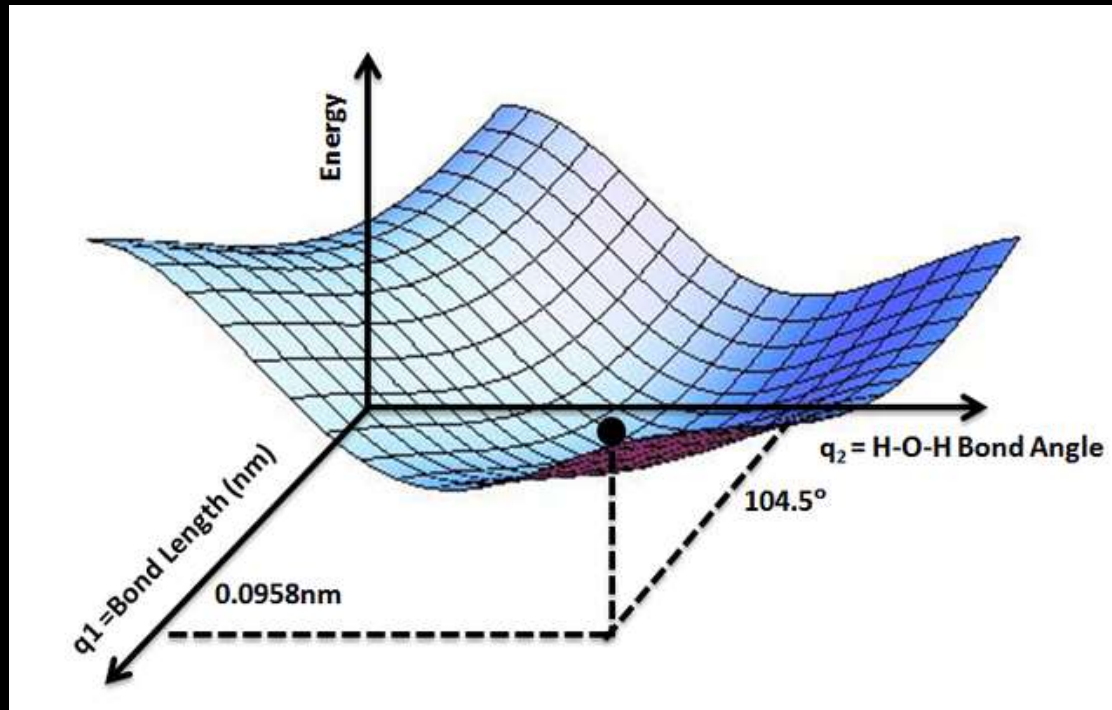
# The Born-Oppenheimer approximation

- ✓ One of the most accurate approximations in quantum chemistry for quite isolated electronic states
- ✓ But fails in presence of close (or degenerate) electronic states (open-shell molecules like ions or radicals) → coupling terms



# At this stage...

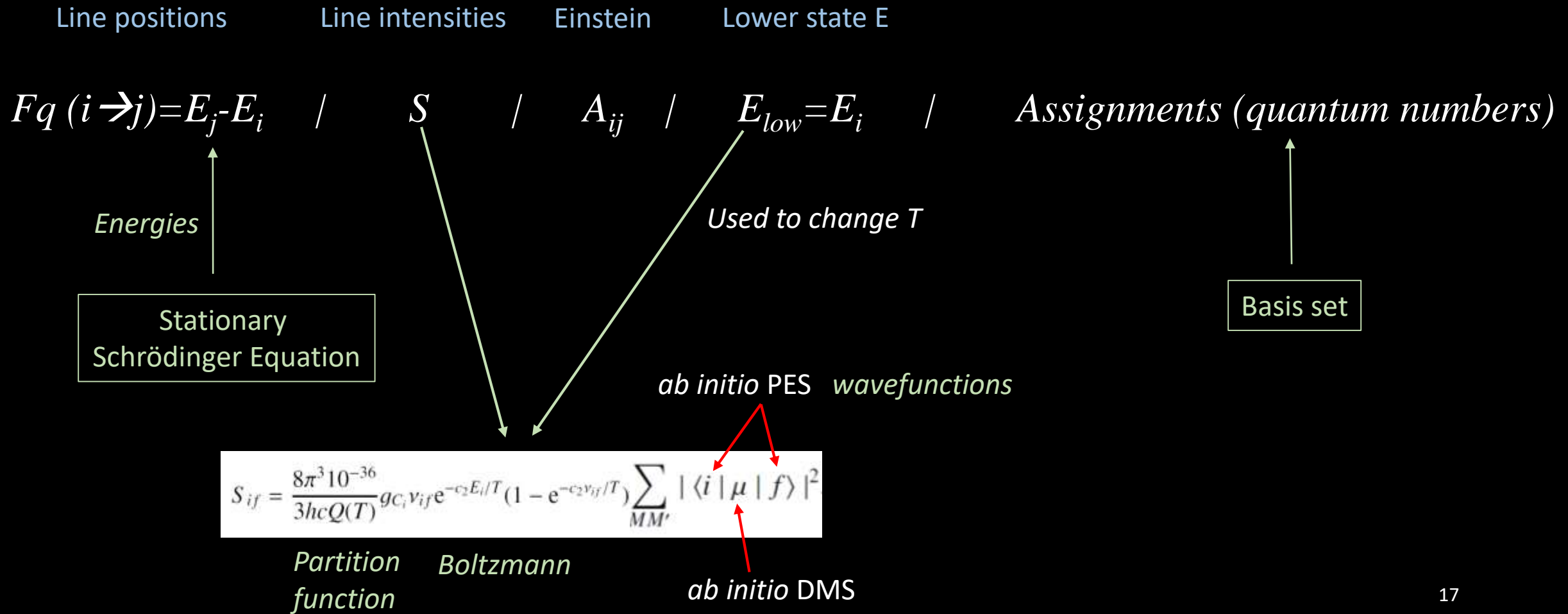
- ✓ Concept of (*ab initio*) Potential Energy (hyper)Surface introduced
- ✓ Need to compute now the dynamics of the nuclei on this surface



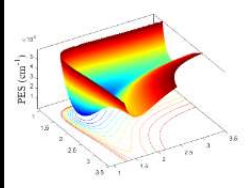
# Nuclear-motion, quantum mechanical calculations



# AIM: Calculated line lists



# Step 1 - The nuclear Hamiltonian model

$$H = T(X, Y, J_\alpha) + V(X) = \text{KEO} + \text{PES} = \text{nuclear motion or initial or untransformed } H$$


$X$  : nuclear coordinates *e.g. curvilinear (valence, radau, jacobi, ...)* or *rectilinear (normal)*

$Y$  : conjugate momenta

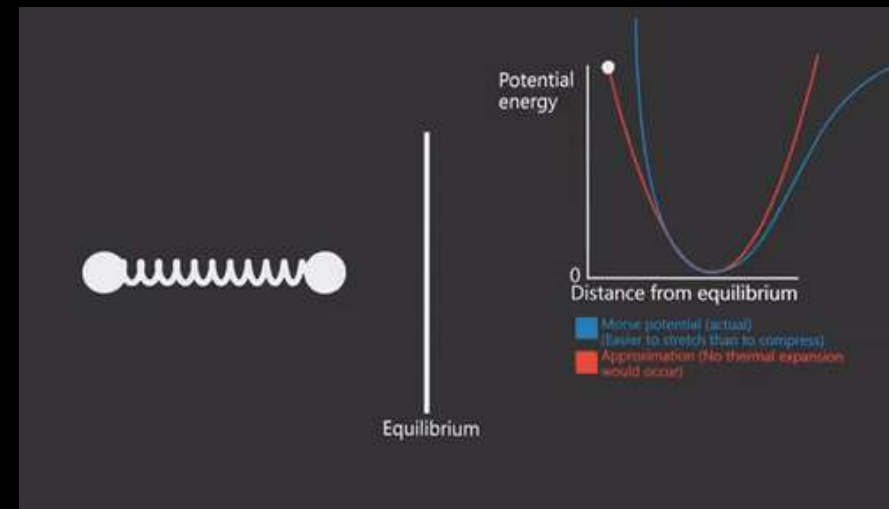
$J_\alpha$  : total angular momentum components (*degree less or equal than 2*)

$V(X)=E_e(X)$  : PES with empirical or *ab initio* or empirically-refined *ab initio* force constants

# A zero-order – HO+RR – approximation

➤ In first approximation, the PES is a quadratic form

✓ Potential = harmonic → harmonic oscillator for the vibration

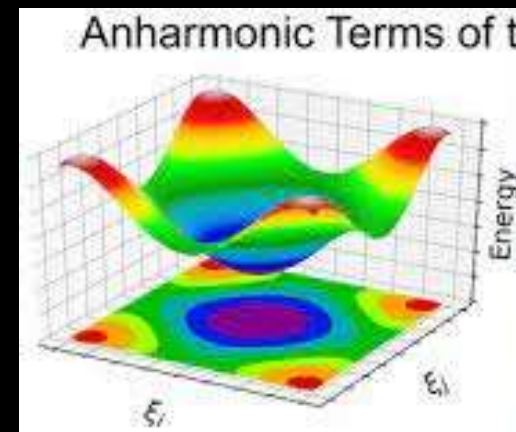


➤ We can use the rigid-rotor approximation

✓ Ex: diatomic molecule →  $\frac{\hbar^2}{2\mu R^2} J^2 \approx \frac{\hbar^2}{2\mu R_e^2} J^2 \rightarrow B_e J(J + 1)$

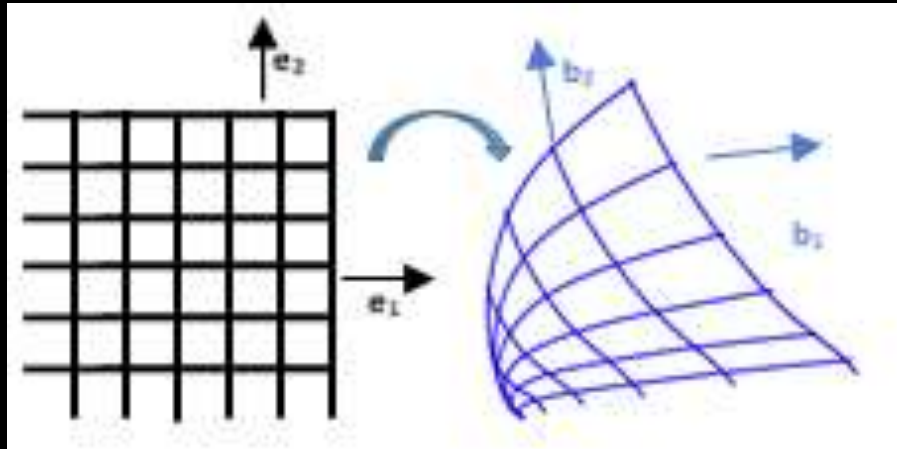
➤ HO+RR =  $\omega(v + 1/2) + B_e J(J + 1)$

Cannot reproduce the experimental data!!



# Nuclear motion Hamiltonian: different strategies

Rectilinear (normal) *versus* curvilinear models?



# Nuclear motion Hamiltonian: different strategies

➤ *The PES is generally expressed in terms of internal (curv.) coordinates (e.g. bond-length, bond-angle)*

➤ For rigid molecules, we have  $H = KEO$  (normal coord.  $Q$ ) +  $PES$  (internal coord.  $R$ )

➔ the way to proceed is to find the nonlinear relation  $R=f(Q)$  in the PES

➔ But, we could also try to derive the nonlinear relation  $Q=g(R)$  in the KEO

➤ For nonrigid molecules, we have either

$$H = KEO(R) + PES(R)$$

or

$$H = KEO(Q, \rho) + KEO(R, \rho) \text{ (mixing curv-rect)}$$

# The Hamiltonian model: rigid molecules

Watson Hamiltonian (nonlinear molecules, 1968)

$$H = \frac{1}{2} \sum_{k\sigma} \omega_k P_{k\sigma}^{2(\Gamma)} + \frac{1}{2} \sum_{\alpha\beta} (J_\alpha - \pi_\alpha) \mu_{\alpha\beta} (J_\beta - \pi_\beta) + U(q) + U_W,$$

Inverse of moment of inertia  
in normal coord.



nuclear KEO



PES *ab initio*  
In normal coord.

# The Hamiltonian model: rigid molecules

If small amplitude vibrations  $\rightarrow$  Taylor series expansion around a single minimum

## Sum of products

$$H = \sum_i h_i (X_1^{m_{1,i}} Y_1^{n_{1,i}}) \cdots (X_{3N-6}^{m_{3N-6,i}} Y_{3N-6}^{n_{3N-6,i}}) \cdots$$

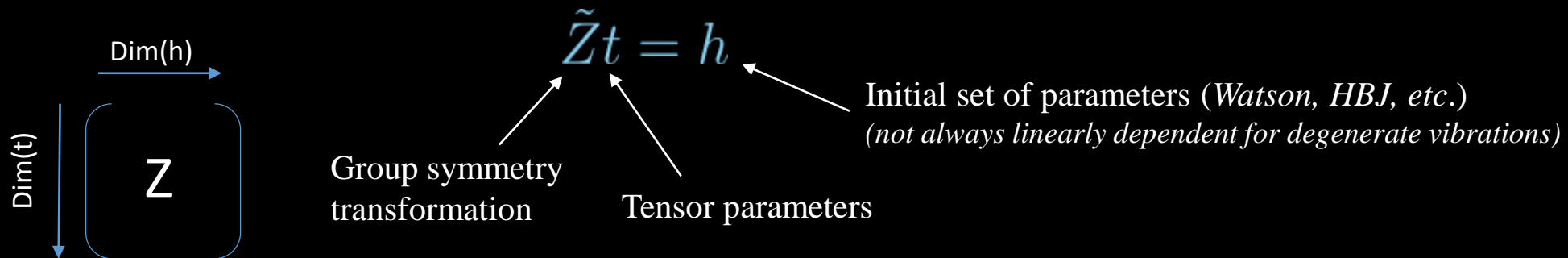
full account of  $\downarrow$  symmetry properties? (Optional)

e.g.  $X$  = coordinate  
 $Y$  = conjugate momentum

$$H^{(\Gamma_0)} = \sum_i t_i ((\mathcal{X}_1 \otimes \mathcal{Y}_1) \otimes \cdots \otimes (\mathcal{X}_{N_m} \otimes \mathcal{Y}_{N_m}))_i^{(\Gamma_0)}$$

$\uparrow$   
#Modes  $\leq 3N-6$

Each matrix is now divided in blocks



# The Hamiltonian model: rigid molecules

Symmetry is one the keys to reduce dimensionality of a given problem

In turn, its implementation in computer codes may be rather involved (e.g. non-Abelian points)

The **TENSOR** computer code (Reims) is able to deal with arbitrary point groups:  $C_n$ ,  $C_{nv}$ ,  $D_n$ ,  $D_{nh}$ ,  $D_{nd}$ ,  $T_d$ ,  $O_h$



# The Hamiltonian model: nonrigid molecules in Hougen-Bunker-Johns

(Benchmark calc. by Hougen, Jensen, Kleiner, Bunker, Coudert, Papousek, Spirko, etc.)

If some vibrations are of large amplitude  $\rightarrow$  Taylor series expansion fails!

$$H^{(\Gamma_0)} = \sum_i t_i ((\mathcal{X}_1 \otimes \mathcal{Y}_1) \otimes \cdots \otimes (\mathcal{X}_{N_m} \otimes \mathcal{Y}_{N_m}))_i^{(\Gamma_0)}$$

**NO !!**

Extension to nonrigid molecules

can be made



$\rho$ -dependent parameters like the Born-Oppenheimer approximation! We form a grid

$$H^{(\Gamma_0)} = \sum_i t_i(\rho) ((\mathcal{I}d_\rho \otimes \mathcal{Y}_\rho) \otimes \cdots \otimes (\mathcal{X}_{N_m} \otimes \mathcal{Y}_{N_m}))_i^{(\Gamma_0)}$$

Nonrigid part  $\omega \sim 10^2 \text{ cm}^{-1}$

Rigid part  $\omega \sim 10^3 \text{ cm}^{-1}$

Analogy with  $\rightarrow$

nuclei = slow motion

electron = fast motion

Quantum chemical calculations.....	OK
Nuclear motion Hamiltonian.....	OK
Solving the nuclear problem.....	??

# Step 2 - Solving the nuclear Schrödinger equation

## ➤ Eigenproblem

$$H\Psi = E\Psi$$

## ➤ Very few exactly solvable models with known, analytical solutions

## ➤ Need to find approximate solutions

- ✓ Approximate the wavefunctions: *variational calculations (part I.)*
- ✓ Approximate the Hamiltonian: *derivation of an effective model (part II.)*

# Part. I. Variational calculations

« *The curse of dimensionality* »

# Why does *ab initio* make sense?



Limitations of the traditional spectroscopic, effective approach



*Include most of the resonances between rovibrational states*

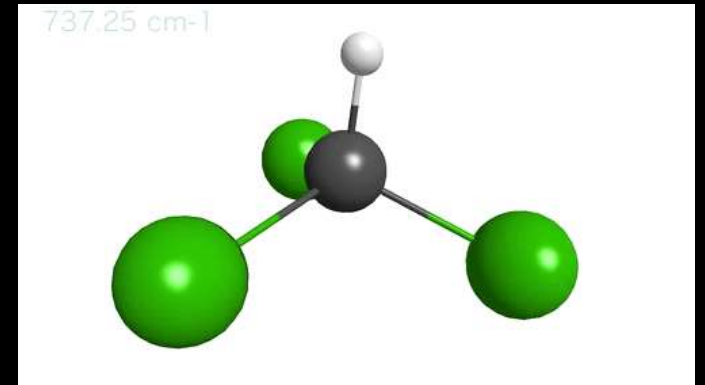
Example 1: For Titan modeling up to  $13400\text{ cm}^{-1}$ , 3800 vibrational  $\text{CH}_4$  sublevels were considered (only 100 from  $H_{\text{eff}}$ )

Example 2: For Exoplanets, more than 10 millions of ro-vibrational  $\text{CH}_4$  energy levels were computed

Example 3: For  $\text{CF}_4$  up to  $4000\text{ cm}^{-1}$ , about 800 vibrational sublevels were considered (only few ones analyzed from  $H_{\text{eff}}$ )

Example 4: For  $\text{SF}_6$  up to  $3000\text{ cm}^{-1}$ , about 2600 vibrational sublevels, 500 CB & HB (only few ones analyzed from  $H_{\text{eff}}$ )

# Solving the vibrational problem



The stationary SE is first solved for  $J=0$  by searching the eigenfunctions as

$$\Psi_{v,k}(\mathbf{X}) = \sum_i c_k^i \phi_{v,i}(\mathbf{X}; [p_1, p_2, \dots])$$

$k^{\text{th}}$  eigenvector

Expansion coefficients deduced from diagonalization

Primitive basis functions

External parameters (optional)

# Primitive functions: example

$$\Psi_{v,k}(\mathbf{X}) = \sum_i c_k^i \phi_{v,i}(\mathbf{X}; [p_1, p_2, \dots])$$

$\phi_{v,i}(\mathbf{X})$  = Harmonic oscillator function are KNOWN

... not “physical” functions BUT a combination of many HO functions

can describe properly the TRUE, UNKNOWN wavefunctions

= the primitive functions have to be conveniently chosen to converge rapidly calc.

# Matrix elements

The matrix elements of  $H$  in the primitive basis

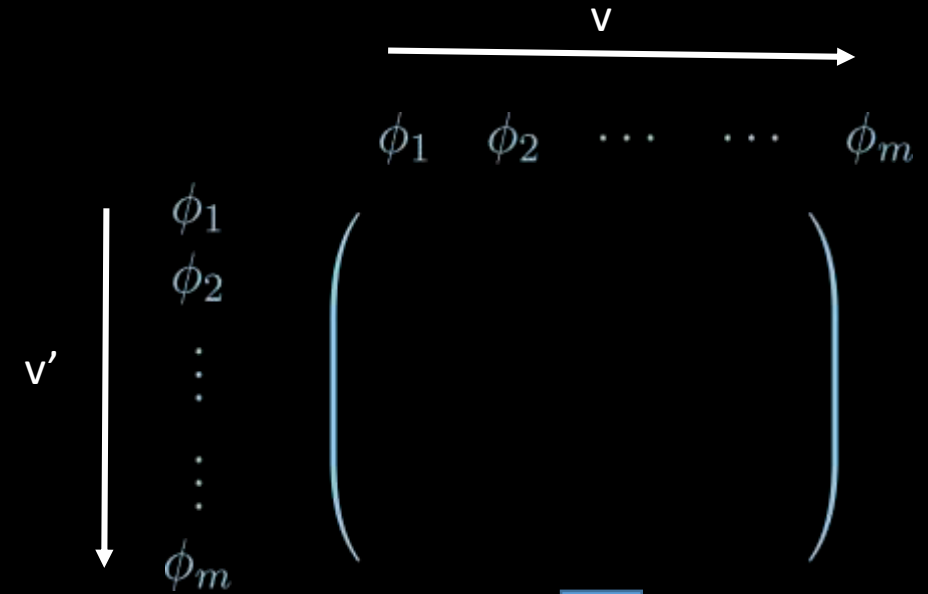
$$\int \phi_{v'}^*(\mathbf{X}) H \phi_v(\mathbf{X}) d\mathbf{X}$$

row

column

can be evaluated

- either analytically / algebraically → exact & fast but not flexible
- or numerically (quadrature) → much more flexible



Diagonalization =  
Energy levels



# Direct product primitive basis set

The simplest way to build a primitive vibrational basis consists in forming a direct product of  $3N-6$  functions

$$\phi_{\mathbf{v}}(\mathbf{X}) = \phi_{v_1}(X_1)\phi_{v_2}(X_2)\cdots\phi_{v_{3N-6}}(X_{3N-6}) \equiv |v_1 v_2 \cdots v_{3N-6}\rangle$$

*Note: non direct product basis sets are also possible*

Imagine 10 functions per degree of freedom

- ✓ Triatomic molecules: number of basis functions =  $10^3 \Rightarrow 0.008$  Gb to store the H matrix
- ✓ Tetraatomic molecules: number of basis functions =  $10^6 \Rightarrow 8$  Tb to store the H matrix in memory !
- ✓ Pentaatomic molecules: number of basis functions =  $10^9 \Rightarrow 8000000$  Tb to store the H matrix !!!

# Direct product primitive basis set

Typically, each time we add an atom, the Hamiltonian matrix is scaled by a factor 1000 without approximation!



Need to find compromises

A drastic dimensionality reduction is required

Several ways to proceed

# Pruning the basis

To drastically reduce dimensionality by several orders of magnitude, a "pruned basis" is introduced and defined by selecting only a limited set of relevant primitive vibrational functions

$$F_{\kappa}(r) \Leftrightarrow \sum_{i=1}^{3N-6} \kappa_i v_i \leq r \in \mathcal{F}(r)$$

Vibrational quantum number

Weight coefficients

Subspace spanned by the functions

with  $v_i = 0, \dots, r$

The dimension of the basis is reduced from  $\sim r^{(3N-6)}$  to  $\sim (3N - 6 + r)! / (3N - 6)! r!$

*Illustration : for a 5-atomic molecule, the number of basis functions is reduced from  $10^9$  to  $10^5$*

# Use of symmetry-adapted functions

The use of symmetry can reduce the dimension of the H matrix up to 1 order of magnitude

$$|v_1 v_2 \cdots v_{3N-6}\rangle \longrightarrow | \underbrace{v_1 v_2 \cdots v_{3N-6}}_{\text{Not good quantum numbers}}; \underbrace{C_v \sigma_v}_{\text{Each symmetry block is characterized by an irrep}} \rangle$$

Trivial for asymm. tops  
More tedious otherwise

*A course on group theory is required here...*



Pruning and symmetry may not be sufficient

# Contracted basis functions

We can consider *reduced* Hamiltonians and solve SE of lower dimension before gathering all eigenfunctions

Imagine a full 6D Hamiltonian

$$H(X_1, Y_1; X_2, Y_2; X_3, Y_3; X_4, Y_4; X_5, Y_5; X_6, Y_6)$$

Let 2 subgroups as

$$G_1 = \{X_1, Y_1; X_2, Y_2; X_3, Y_3; X_4, Y_4\}$$

$$G_2 = \{X_5, Y_5; X_6, Y_6\}$$

such that

$$H = H_{G_1} + H_{G_2} + H_{G_1-G_2}$$

# Contracted basis functions

We solve separately the SE

$$H_{G_i} \Psi_{G_i} = E_{G_i} \Psi_{G_i}$$

$$\Psi_{G_i} = \mathbf{U}_{G_i}^{-1} \Phi_{G_i} \quad \text{with} \quad \mathbf{U}_{G_i} \in \mathbb{R}^{m_i \times m_i}$$

In practice, we retain only  $n_i \ll m_i$  eigenvectors to reduce dimensionality without almost no loss of precision

$$\begin{array}{c} \phi_{1G} \\ \phi_{2G} \\ \vdots \\ \vdots \\ \phi_{mG} \end{array} \left( \begin{array}{cccc} \Psi_{1G} & \Psi_{2G} & \cdots & \cdots & \Psi_{mG} \\ \mathbf{U}_{G_i} \in \mathbb{R}^{m_i \times n_i} \end{array} \right)$$



# Contracted basis functions

- In the primitive basis  $\Phi_{G_1} \times \Phi_{G_2}$  the Hamiltonian matrix is huge, making calculations not tractable
- In the eigenvector basis  $\Psi_{G_1} \times \Psi_{G_2}$  the matrix representation of  $H = H_{G_1} + H_{G_2} + H_{G_1-G_2}$  reads

$$\mathbf{H} = \underbrace{\mathbf{E}_{G_1} + \mathbf{E}_{G_2}}_{\text{Diagonal matrix}} + \mathbf{U}^{-1} \mathbf{h} \mathbf{U}$$

Matrix of  $H_{G_1-G_2}$  in the primitive basis = huge !

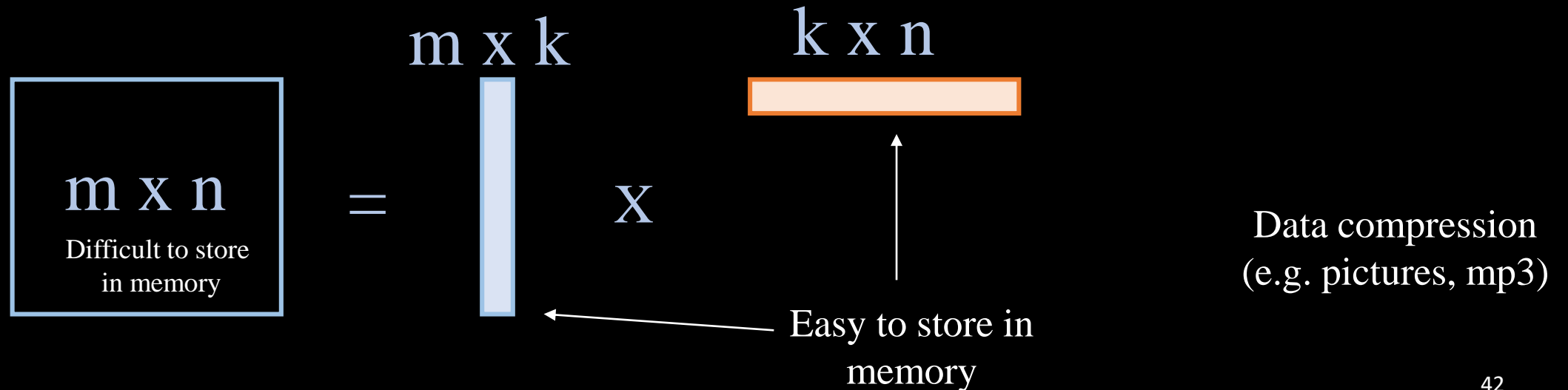
Matrix in the eigen-basis = small !

*Ex:  $H_{G_1}$ =Stretch,  $H_{G_2}$ =Bend*

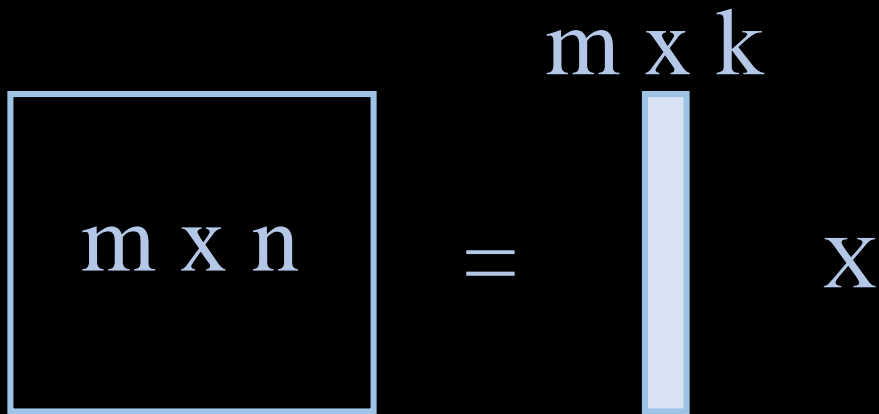
*$H_{G_1}$ =molecule 1,  $H_{G_2}$ = molecule 2  $\rightarrow H = \text{van der Waals complex}$*

# Reducing the memory cost of the matrix multiplication

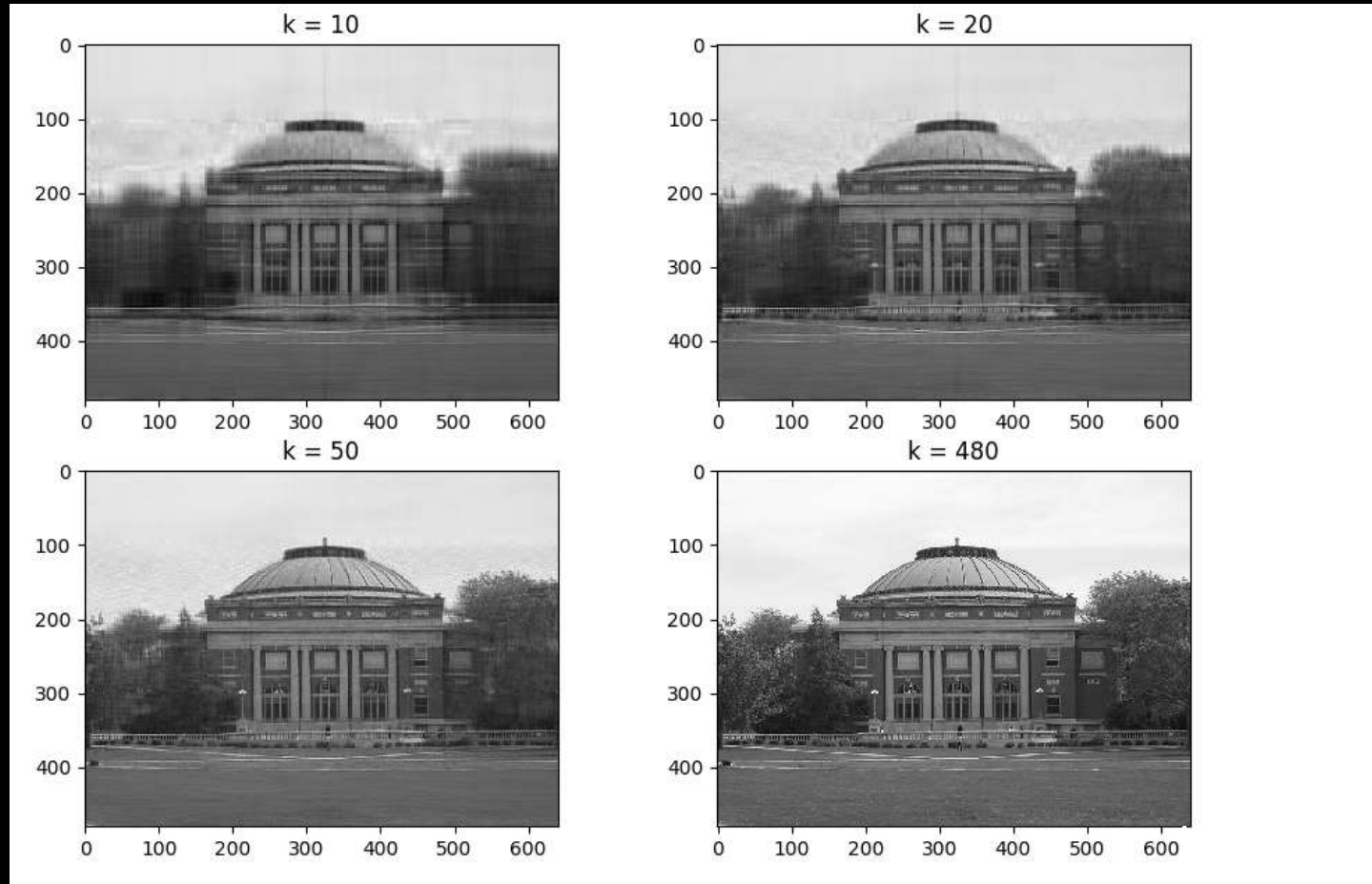
- Principal Component Analysis (PCA), SVD
- Low-rank tensor approximations (canonical polyadic, Tucker format, tensor train decomposition) (*MCTDH-type calculations*)



# Reducing the memory cost / compromise with accuracy



$m=n=k=480 = \text{Full rank here}$



# Choice of the eigensolver

If at the end of the procedure ....

- $\text{Dim}(\text{Matrix}) < 100000 \times 100000$  → direct eigensolvers (Jacobi, householder, etc): LAPACK library  
Fit in memory
- $\text{Dim}(\text{Matrix}) > 100000 \times 100000$  → iterative methods (Lanczos/Arnoldi) will be preferred  
Does not fit in memory

# Lanczos: basic principles

- Avoids diagonalization of huge matrices - Not demanding
- The basic idea is to transform the **HUGE** H matrix into a tri-diagonal matrix

$$Q^t H Q = T$$

Lanczos vectors

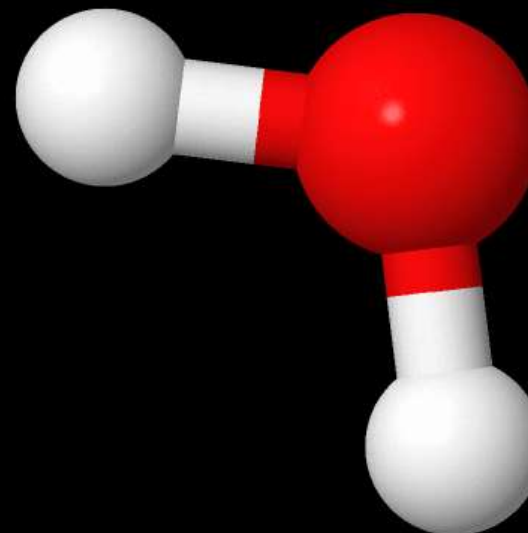
Tri-diagonal, same eigenvalues as H

- T is built iteratively (Lanczos iterations) - The exact arithmetic algorithm is very easy to implement
- The eigenvalues converge rapidly (from the bottom and the top) if the spectrum is not too dense
- .... *But to be used with care* .... the orthogonality of the Lanczos vectors may be lost due to rounding errors

# Vibrational part solved

## Next step : introduction of the molecular rotation

3 additional degrees of freedom



Not good quantum numbers

Variational calculations

$$|\gamma, J, C\rangle = |v_1 v_2 \cdots v_{3N-6}; C_v\rangle \otimes |J, (K); C_r\rangle$$

Block diagonal

To be further reduced!

!!! Huge dimension !!!

# Introduction of the molecular rotation

- For high  $J$  calculations, I have introduced so-called *reduced* vibrational eigenfunctions of lower dimension

$$\Psi_{v,i}^{(C_v)} = \sum_{j \in \mathcal{F}_p} U_{j,i}^{(C_v)} \phi_{v,j}^{(C_v)} \quad \mathbf{U} \in \mathbb{R}^{M \times M}$$

↓

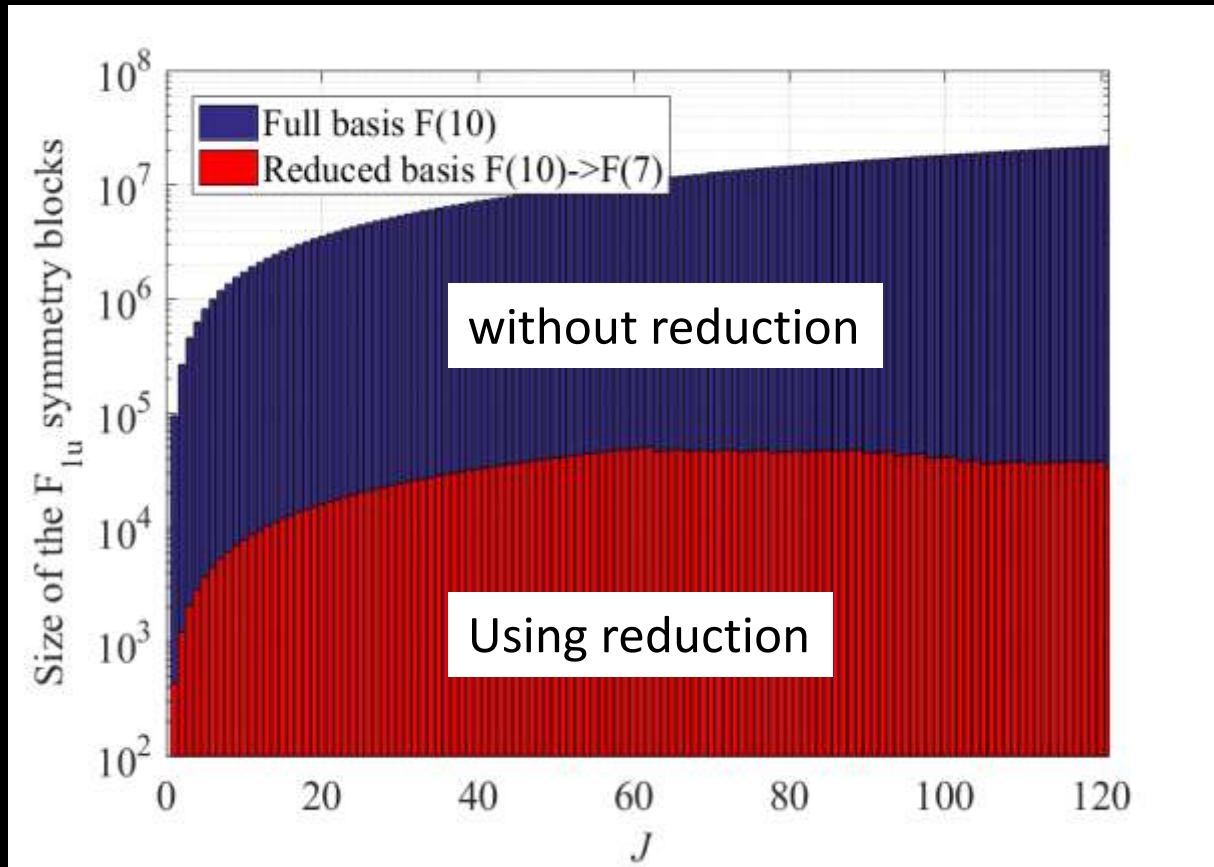
$$\Psi_{v,i}^{(C_v)} = \sum_{j \in \mathcal{F}_{p'}} U_{j,i}^{(C_v)} \phi_{v,j}^{(C_v)} + \boxed{\sum_{k \notin \mathcal{F}_{p'}} U_{k,i}^{(C_v)} \phi_{v,k}^{(C_v)}} \quad \text{Small in the range of OBS}$$

↓

$$\Psi_{\text{app},v,i}^{(C_v)} = \sum_{j \in \mathcal{F}_{p'}} U_{\text{app},j,i}^{(C_v)} \phi_{v,j}^{(C_v)} \quad \mathbf{U}_{\text{app}} \in \mathbb{R}^{M' \times M'} \quad (M' \ll M)$$

↙ Gram-Schmidt

# Illustration on the first full-dimensional quantum mechanical calculations for a 7-atomic molecule: Case of SF<sub>6</sub>



## Key results

- 2600 calc. band centers up to 3000 cm<sup>-1</sup>
- 3 millions of levels up to  $J=120$
- 6 billion lines in RT spectra up to 3000 cm<sup>-1</sup>



# Quality of the calculation: Precision *versus* Accuracy

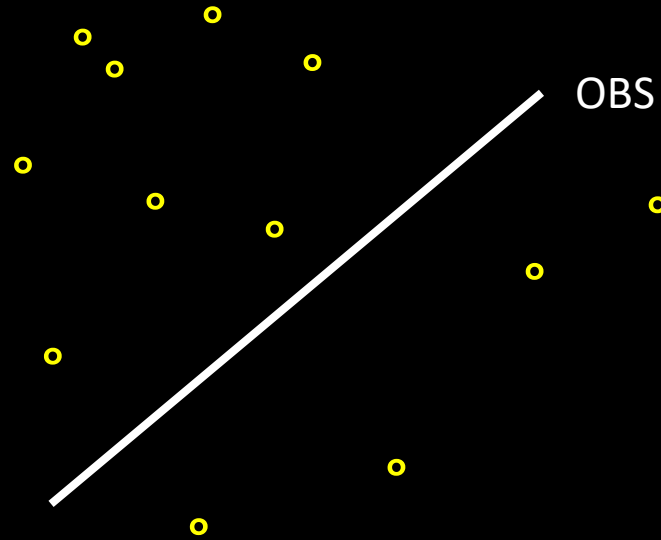
➤ 2 ways that scientists think about error

- ✓ Precision is how close different calculations are to each other
- ✓ Accuracy is how close a calculation is to experiment

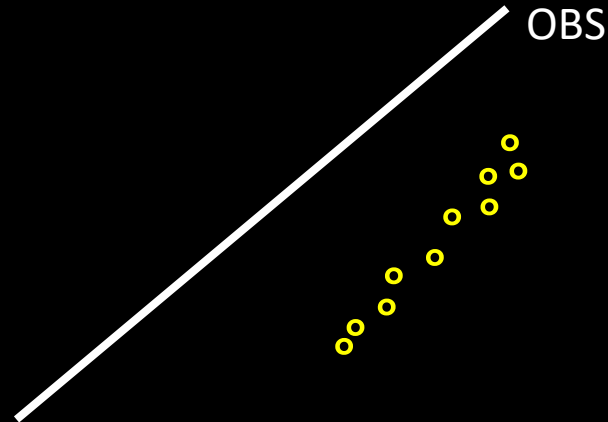
We have to control the precision of calculation to reach high accuracy

# Precision *versus* Accuracy

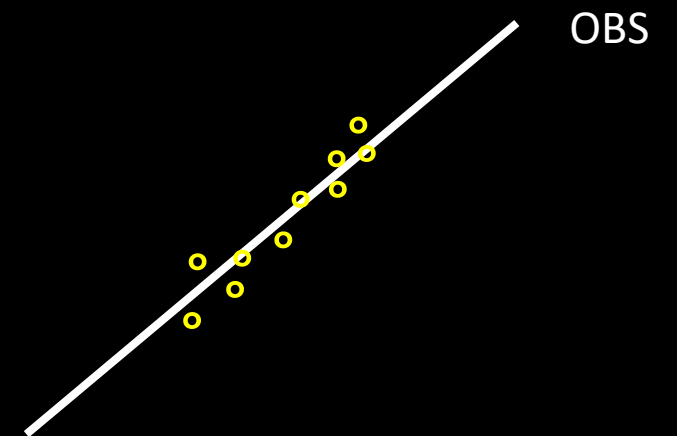
*Not precise, not accurate*



*precise, not accurate*



*precise, accurate*



*Non converged energy levels  
or errors during calculations (loss of  
precision, bug, etc)*

*Good calculation  
but « bad » PES*

*Good calculation  
using a refined or accurate PES*

# Accuracy of *ab initio* calculations

## Line positions

'Pure' *ab initio* PES  
~ 0.01 - 0.1-10 cm<sup>-1</sup>  
rotation      vibration



Refined PES  
~ 0.001 - 0.01 cm<sup>-1</sup>  
rotation      vibration

Geometry -  
Force constants

## Line intensities

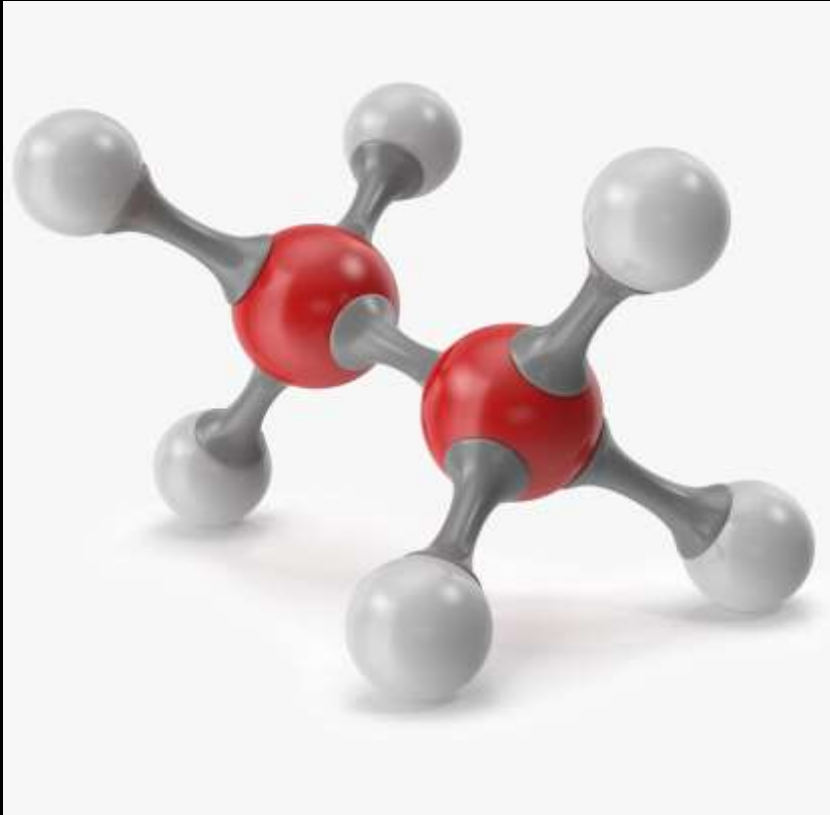
*ab initio* DMS  
~ few % on strong lines

Ex. 1-5% for (stable) strong lines with respect  
to the best accurate experimental  
works (CRDS,FTS)

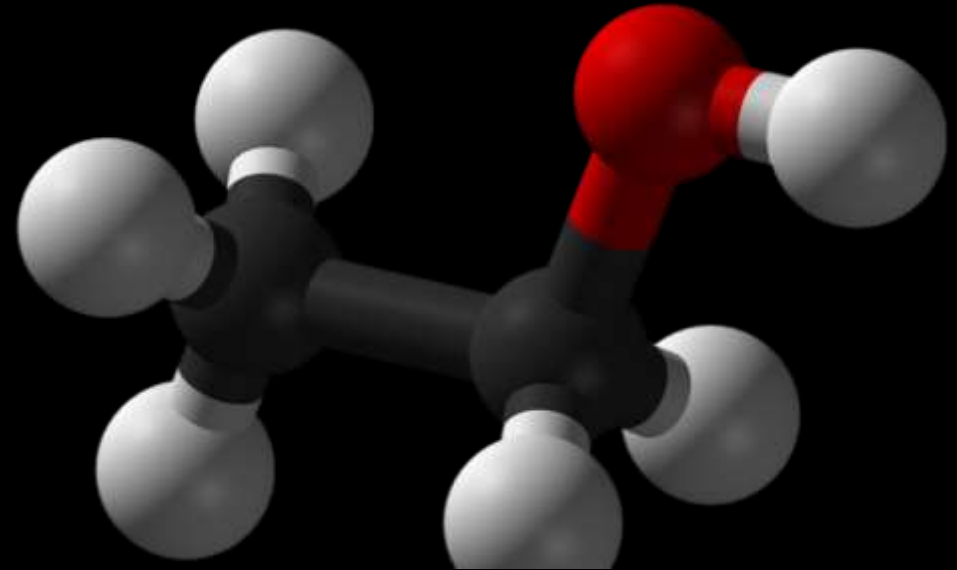
In general, much more consistent than  
those derived from empirical models  
for large spectral ranges

# Finally, why such theoretical developments?

- Example 1 : calculation of the molecular line list for methanol & ethane

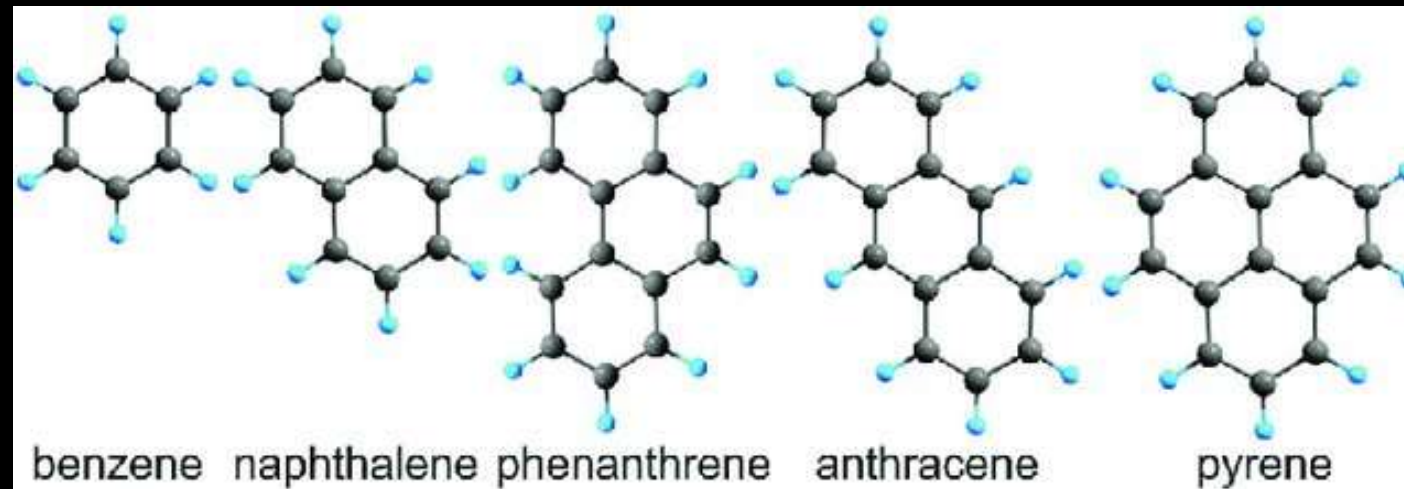


Many degrees of freedom + large amplitude → great challenge



# Finally, why such theoretical developments?

- Example 2: studying small PAH (Polycyclic Aromatic Hydrocarbons) in a near future, why not?



High symmetry

PES available

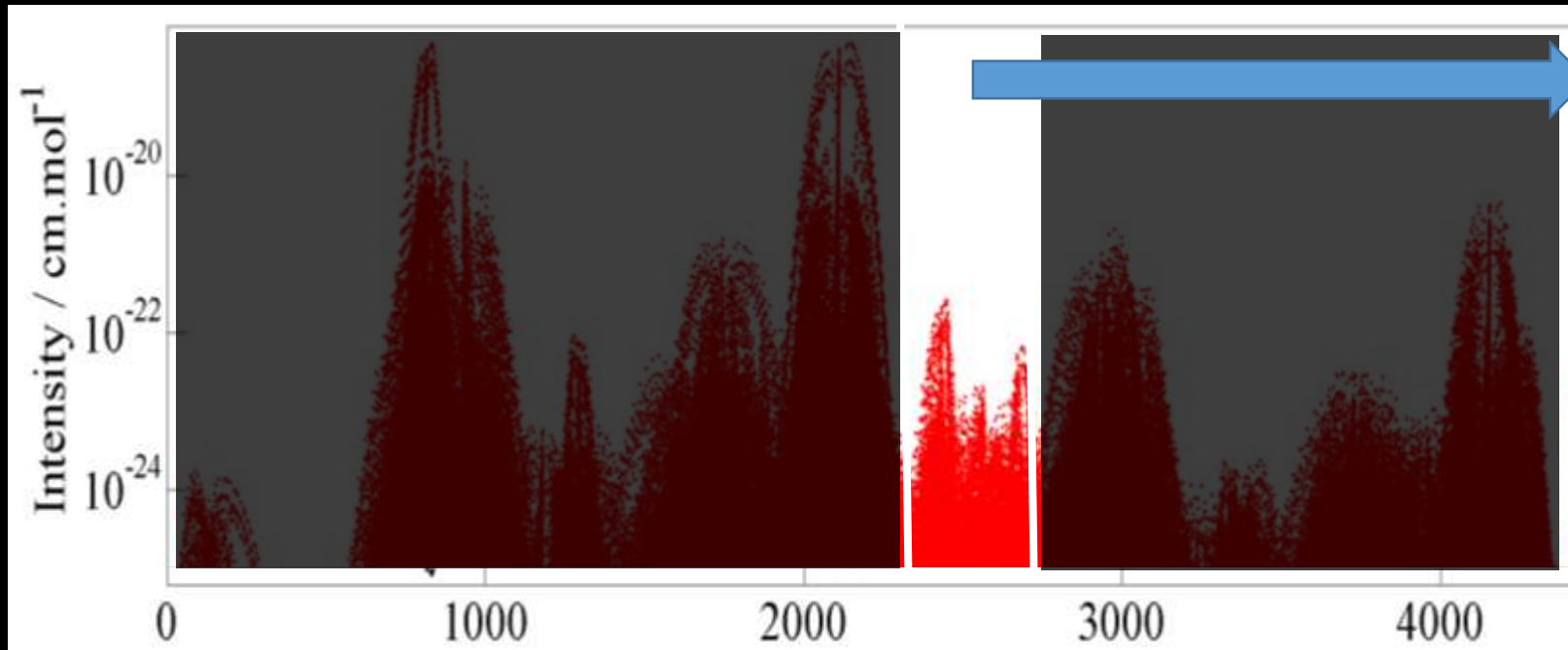
# At this stage

- (1) PES & DMS ..... OK (commercial codes)
- (2) Solving the Schrödinger equation ..... OK (home-made codes)

(1) + (2) = theoretical line lists

DMS (quantum chemists) + variational eigenfcts

# Converging integrated intensity for consistent opacity calculation



*Convergence is governed by 3 parameters*

1. J angular rot. Momentum
2. E<sub>low</sub> value for including HB
3. I<sub>cutoff</sub> value

**WARNING**

Need to be converged simultaneously !!

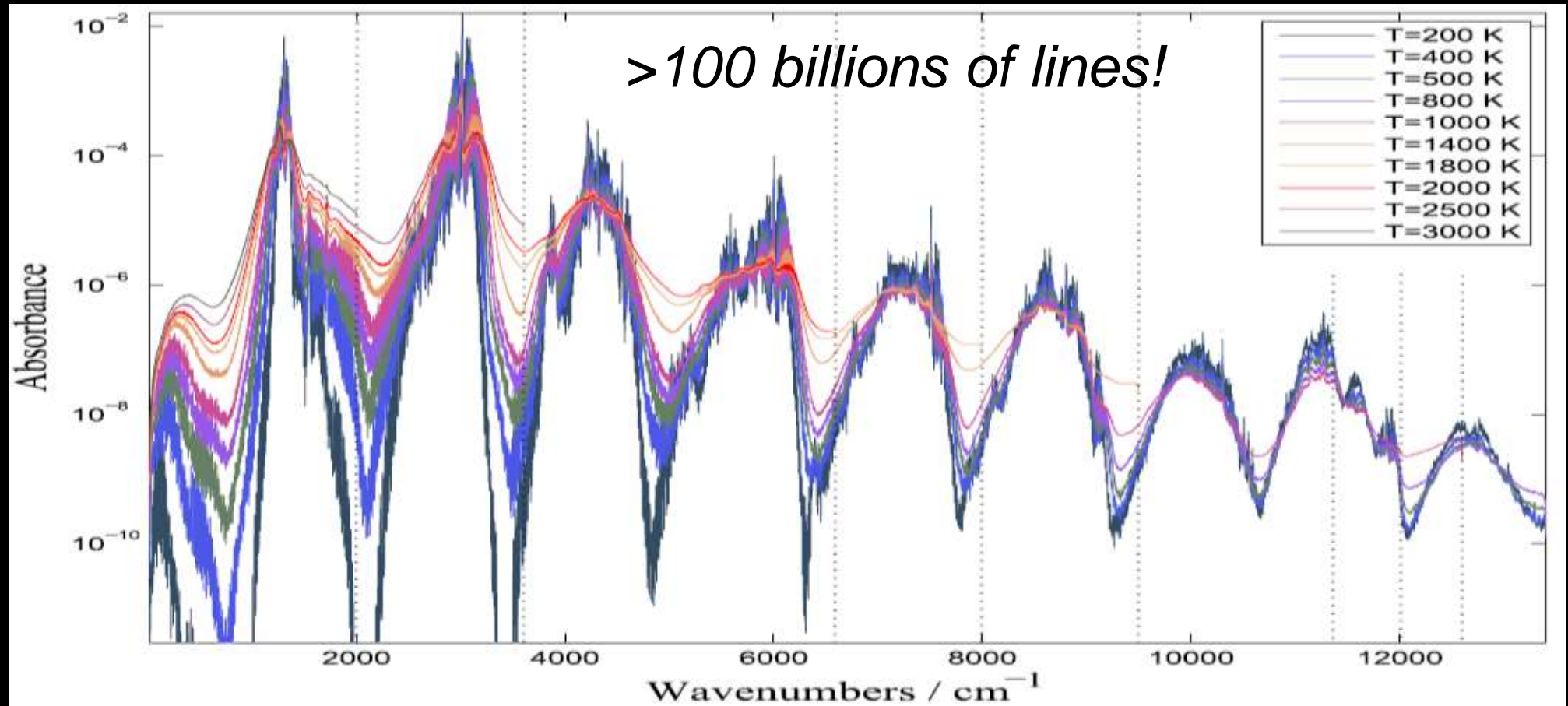
The “E<sub>low</sub>” parameter which is used to change  $T$  is for sure the most limiting factor in **empirical effective models** because it requires knowledge of highly-excited vibrational levels

# Example: methane spectra

Titan



Exoplanètes

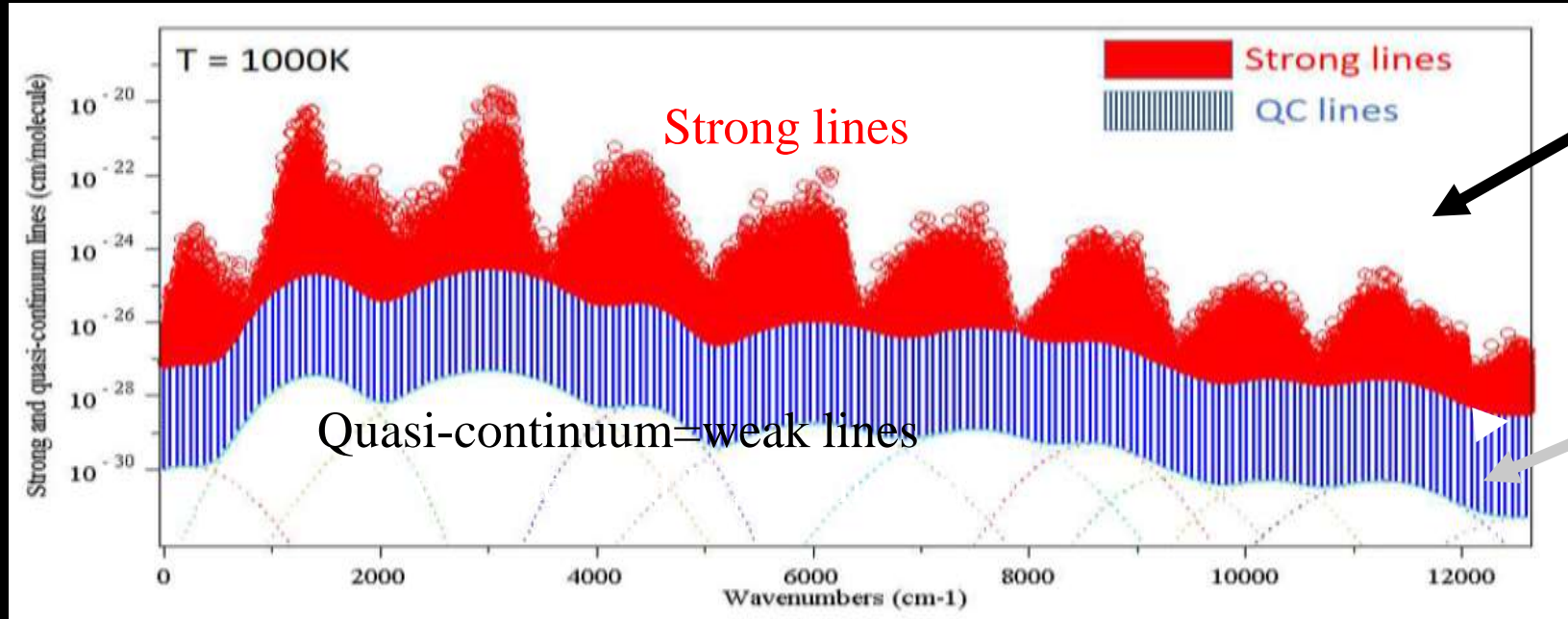




# Managing the huge number of lines

Q: How to manage billions of lines?

R: data compression using “superlines”: from several billions to few millions !! The user is now HAPPY ☺

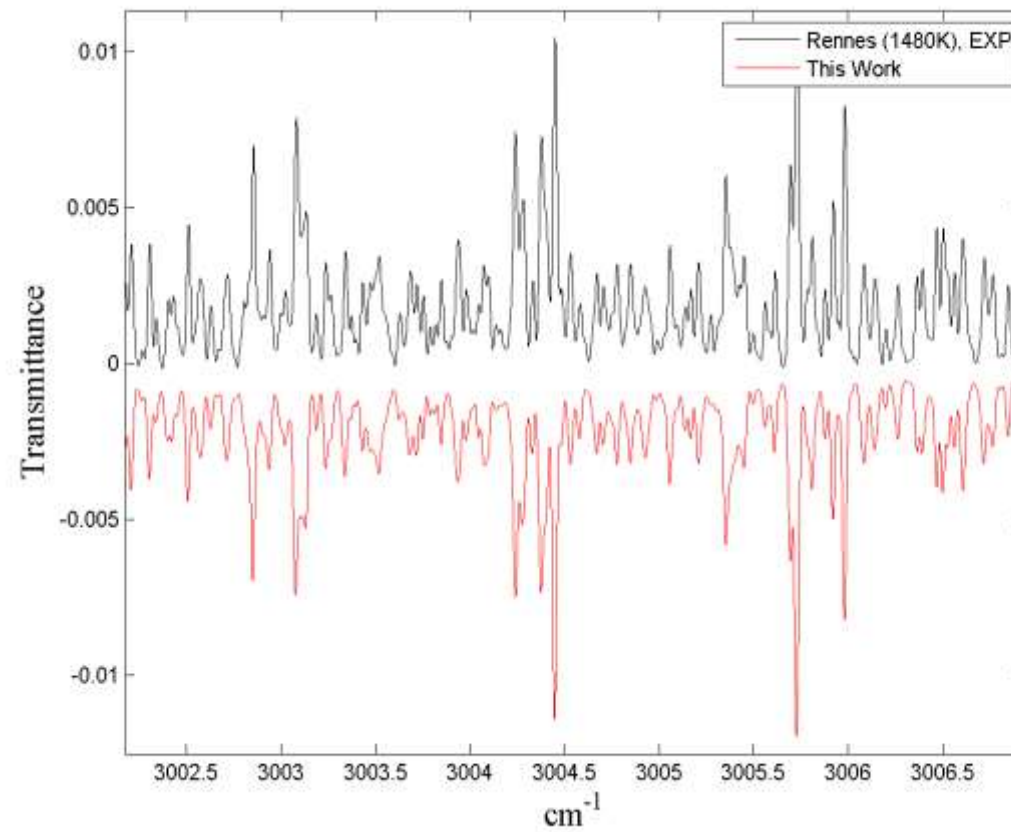
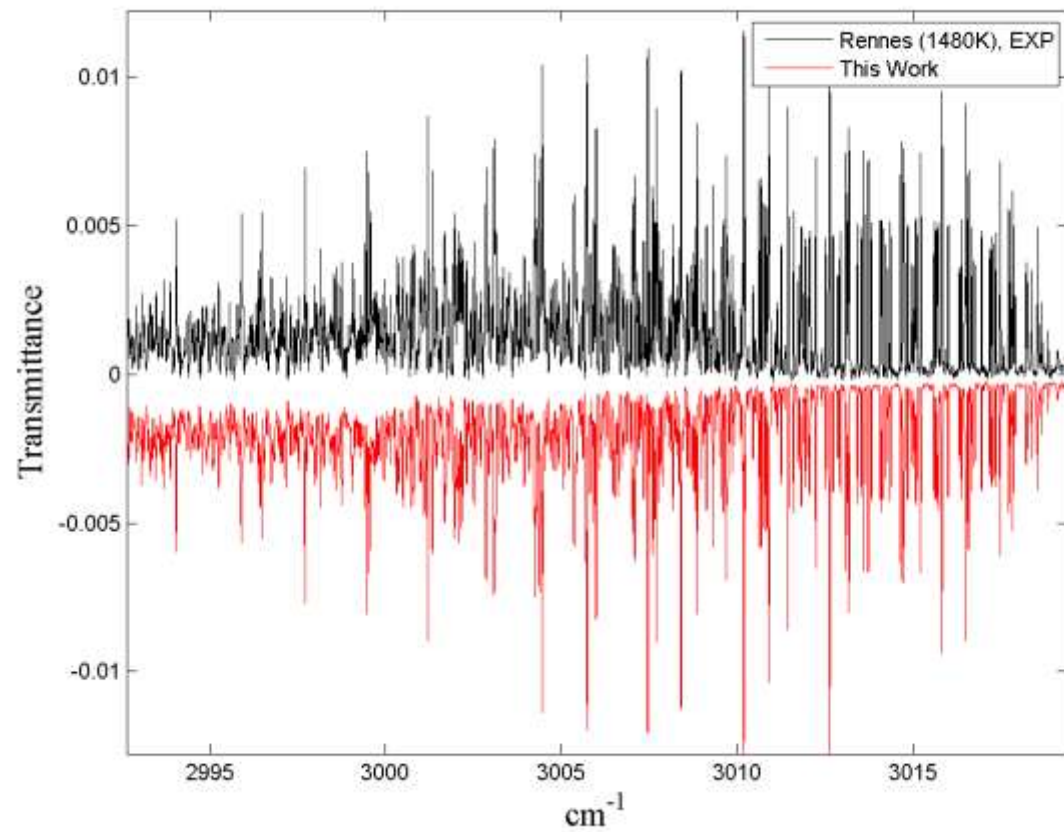


“Usual” treatment  
(few Mb)

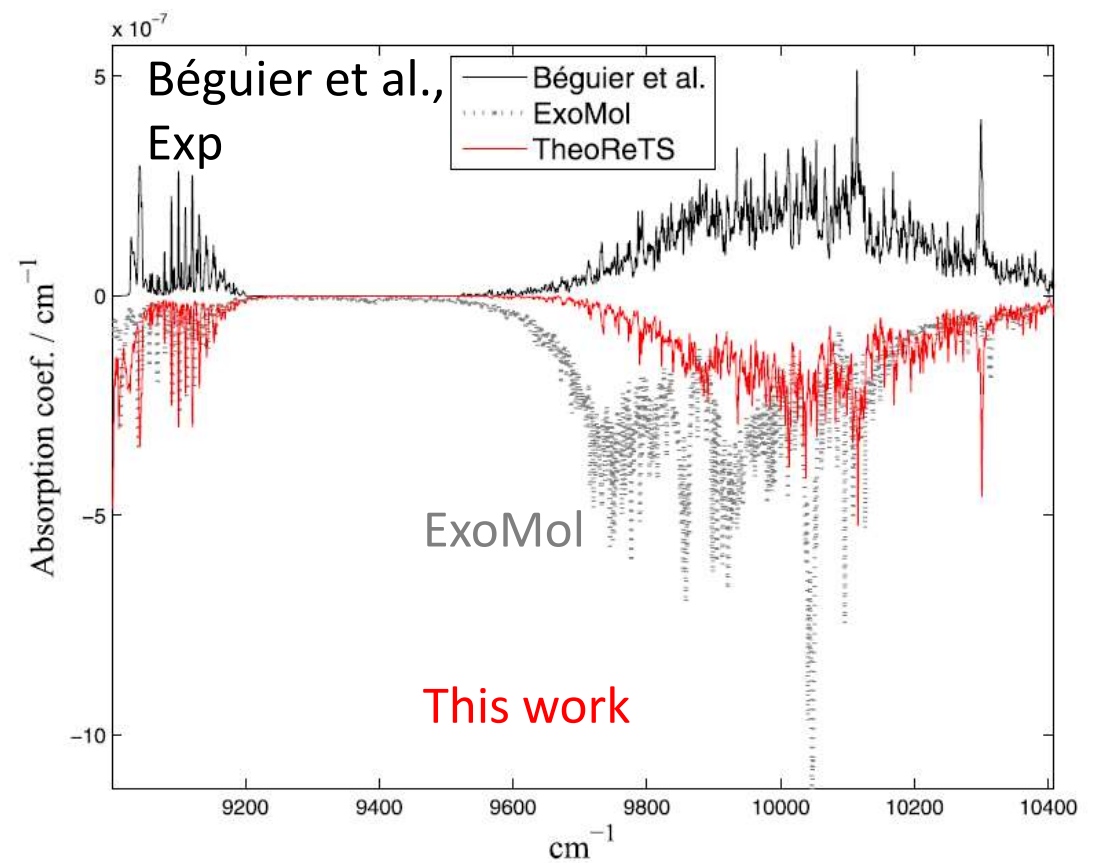
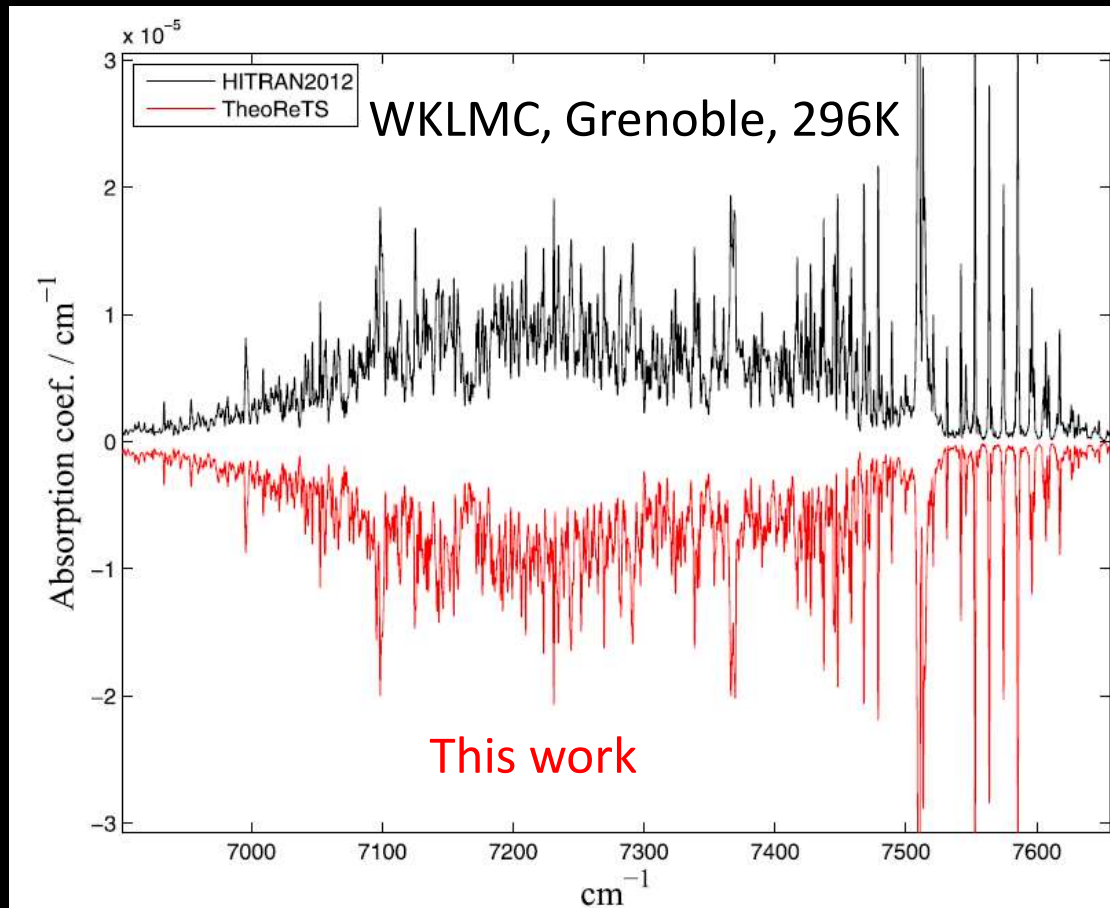
“Superline”  
Treatment  
(several Tb to few Mb)

# Validation @3 $\mu$

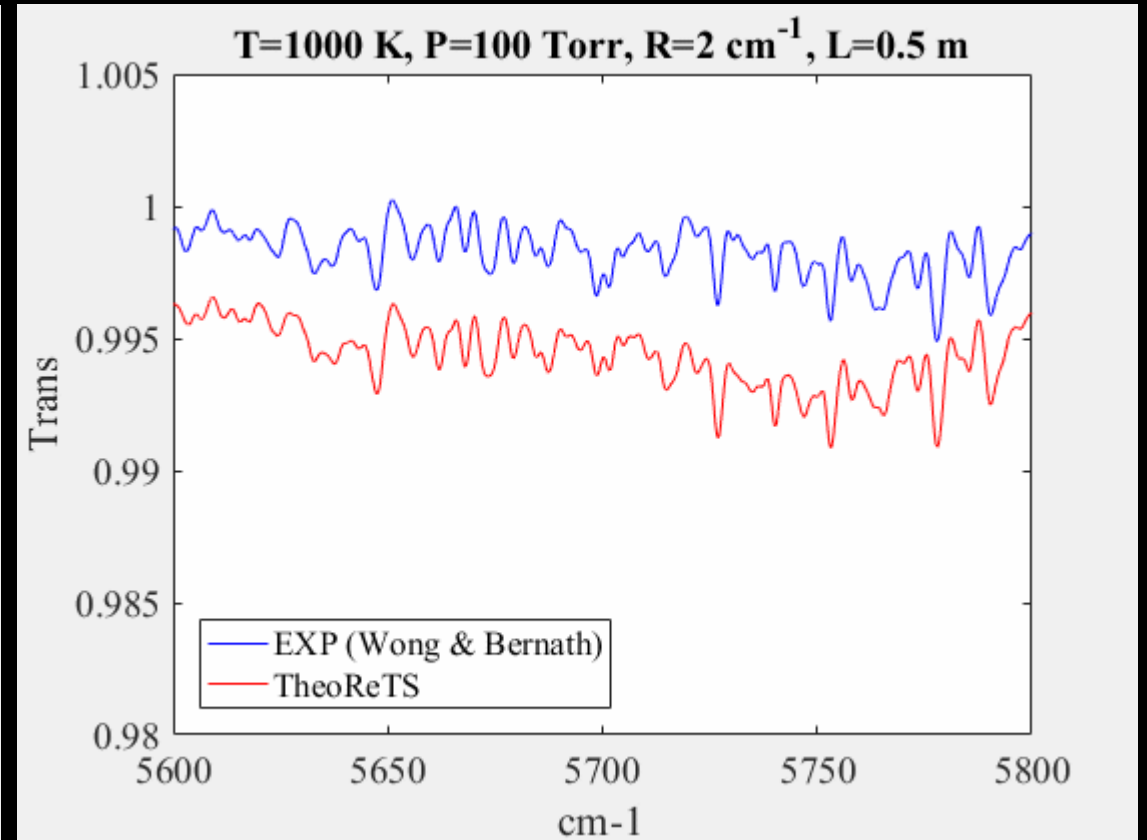
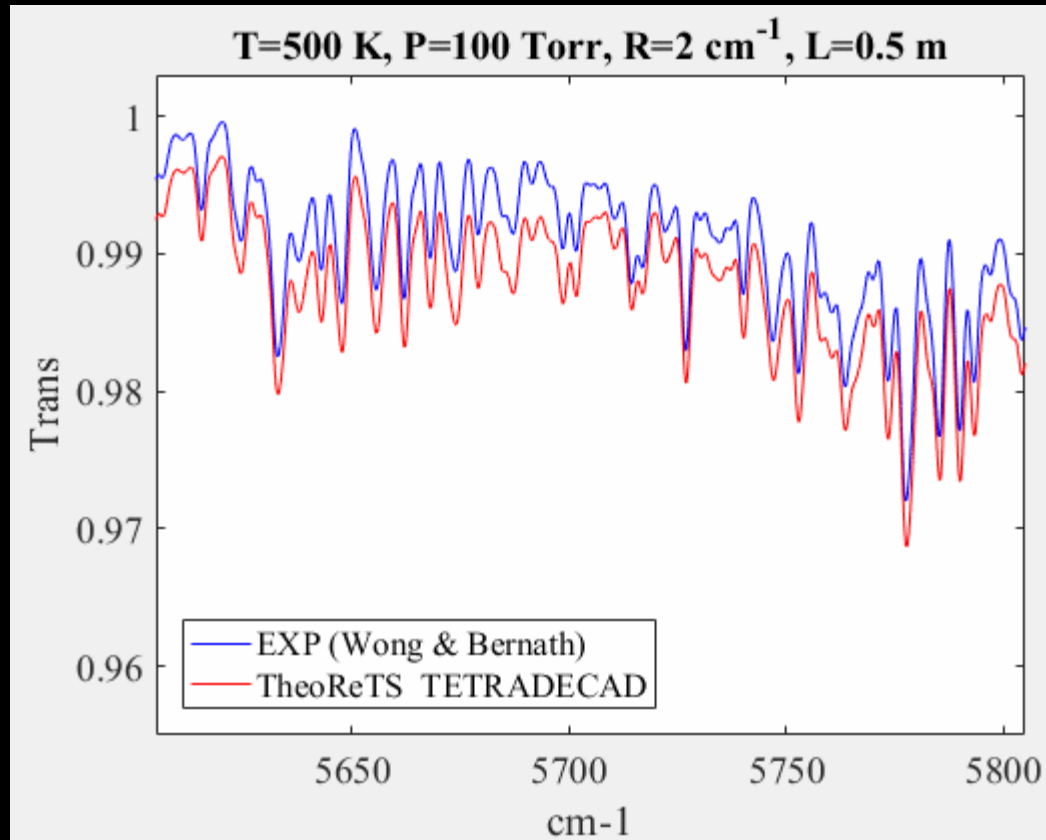
CH<sub>4</sub> EXP : R. Georges et al. (Rennes) 1480K



# Validation @ 1.3 & 1 $\mu$

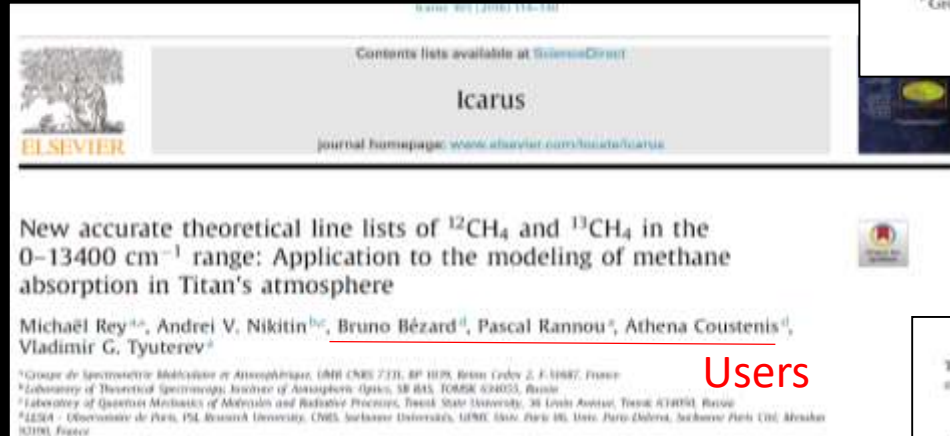


# Validation @ high T (500 and 1000 K)



# Major methane publications

<http://theorets.univ-reims.fr>



Contents lists available at ScienceDirect  
**Icarus**  
journal homepage: [www.elsevier.com/locate/icarus](http://www.elsevier.com/locate/icarus)

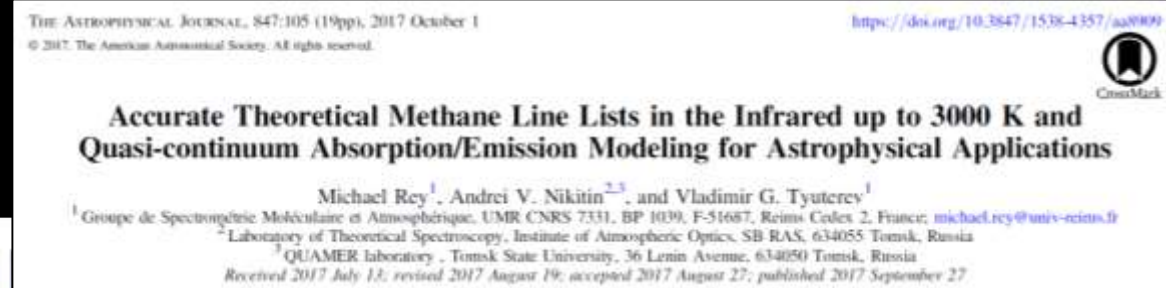
**New accurate theoretical line lists of  $^{12}\text{CH}_4$  and  $^{13}\text{CH}_4$  in the 0–13400  $\text{cm}^{-1}$  range: Application to the modeling of methane absorption in Titan's atmosphere**

Michaël Rey<sup>a,c</sup>, Andrei V. Nikitin<sup>b,c</sup>, Bruno Bézard<sup>d</sup>, Pascal Rannou<sup>e</sup>, Athena Coustenis<sup>d</sup>, Vladimir G. Tyuterev<sup>a</sup>

<sup>a</sup>Groupe de Spectrométrie Moléculaire et Atmosphérique, UMR CNRS 7331, BP 1039, Reims Cedex 2, F-51687, France  
<sup>b</sup>Laboratory of Theoretical Spectroscopy, Institute of Atmospheric Optics, SB RAS, TOMSK 634055, Russia  
<sup>c</sup>Laboratory of Quantum Mechanics of Molecules and Radiative Processes, Tomsk State University, 36 Lenin Avenue, Tomsk 634051, Russia  
<sup>d</sup>LESIA – Observatoire de Paris, PSL Research University, CNRS Sorbonne Université, UMR 8150, Observatoire de Paris, 91196, Paris Cedex 12, France  
<sup>e</sup>OSIRIS – Observatoire de Paris, PSL Research University, CNRS Sorbonne Université, UMR 8150, Observatoire de Paris, 91196, Paris Cedex 12, France

Users

Validation Titan & high T



THE ASTROPHYSICAL JOURNAL, 847:105 (19pp), 2017 October 1  
© 2017. The American Astronomical Society. All rights reserved.  
<https://doi.org/10.3847/1538-4357/aa8009>

**Accurate Theoretical Methane Line Lists in the Infrared up to 3000 K and Quasi-continuum Absorption/Emission Modeling for Astrophysical Applications**

Michael Rey<sup>1</sup>, Andrei V. Nikitin<sup>2,3</sup>, and Vladimir G. Tyuterev<sup>1</sup>

<sup>1</sup>Groupe de Spectrométrie Moléculaire et Atmosphérique, UMR CNRS 7331, BP 1039, F-51687, Reims Cedex 2, France; [michael.rey@univ-reims.fr](mailto:michael.rey@univ-reims.fr)  
<sup>2</sup>Laboratory of Theoretical Spectroscopy, Institute of Atmospheric Optics, SB RAS, 634055 Tomsk, Russia  
<sup>3</sup>QUAMER laboratory, Tomsk State University, 36 Lenin Avenue, 634050 Tomsk, Russia  
Received 2017 July 13; revised 2017 August 19; accepted 2017 August 27; published 2017 September 27



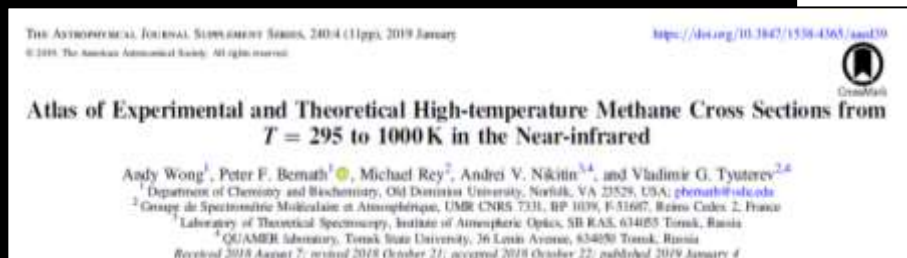
THE ASTROPHYSICAL JOURNAL SUPPLEMENT SERIES, 247:55 (19pp), 2020 April  
© 2020. The American Astronomical Society. All rights reserved.  
<https://doi.org/10.3847/1538-4367/ab7a1a>

**An Accurate, Extensive, and Practical Line List of Methane for the HITEMP Database**

Robert J. Hargreaves<sup>1</sup>, Joshi E. Gordon<sup>1</sup>, Michael Rey<sup>2</sup>, Andrei V. Nikitin<sup>3</sup>, Vladimir G. Tyuterev<sup>2,4</sup>, Roman V. Kochanov<sup>3,4</sup>, and Laurence S. Rothman<sup>1</sup>

<sup>1</sup>Center for Astrophysics | Harvard & Smithsonian, Atomic and Molecular Physics Division, 60 Garden Street, Cambridge, MA 02138, USA  
[robert.hargreaves@csa.harvard.edu](mailto:robert.hargreaves@csa.harvard.edu)  
<sup>2</sup>Groupe de Spectrométrie Moléculaire et Atmosphérique, UMR CNRS 7331, BP 1039, F-51687, Reims Cedex 2, France  
<sup>3</sup>V.E. Zuev Institute of Atmospheric Optics, Laboratory of Theoretical Spectroscopy, Russian Academy of Sciences, 1 Akademicheskoy Avenue, 634055 Tomsk, Russia  
<sup>4</sup>QUAMER laboratory, Tomsk State University, 36 Lenin Avenue, 634050 Tomsk, Russia  
Received 2020 January 13; revised 2020 February 18; accepted 2020 February 24; published 2020 April 1

Integrated in the HITEMP database



THE ASTROPHYSICAL JOURNAL SUPPLEMENT SERIES, 240:4 (11pp), 2019 January  
© 2019. The American Astronomical Society. All rights reserved.  
<https://doi.org/10.3847/1538-4367/aae139>

**Atlas of Experimental and Theoretical High-temperature Methane Cross Sections from  $T = 295$  to  $1000$  K in the Near-infrared**

Andy Wong<sup>1</sup>, Peter F. Bernath<sup>1</sup>, Michael Rey<sup>2</sup>, Andrei V. Nikitin<sup>3,4</sup>, and Vladimir G. Tyuterev<sup>2,4</sup>

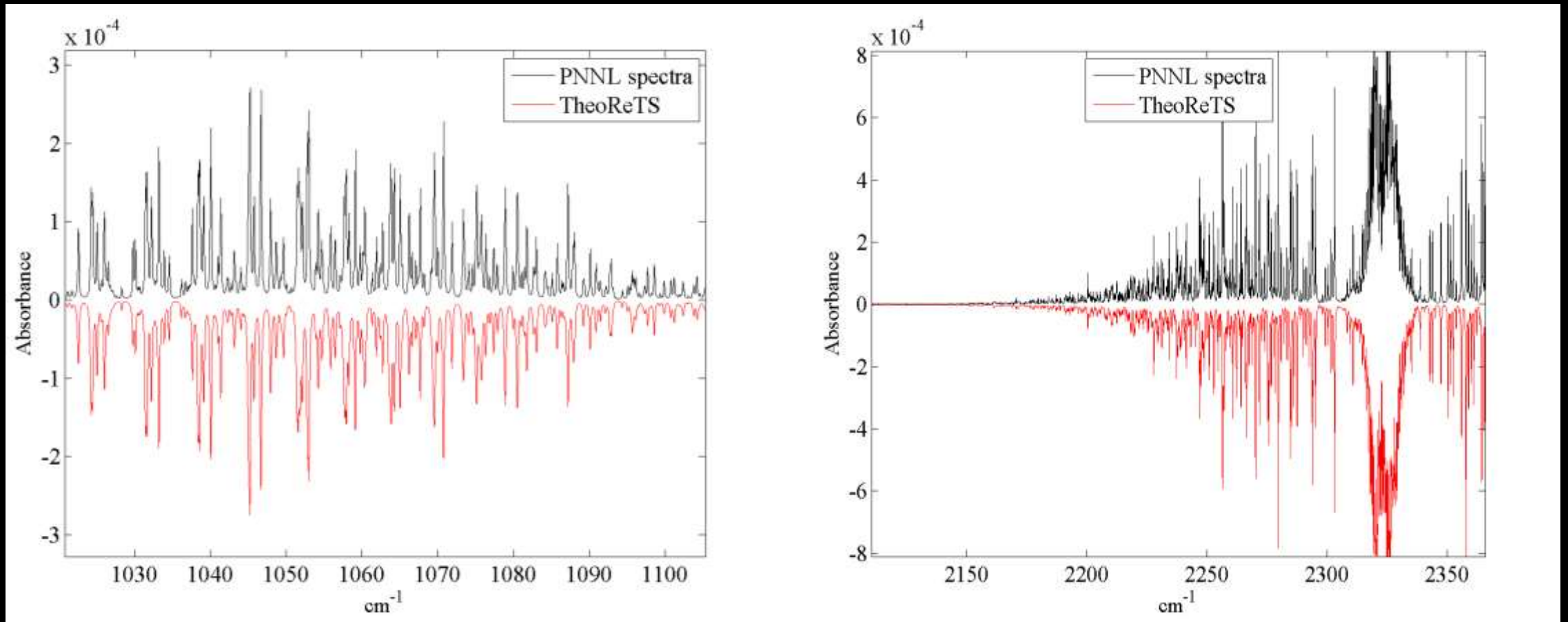
<sup>1</sup>Department of Chemistry and Biochemistry, Old Dominion University, Norfolk, VA 23529, USA; [pbernath@odu.edu](mailto:pbernath@odu.edu)  
<sup>2</sup>Groupe de Spectrométrie Moléculaire et Atmosphérique, UMR CNRS 7331, BP 1039, F-51687, Reims Cedex 2, France  
<sup>3</sup>Laboratory of Theoretical Spectroscopy, Institute of Atmospheric Optics, SB RAS, 634055 Tomsk, Russia  
<sup>4</sup>QUAMER laboratory, Tomsk State University, 36 Lenin Avenue, 634050 Tomsk, Russia  
Received 2018 August 7; revised 2018 October 21; accepted 2018 October 22; published 2019 January 4

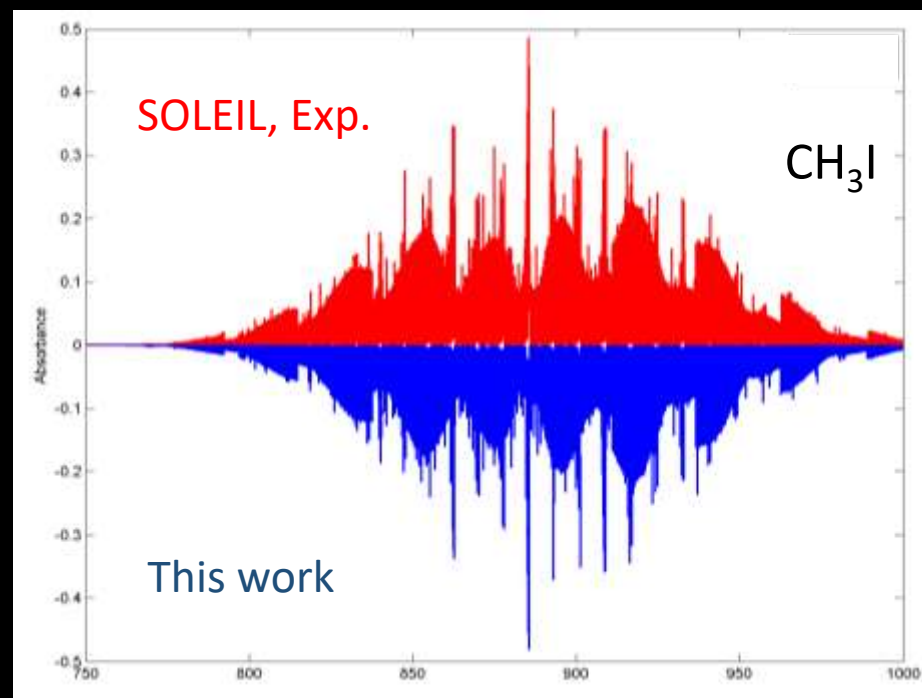
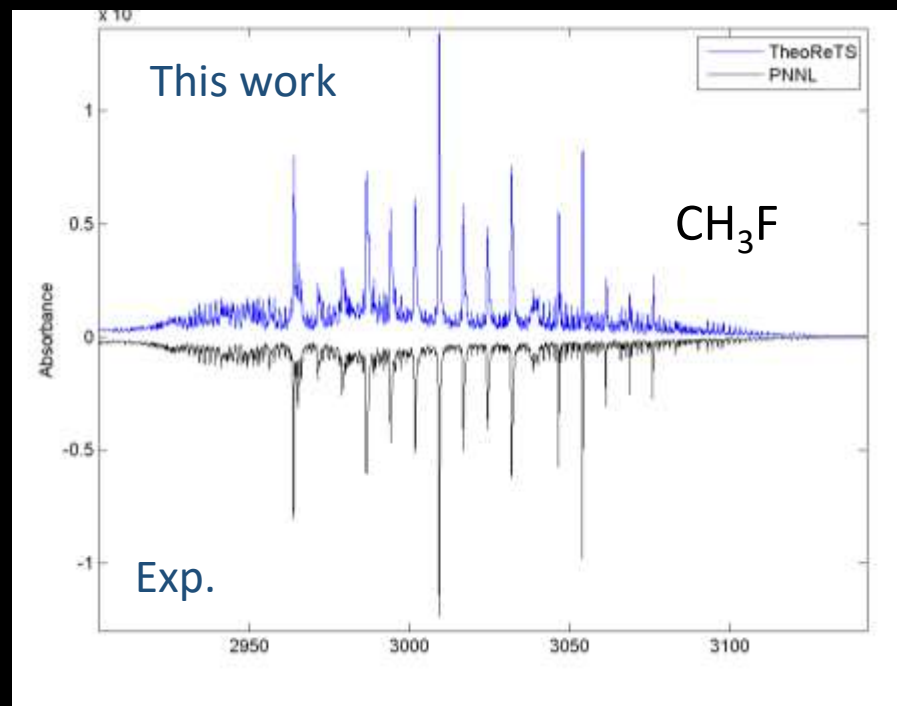
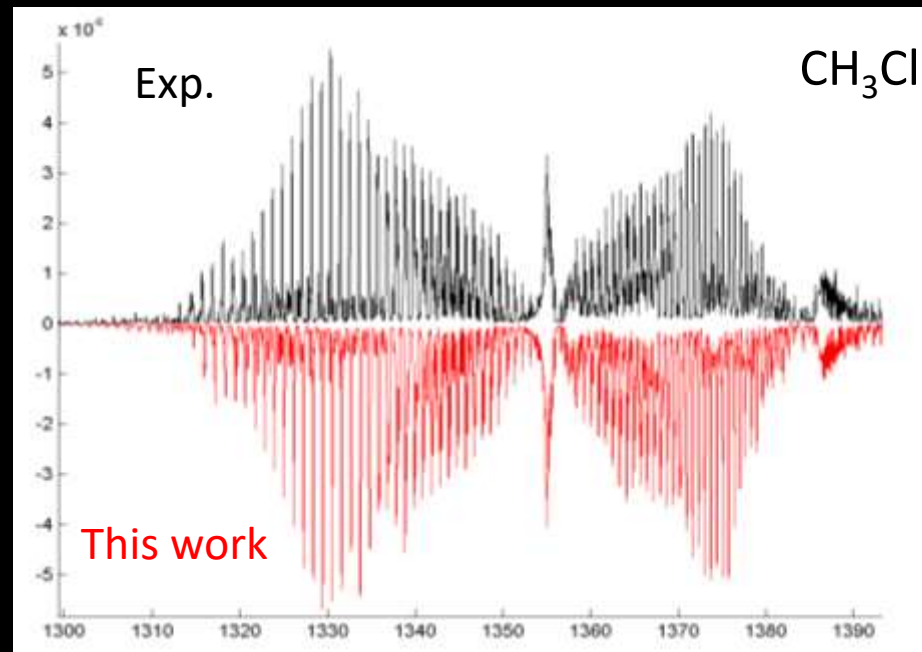
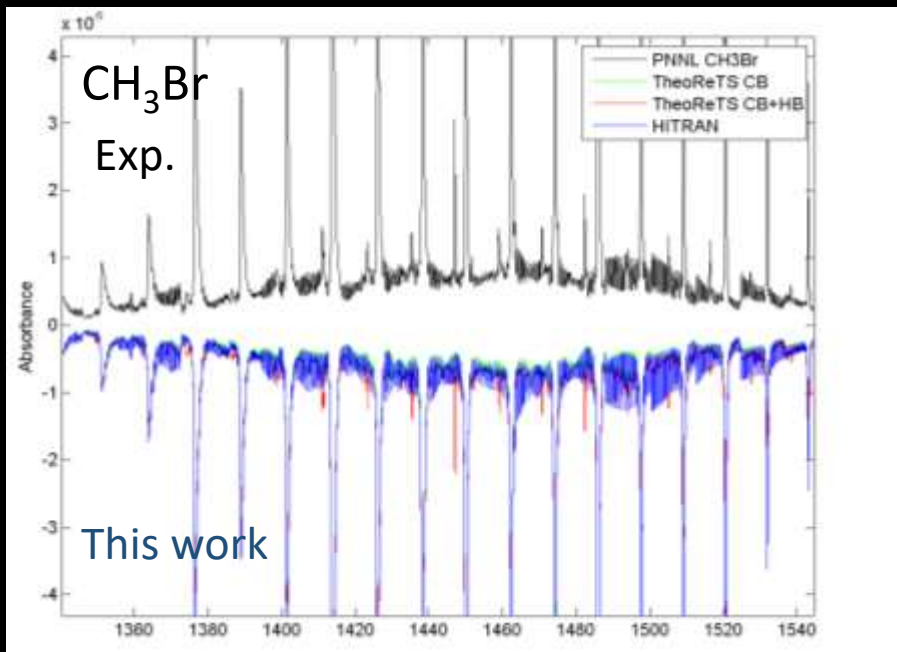
# Other molecules



# Phosphine

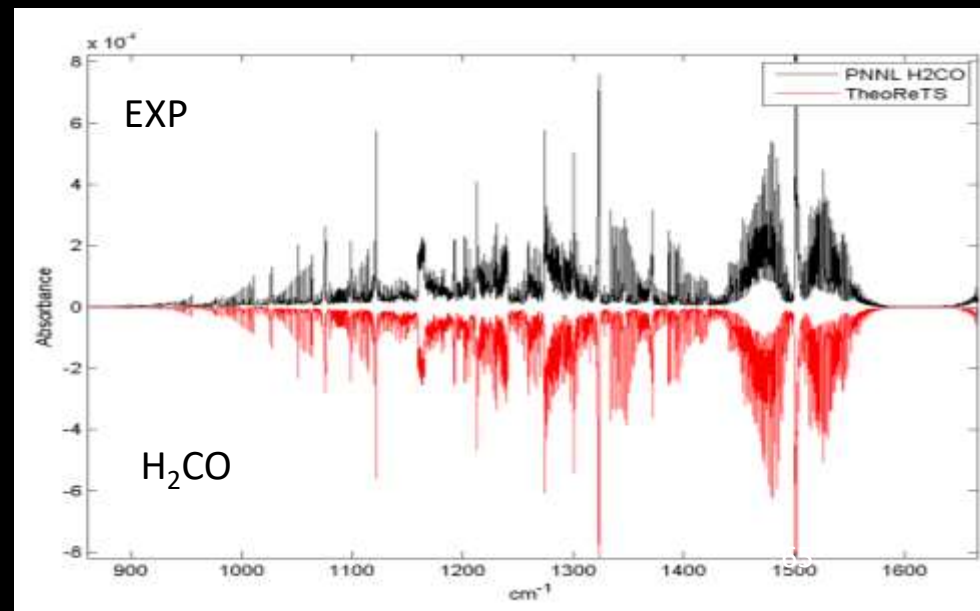
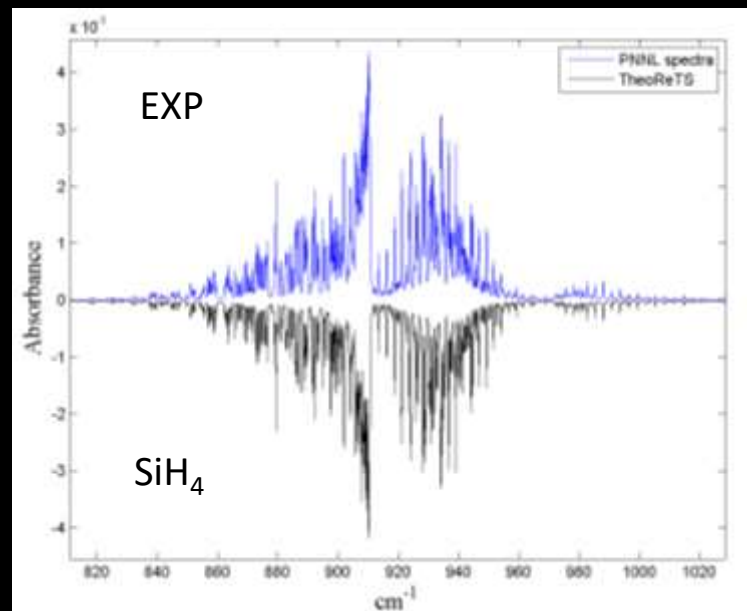
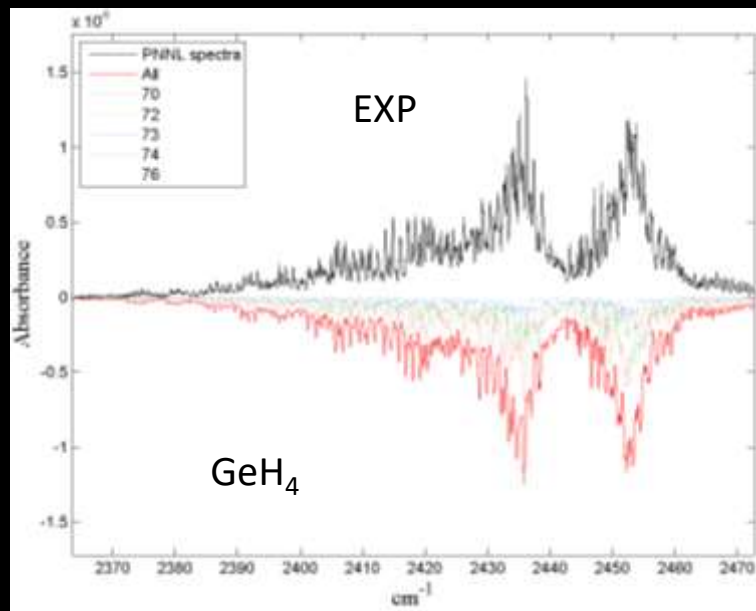
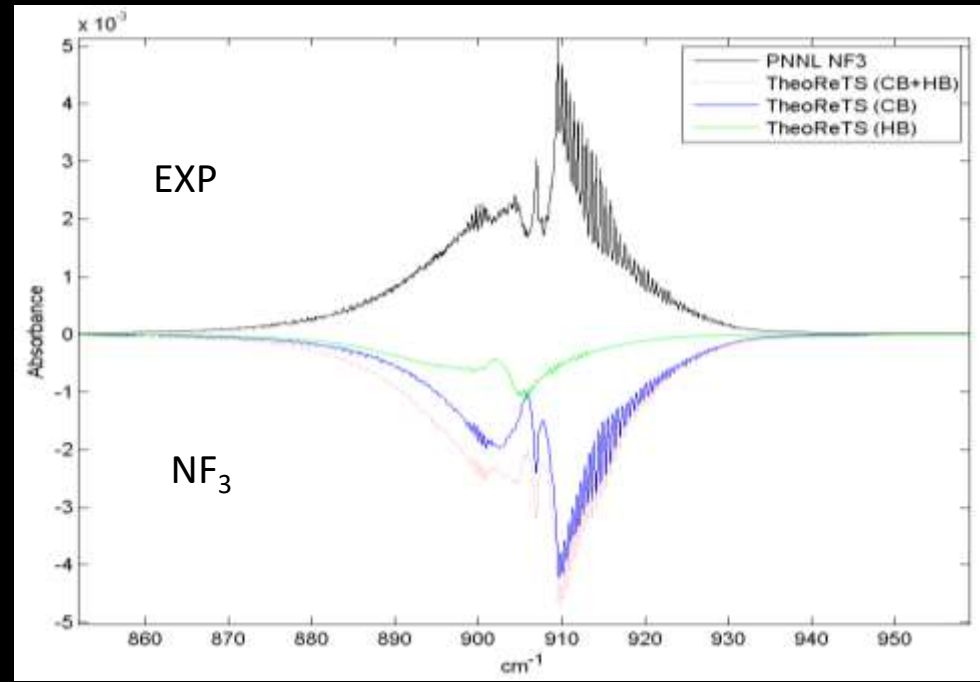
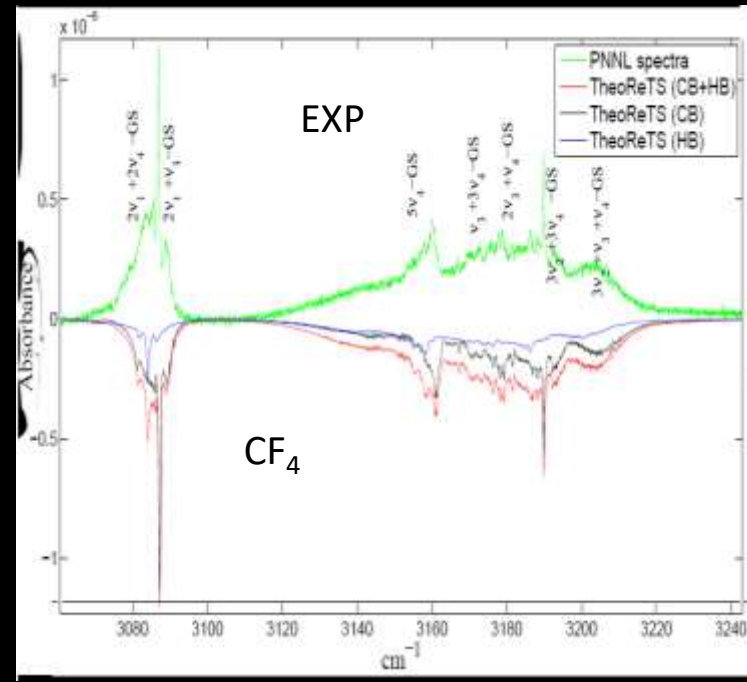
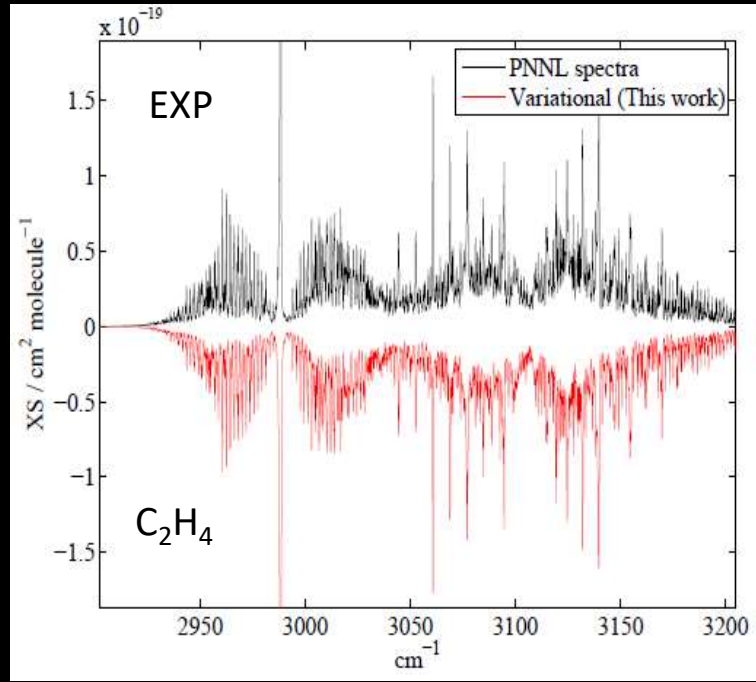
Same strategy as  $\text{CH}_4$   $\rightarrow$  empirically corrected line lists (for positions) based on Andrei Nikitin's analysis  
Best of both worlds  $\rightarrow$  accurate line positions for cold & hot bands + accurate *ab initio* intensities







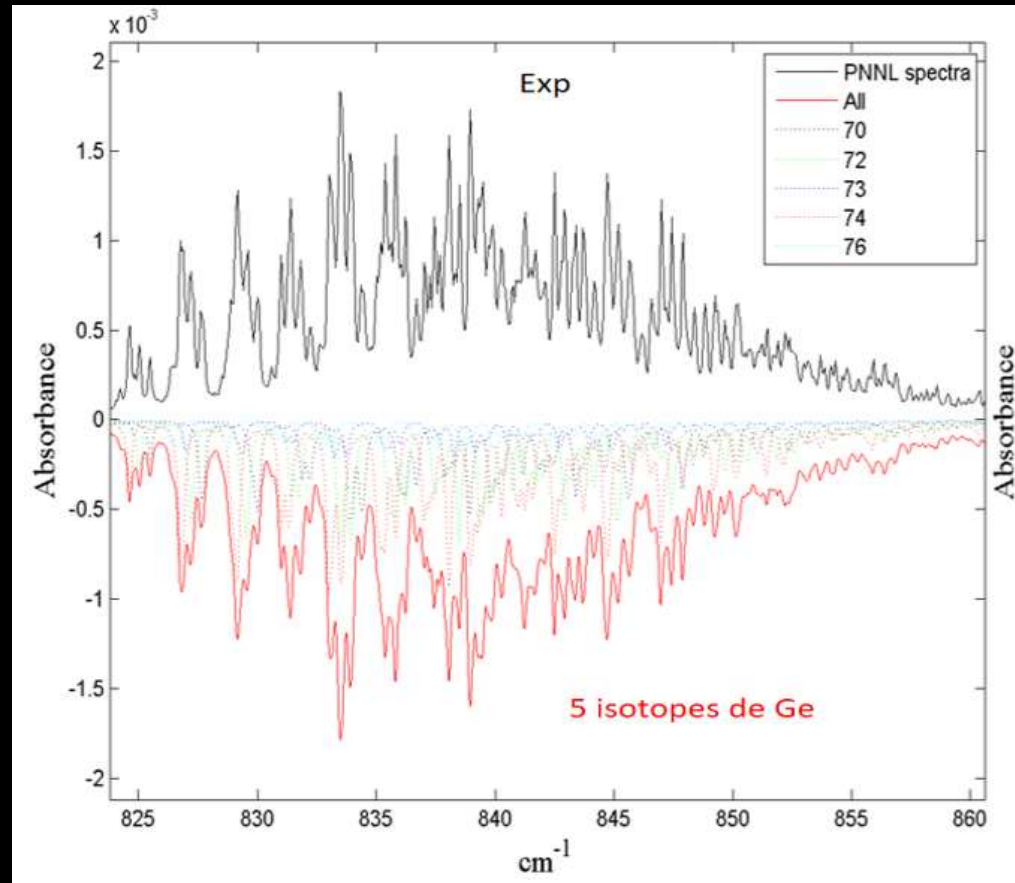
# All vibrational bands are systematically taken into account



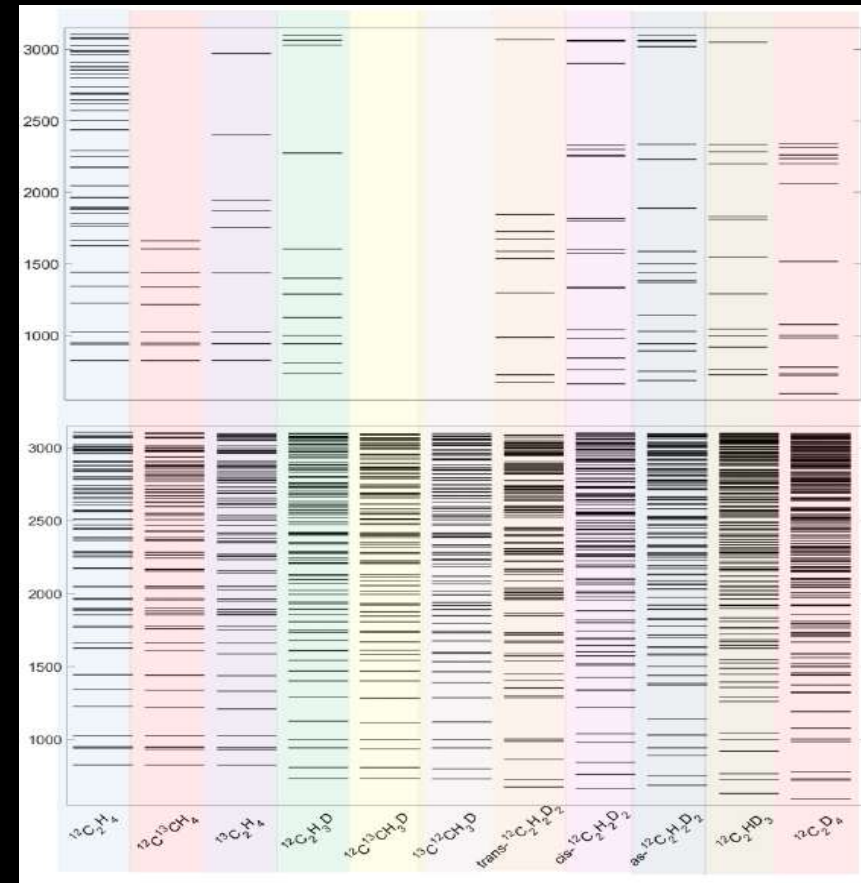
# Isotopic species

- Predicting all isotopologues almost simultaneously

Germane molecule



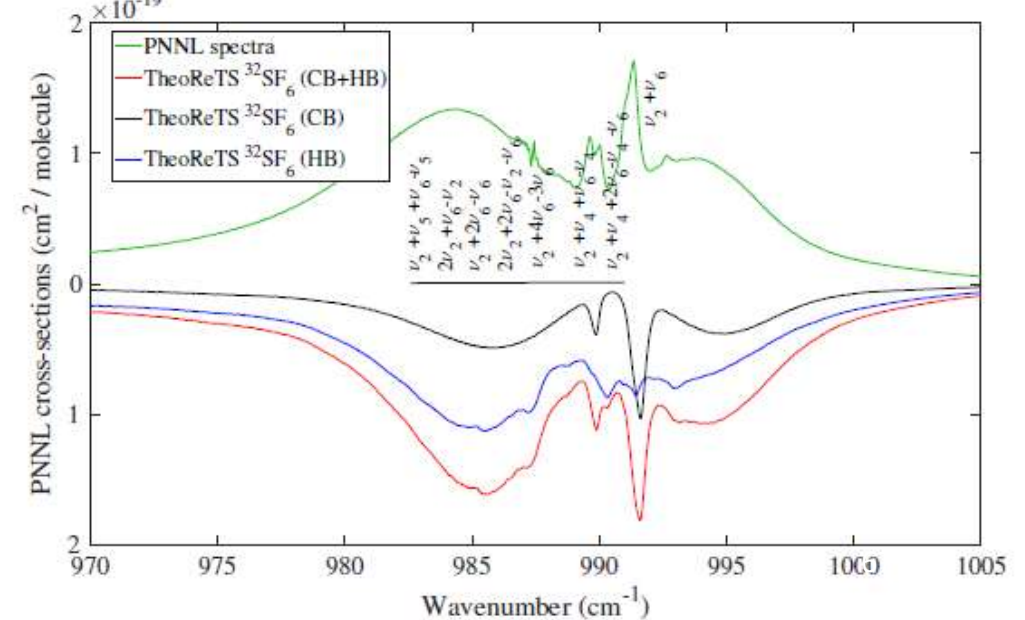
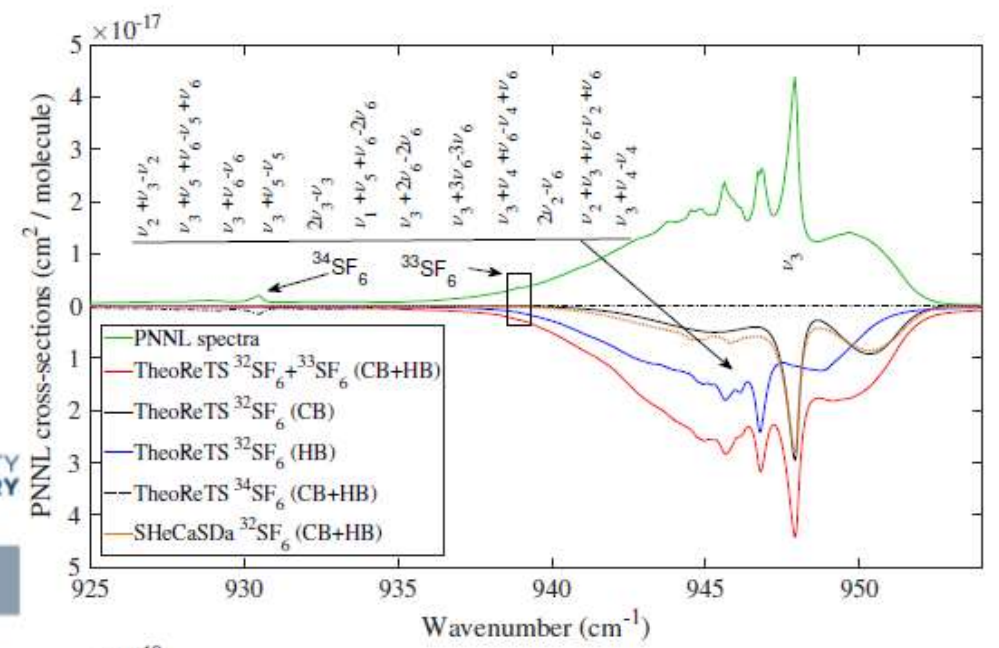
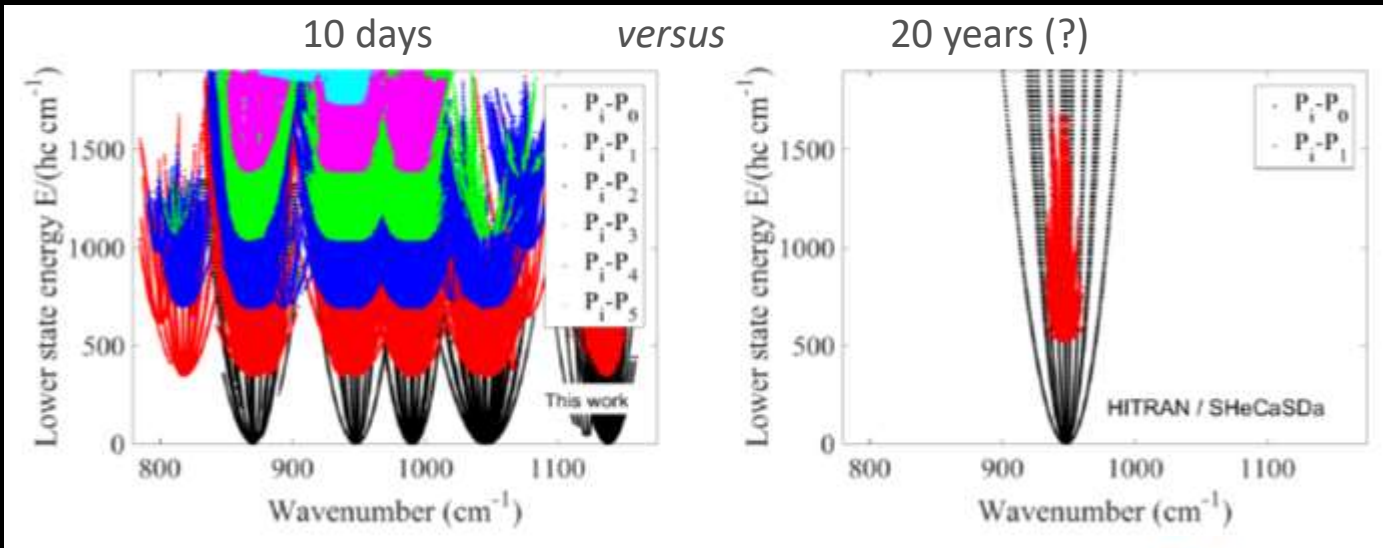
Ethylene: 11 isotopologues



151 "obs" band centers

1252 "calc" band centers

# $^{32}\text{SF}_6 + ^{33}\text{SF}_6 + ^{34}\text{SF}_6$ spectra



PCCP  
PAPER

ROYAL SOCIETY OF CHEMISTRY

(2021)

Table 4 Sum of experimental PNNL cross-sections ( $\text{cm}^2/\text{molecule}$ ) for  $\text{SF}_6$  at room temperature and comparison with simulations using the TheoReTS line list (this work) and the SheCaSDa database<sup>32</sup>

Region ( $\text{cm}^{-1}$ )	TheoReTS (TW)	PNNL	Error (%)
560-650	$1.98 \times 10^{-16}$	$2.23 \times 10^{-16}$	11.2
820-920	$1.55 \times 10^{-17}$	$1.63 \times 10^{-17}$	4.9
920-965	$3.12 \times 10^{-15}$	$3.20 \times 10^{-15}$	2.3
965-1005	$4.15 \times 10^{-17}$	$4.01 \times 10^{-17}$	-3.4
1005-1500	$7.44 \times 10^{-18}$	$7.62 \times 10^{-18}$	2.4
1550-1730	$3.23 \times 10^{-17}$	$3.47 \times 10^{-17}$	6.9

Region ( $\text{cm}^{-1}$ )	SheCaSDa <sup>32</sup>	PNNL	Error (%)
560-650	$1.01 \times 10^{-16}$	$2.23 \times 10^{-16}$	54.7
910-965	$1.19 \times 10^{-15}$	$3.20 \times 10^{-15}$	62.8

Towards a complete elucidation of the ro-vibrational band structure in the  $\text{SF}_6$  infrared spectrum from full quantum-mechanical calculations†

Michael Rey,<sup>1</sup> Iana S. Chizhnikova,<sup>2</sup> Andrei V. Nikitin<sup>3</sup> and Vladimir G. Tyuterev<sup>4</sup>

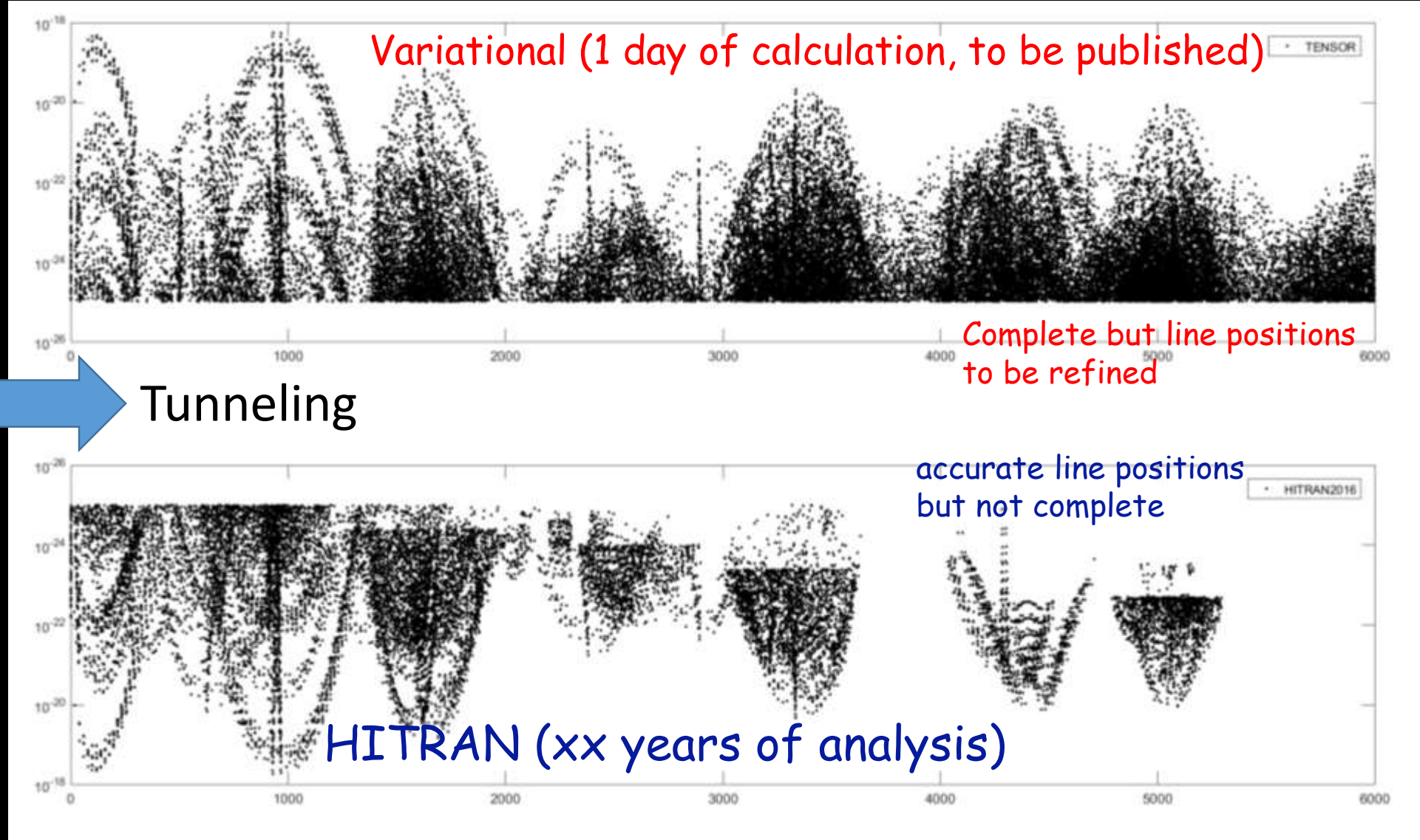
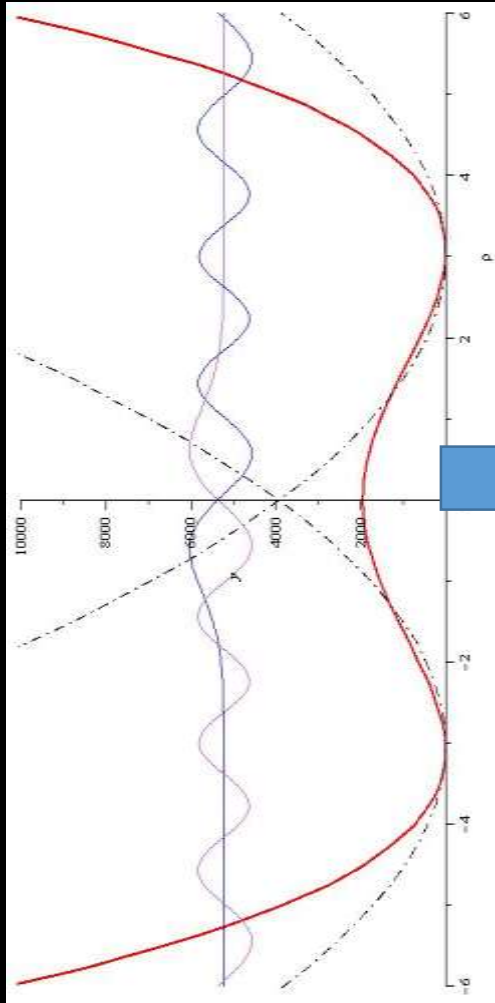
TheoReTS

Atmospheric windows at 296K:  
2,3% vs 63% err on the opacity

HITRAN



# Ammonia (nonrigid)



# Variational calculation: summary

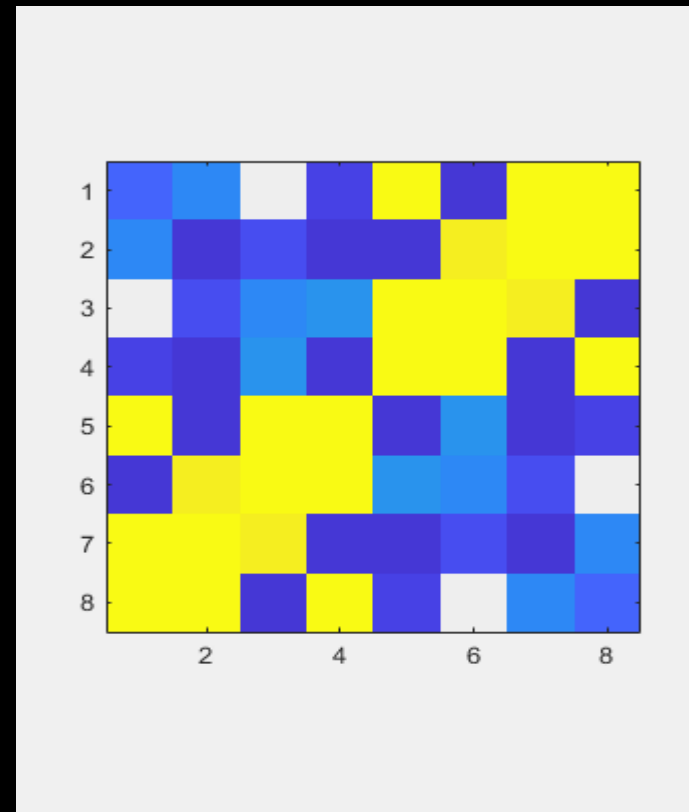
- ✓ Completeness OK
- ✓ Consistent opacity calculation because all resonances are taken into account
- ✓ Relevant for planetary applications

BUT .....

- ✓ Very involved calculations - it is difficult to refine the PES
- ✓ Not able to reach the HR spectroscopic accuracy ( $\sim 0.001 \text{ cm}^{-1}$  in the infrared)

## Part. II. Effective models

- ✓ Small dimensionality: block-diagonal transformation of the Hamiltonian
- ✓ Can reach spectroscopic accuracy – only a small spectral range can be studied
- ✓ Assist a spectroscopist in analysis



# Basic principles of the (empirical) effective approach

Transform a full problem into a series of much smaller problem = POLYADS

$$\tilde{H}^{(\Gamma_0)} = \sum_i \tilde{t}_i (V \otimes R)_i^{(\Gamma_0)}$$

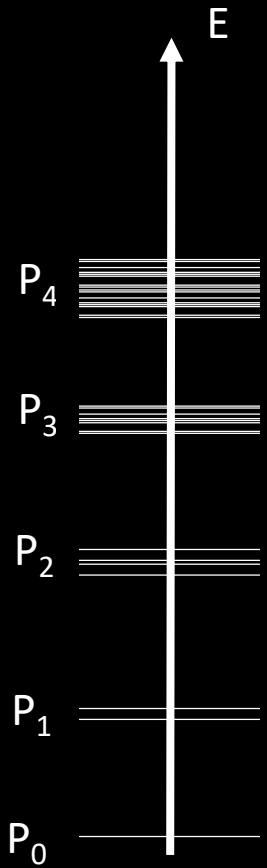
Unknown Spectroscopic parameters      Molecular vibration      Molecular rotation

→ Describes a small group of interacting vibrational states = **1 effective Hamiltonian per group**

$$\text{Line position} = E_j(\tilde{t}) - E_i(\tilde{t})$$

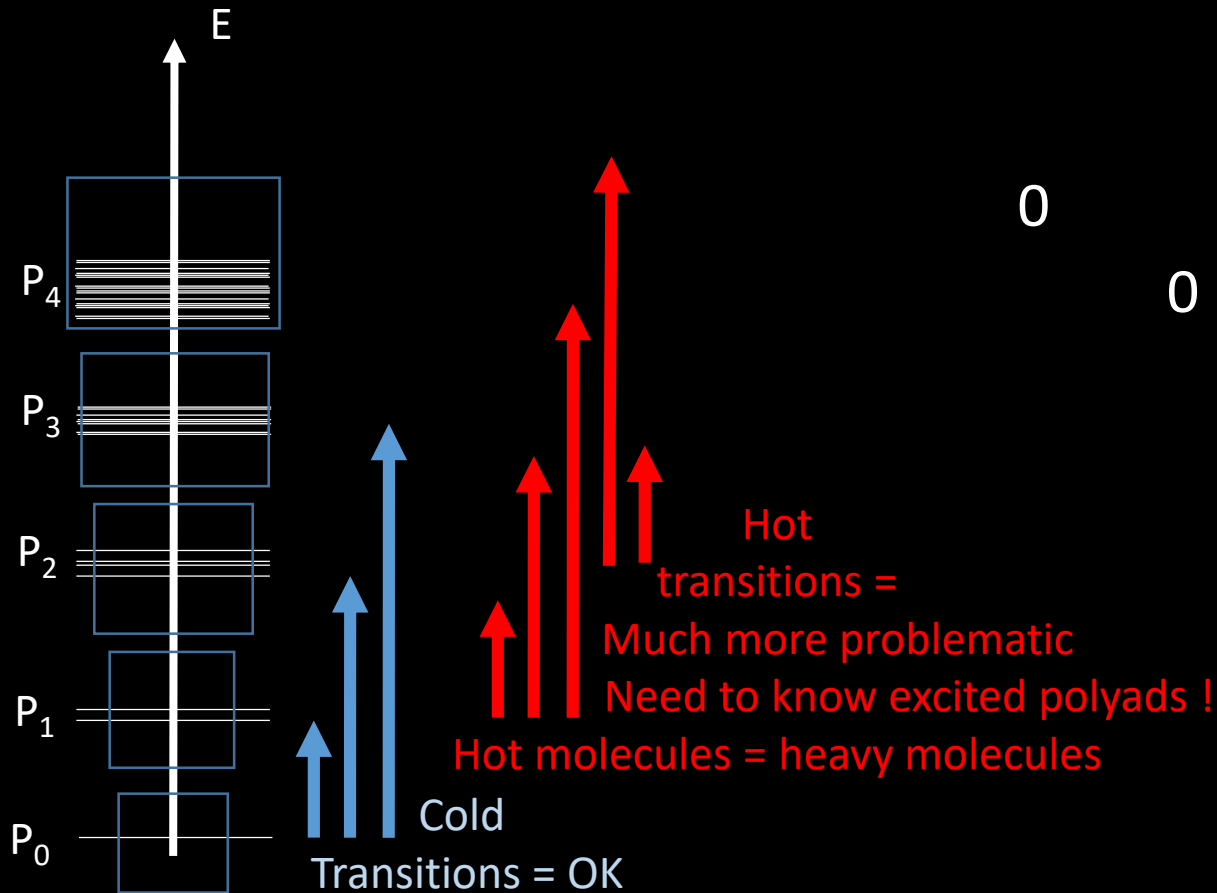
Least squares fitting to determine the parameters – data reduction

# Empirical effective Hamiltonians: *ideal case*





# Empirical effective Hamiltonians: ideal case



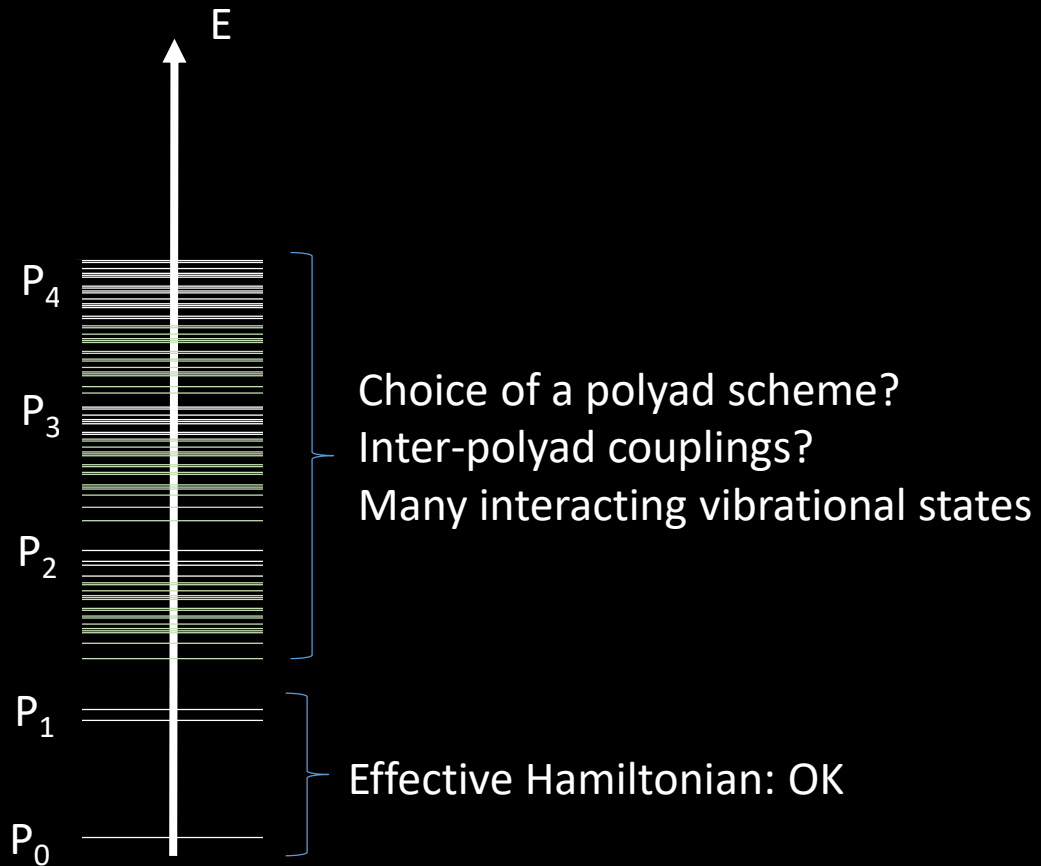
Block-diagonal Hamiltonian matrix

0  
0  
0  
0  
0

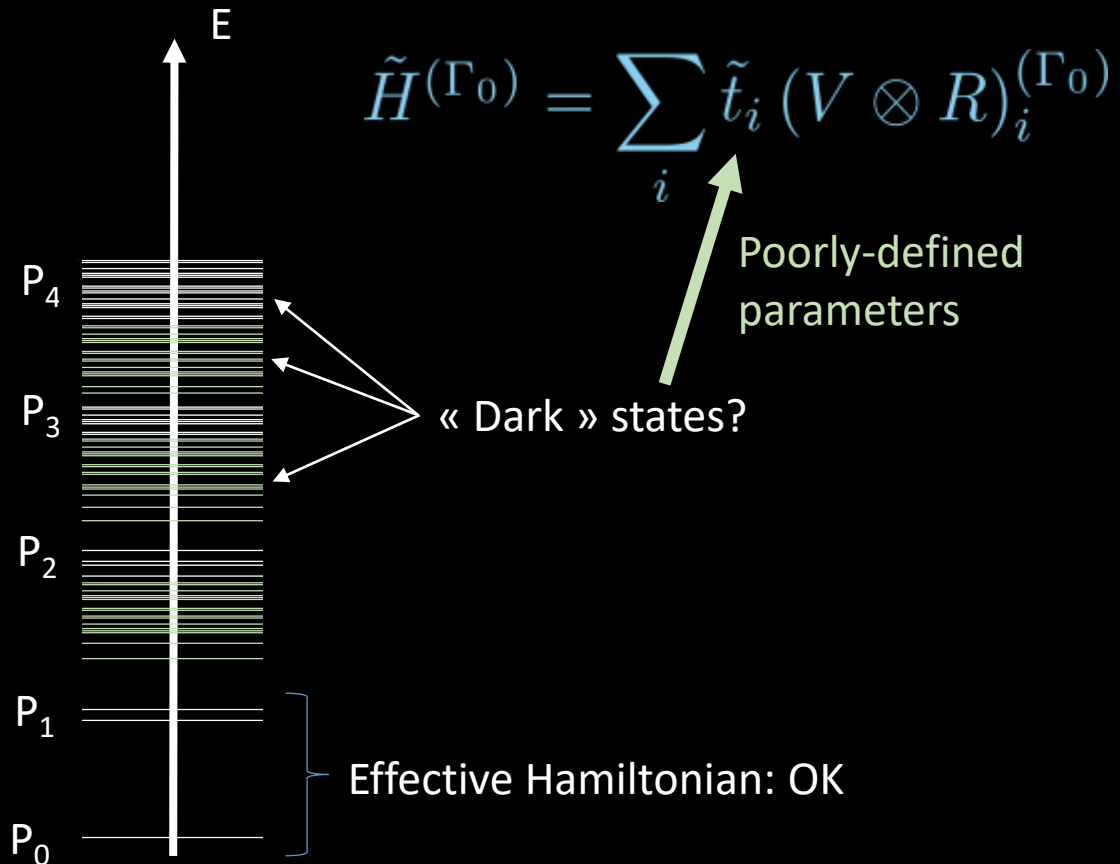
$$= \tilde{H}^{(\Gamma_0)} = \sum_i \tilde{t}_i (V \otimes R)_i^{(\Gamma_0)}$$

Fitted to obs

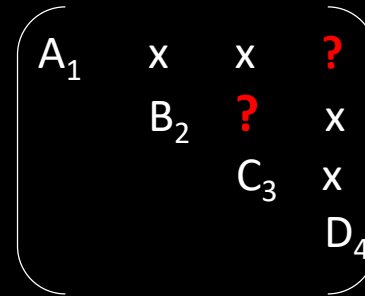
# Empirical effective Hamiltonians: practical case



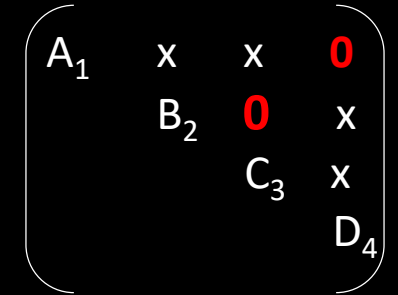
# Empirical effective Hamiltonians: *practical case*



No information on dark states

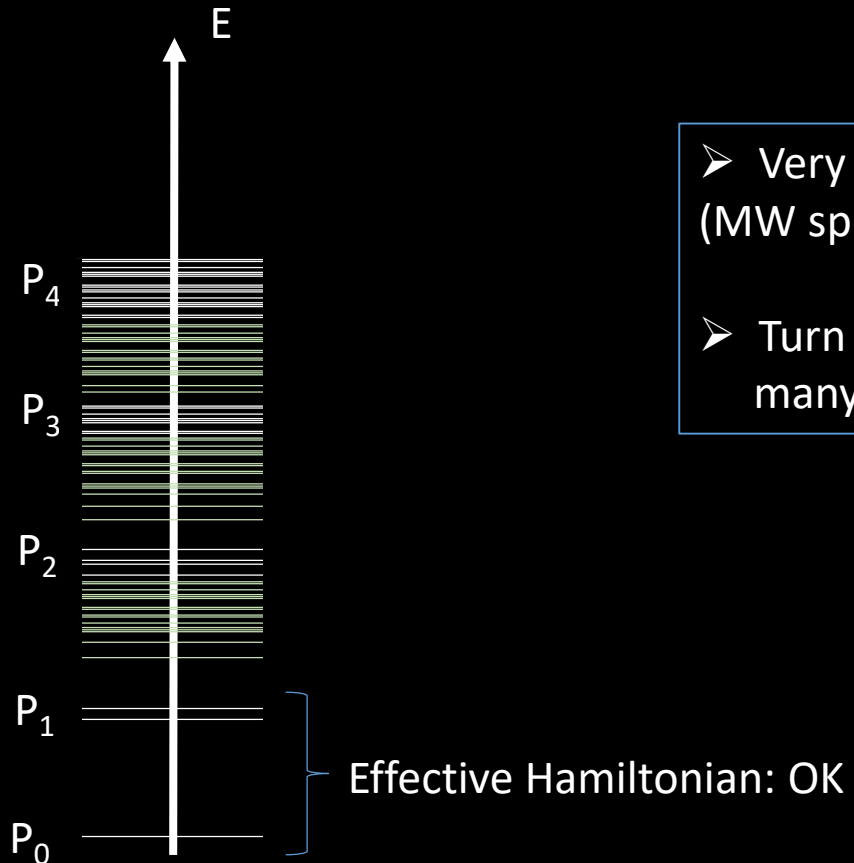


Constraints



Bad wavefunctions

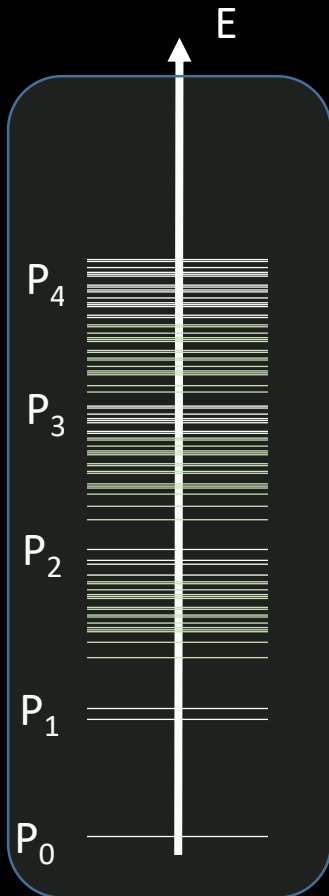
# Empirical effective Hamiltonians



- Very efficient for isolated polyads (small dimensionality=accurate models) (MW spectroscopy, few vibrational bands)
- Turn out very limited for complex polyads involving many interacting vibrational states

# Alternative: variational approach (based on *ab initio* PES)

Global calculation – much more consistent  
All the resonance coupling terms are taken into account  
Very good representation of the wavefunctions for line intensities

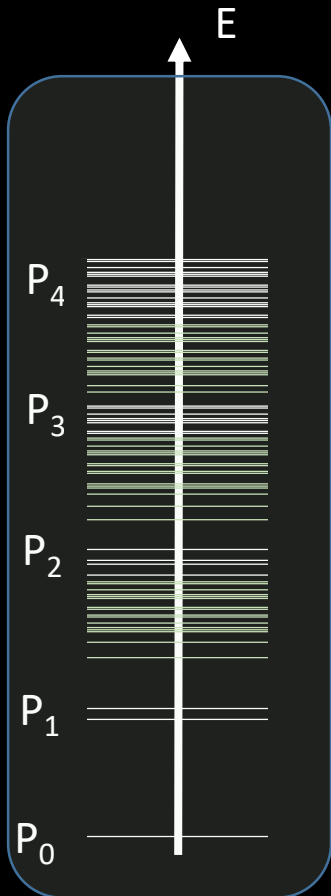


$$\Psi_{v,k}(\mathbf{X}) = \sum_i c_k^i \phi_{v,i}(\mathbf{X})$$

$k^{\text{th}}$  eigenvector      Expansion coefficients to be determined      Primitive basis functions

# Alternative: variational approach (based on *ab initio* PES)

Global calculation – much more consistent  
All the resonance coupling terms are taken into account  
Very good representation of the wavefunctions for line intensities



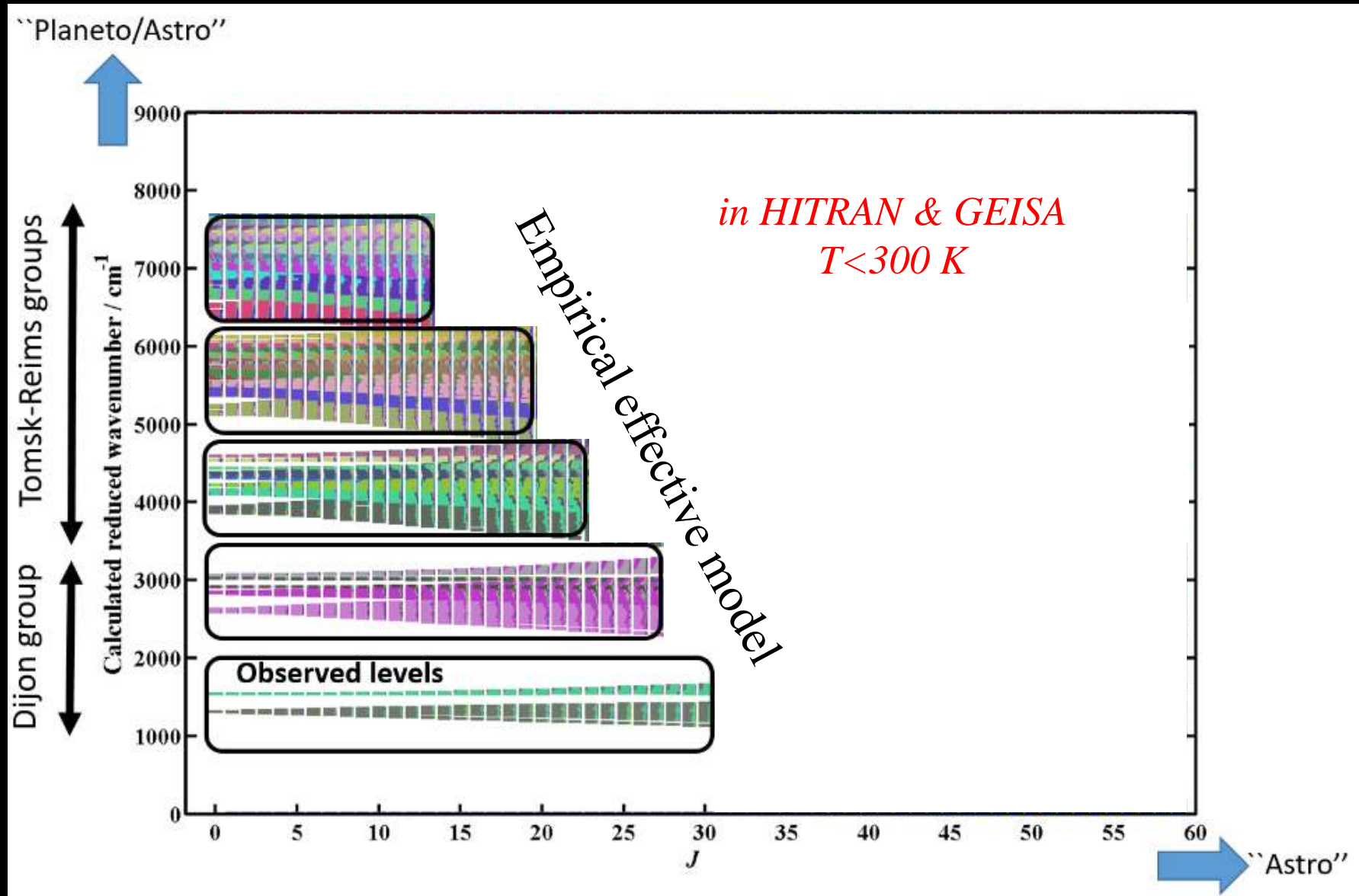
$$\Psi_{v,k}(\mathbf{X}) = \sum_i c_k^i \phi_{v,i}(\mathbf{X})$$



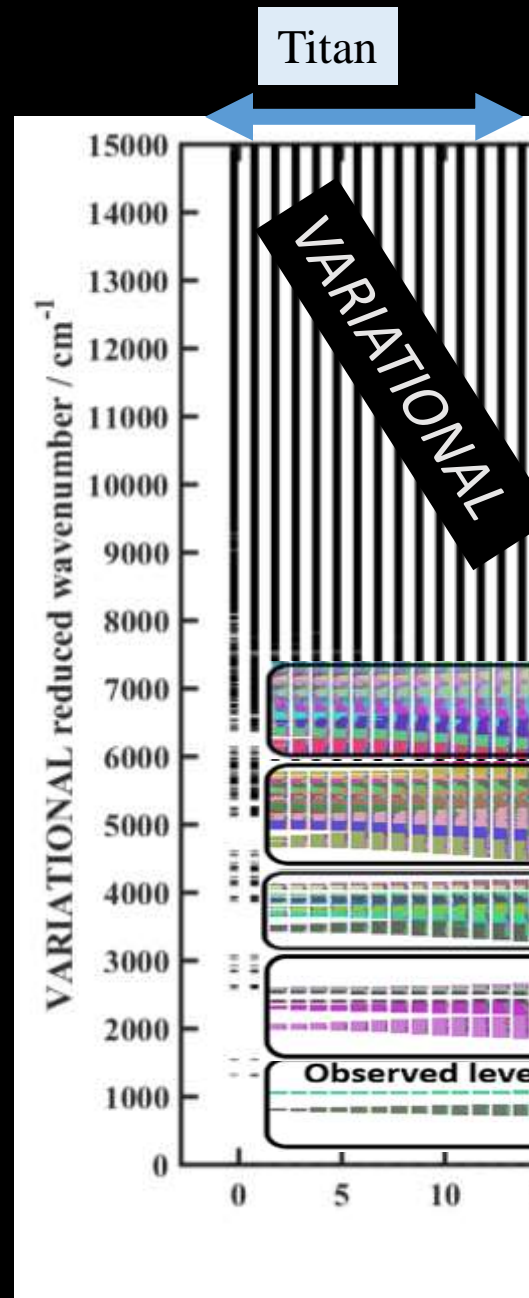
HUGE matrix to be diagonalized ☹️

# Energy levels of methane: effective vs. variational

40 years of analysis!



# Energy levels of methane: effective vs. variational



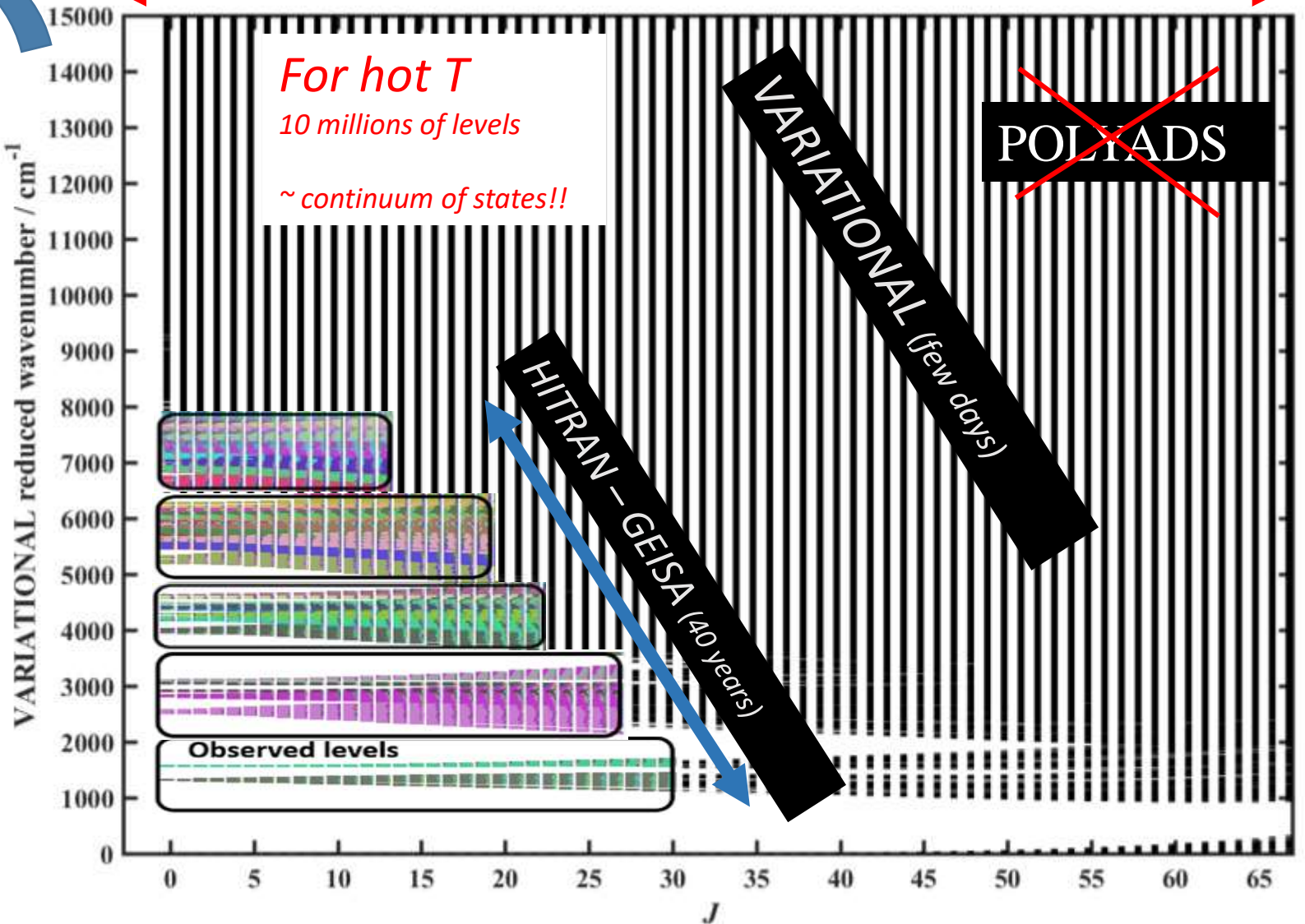
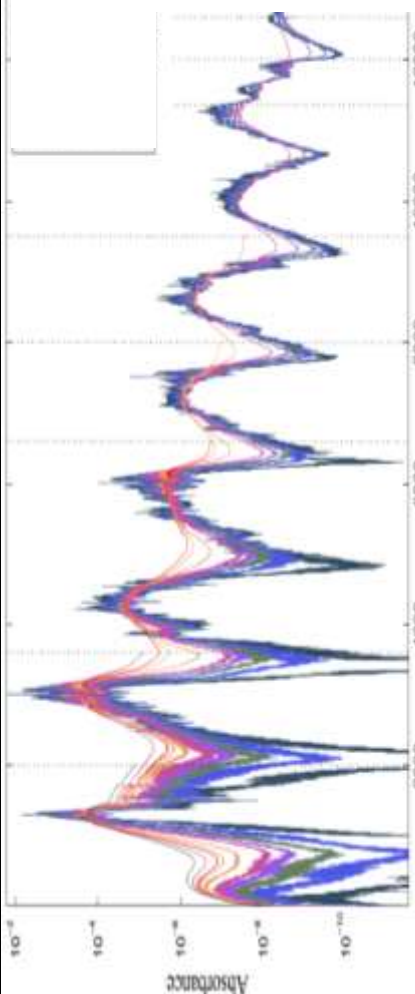


Titan

Exoplanets



>100 billion transitions



*For hot T*  
 10 millions of levels  
 ~ continuum of states!!

VARIATIONAL (few days)

~~POLYADS~~

HITRAN – GEISA (40 years)

Observed levels

# Combining the best of both worlds ? *ab initio* effective approach

Transform a full problem into a series of much smaller problem

$$\tilde{H}^{(\Gamma_0)} = \sum_i \tilde{t}_i (V \otimes R)_i^{(\Gamma_0)}$$

→ Describes a small group of interacting vibrational states = **1 effective Hamiltonian per group**

Molecular vibration

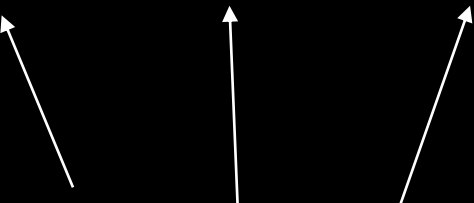
Molecular rotation

Determine from both the PES & geometry

- ✓ Small dimensionality
- ✓ Almost as complete as variational calculations

# *ab initio* effective model (Van Vleck algebraic procedure)

## Transformation of the nuclear Hamiltonian

Usual perturbative procedure  
 $\exp(-i\lambda S_1) * \exp(-i\lambda^2 S_2) * \exp(-i\lambda^3 S_3) \dots \rightarrow$   
  
 Generators to be found

$$\begin{aligned} \mathbf{H}_0^{(1)} &= \mathbf{H}_0, \\ \mathbf{H}_1^{(1)} &= \mathbf{H}_1 + i[\mathbf{S}_1, \mathbf{H}_0], \\ \mathbf{H}_2^{(1)} &= \mathbf{H}_2 + i[\mathbf{S}_1, \mathbf{H}_1] - \frac{1}{2}[\mathbf{S}_1, [\mathbf{S}_1, \mathbf{H}_0]], \\ \mathbf{H}_3^{(1)} &= \mathbf{H}_3 + i[\mathbf{S}_1, \mathbf{H}_2] - \frac{1}{2}[\mathbf{S}_1, [\mathbf{S}_1, \mathbf{H}_1]] - \frac{1}{6}i[\mathbf{S}_1, [\mathbf{S}_1, [\mathbf{S}_1, \mathbf{H}_0]]], \\ \mathbf{H}_4^{(1)} &= \mathbf{H}_4 + i[\mathbf{S}_1, \mathbf{H}_3] - \frac{1}{2}[\mathbf{S}_1, [\mathbf{S}_1, \mathbf{H}_2]] - \frac{1}{6}i[\mathbf{S}_1, [\mathbf{S}_1, [\mathbf{S}_1, \mathbf{H}_1]]] \\ &\quad + \frac{1}{24}[\mathbf{S}_1, [\mathbf{S}_1, [\mathbf{S}_1, [\mathbf{S}_1, \mathbf{H}_0]]]] \end{aligned}$$

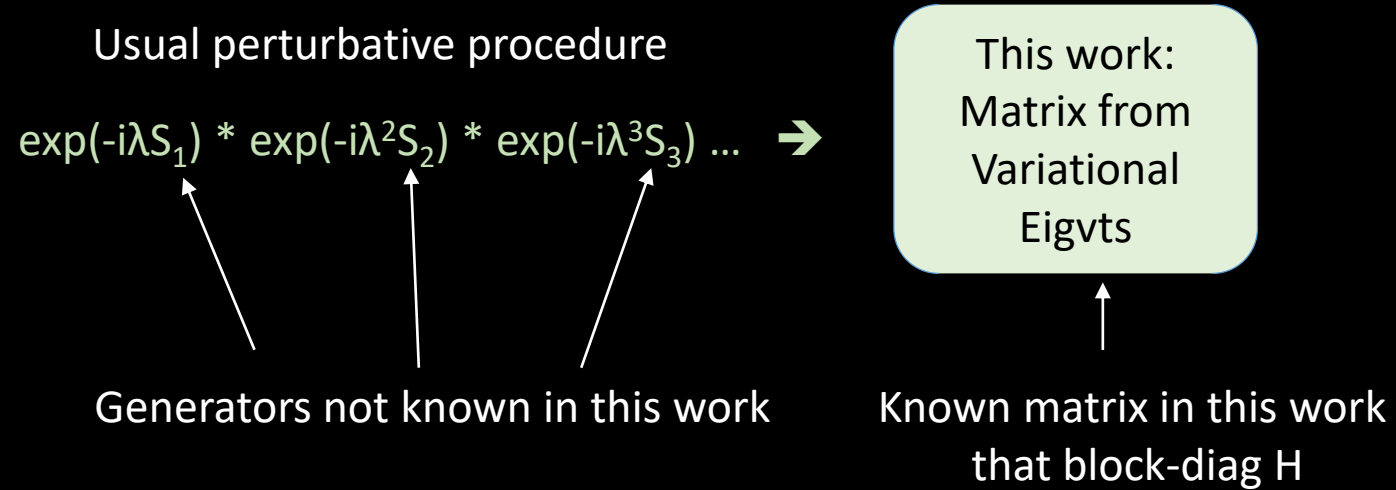
Millions of commutators for polyatomic molecules  
 Transformed dipole moment – tricky task

$$\mathbf{H}_n^{(1)} = \mathbf{H}_n + \sum_{m=0}^{n-1} (i^{n-m}/(n-m)!) \underbrace{[\mathbf{S}_1, [\mathbf{S}_1, \dots, [\mathbf{S}_1, \mathbf{H}_m] \dots]]}_{n-m}.$$

# Matrix transformation

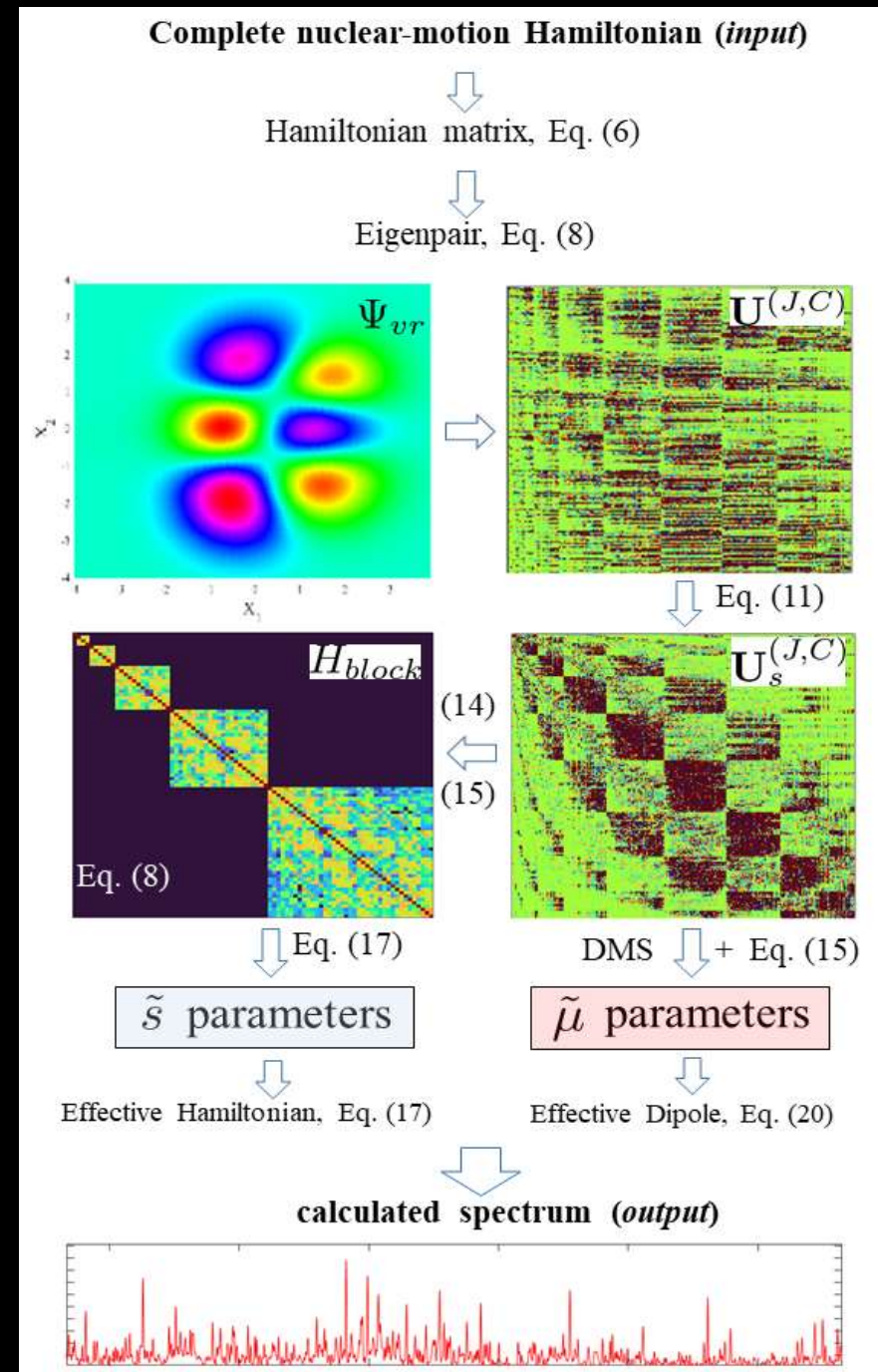
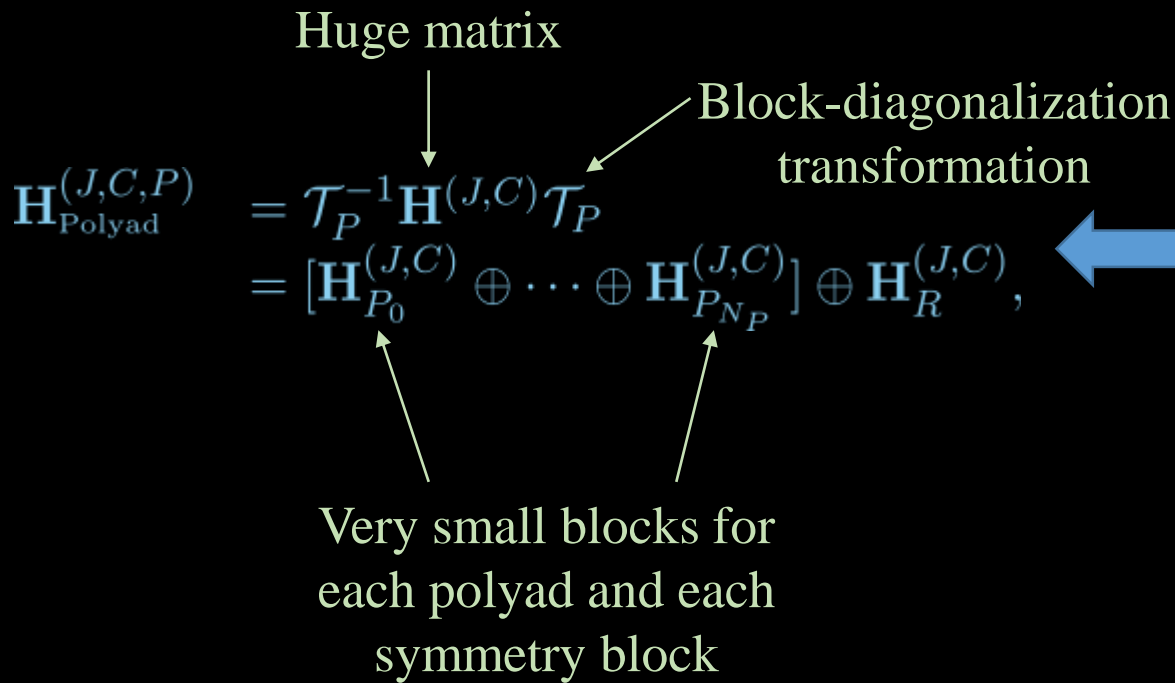
- ✓ Without using perturbation theory - Obviate the need to perform very involved CT
- ✓ Numerical approach for the block diagonalization (no need to compute commutators)

# Numerical procedure?

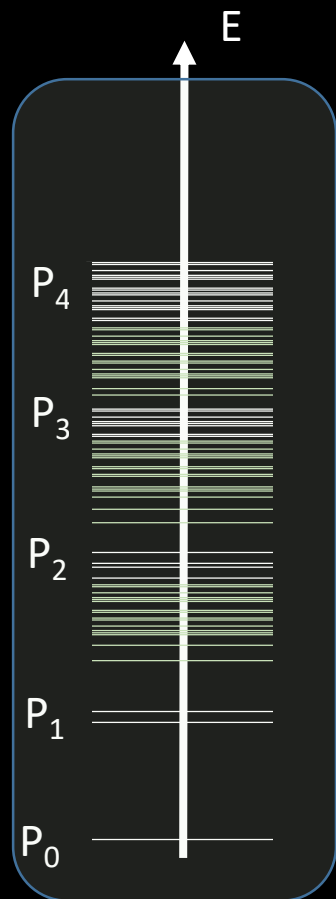


# Basic principles : numerical transformation of selected variational eigenpairs

$$\{E, \Psi = \mathbf{U}^{-1} \Phi\}$$

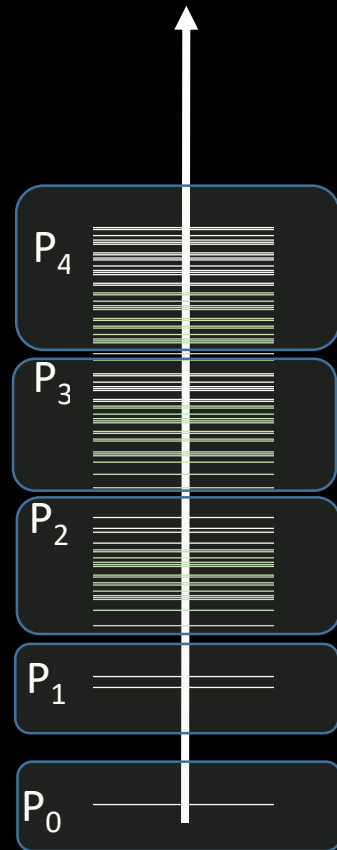


# *ab initio* effective Hamiltonian



Block-diagonal

transformation



Good initial set of  
Parameters to be refined on experiment  
(keeping fixed the coupling parameters)

$$\tilde{H}^{(\Gamma_0)} = \sum_i \tilde{t}_i (V \otimes R)_i^{(\Gamma_0)}$$

Well-defined  
parameters

« Dark » states OK

with all resonant states =  
Good wavefunctions

$E_1$	x	x	OK
	$E_2$	OK	x
		$E_3$	x
			$E_4$

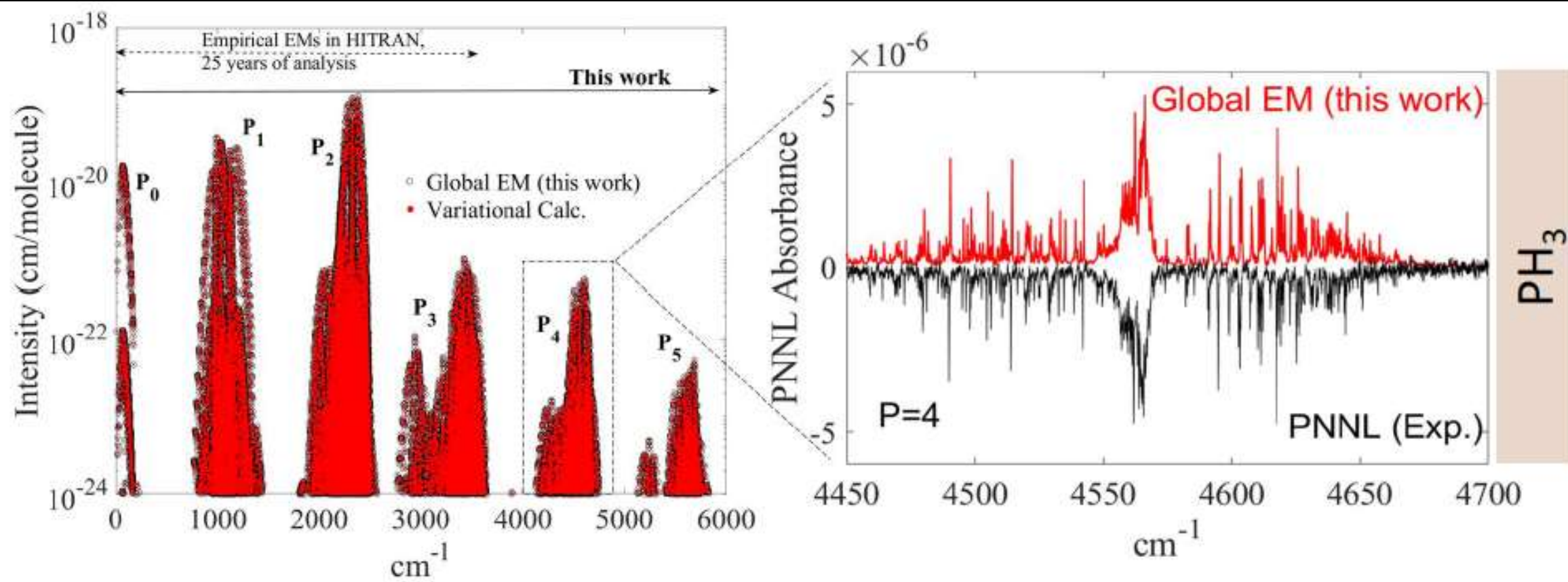


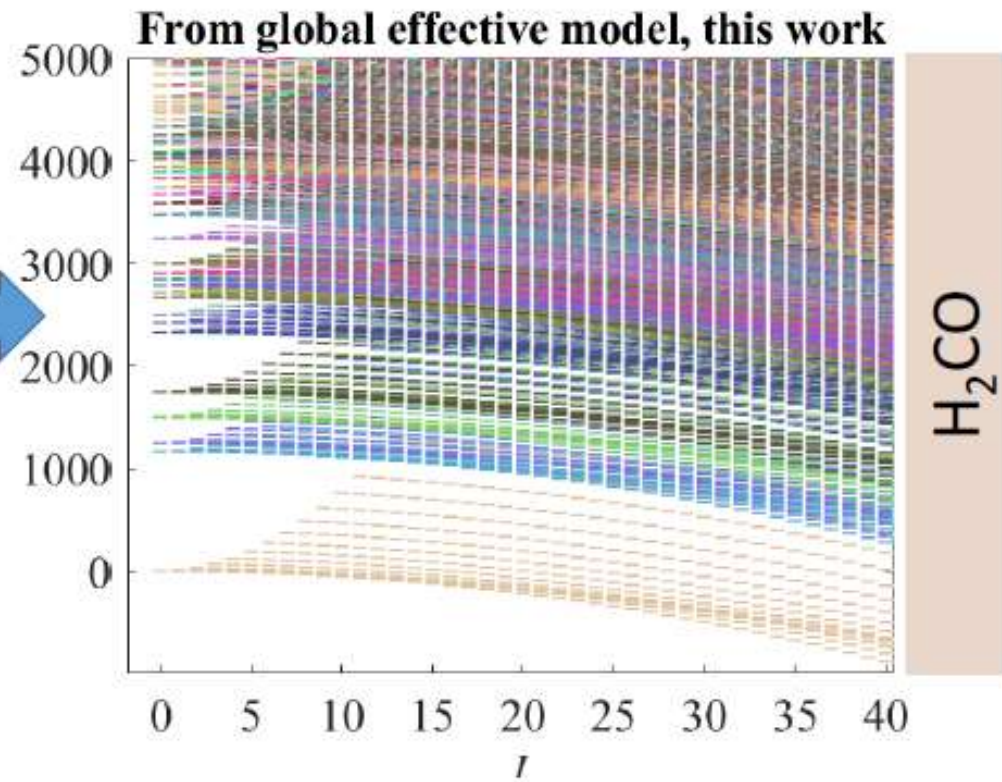
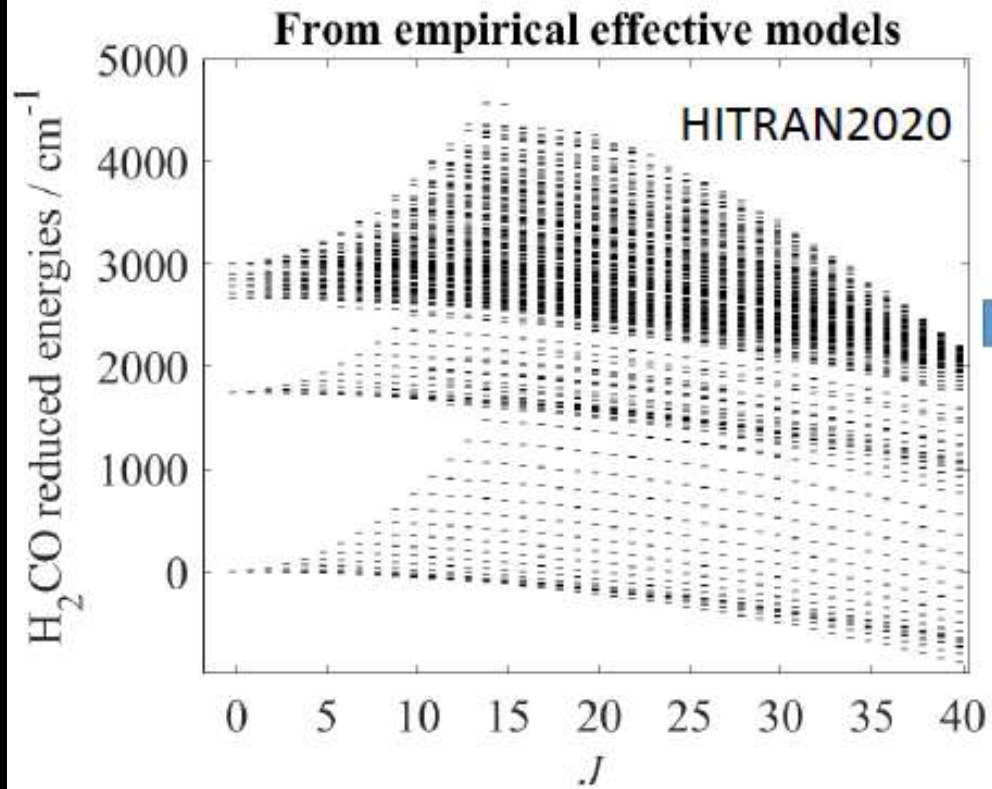
# Illustration: PH<sub>3</sub> parameters for the dyad

Operator	$\bar{s}$ , Eq. (19)	$\bar{s}$ , fit <sup>a</sup>
Ground state ( $P = 0$ )	<b>From PES, this work</b>	<b>From FIT</b>
$R^{2(2,0A1)}$	$-1.08859121 \times 10^{-1}$	$-1.08856(2) \times 10^{-1}$
$R^{2(0,0A1)}$	$-1.85097033$	$-1.850969(1)$
$R^{4(4,0A1)}$	$-4.21792347 \times 10^{-6}$	$-4.224(3) \times 10^{-6}$
$R^{4(4,3A1)}$	$6.35064638 \times 10^{-6}$	$6.393(9) \times 10^{-6}$
$R^{4(2,0A1)}$	$-4.54280135 \times 10^{-6}$	$-4.530(5) \times 10^{-6}$
$R^{4(0,0A1)}$	$-1.91476610 \times 10^{-5}$	$-1.9143(3) \times 10^{-5}$
	RMS=0.0018	RMS=0.00013 <sup>b</sup>
Dyad ( $P = 1$ )		
$R^{0(0,0A1)}(a_2^+ \otimes a_2)^{(A_1)}$	992.134856	992.1354(1)
$R^{2(2,0A1)}(a_2^+ \otimes a_2)^{(A_1)}$	$6.11040167 \times 10^{-3}$	$5.877(5) \times 10^{-3}$
$R^{2(0,0A1)}(a_2^+ \otimes a_2)^{(A_1)}$	$-2.85659105 \times 10^{-3}$	$-2.863(6) \times 10^{-3}$
$R^{0(0,0A1)}(a_4^+ \otimes a_4)^{(A_1)}$	1581.52444	1581.5238(1)
$R^{2(2,0A1)}(a_4^+ \otimes a_4)^{(A_1)}$	$-1.05612963 \times 10^{-2}$	$-1.0614(5) \times 10^{-2}$
$R^{2(0,0A1)}(a_4^+ \otimes a_4)^{(A_1)}$	$-1.12134942 \times 10^{-3}$	$-1.119(6) \times 10^{-3}$
$R^{2(2,1E)}(a_4^+ \otimes a_4)^{(E)}$	$2.18084810 \times 10^{-2}$	$2.176(3) \times 10^{-2}$
$R^{2(2,2E)}(a_4^+ \otimes a_4)^{(E)}$	$-5.13139342 \times 10^{-5}$	$-3.52(7) \times 10^{-5}$
	RMS=0.019	RMS=0.00057 <sup>b</sup>

Good starting point for analysis  
(90% fixed to *ab initio*, 10% refined)







**Hamiltonian parameters for  $H_2CO$**

```

1.671940685E+00 R 2 ( 2, 0A1 ) Pol(0) A1 0 0 0 0 0 0 0 0 0 0 0 0
2.854098592E-02 R 2 ( 2, 2A1 ) Pol(0) A1 0 0 0 0 0 0 0 0 0 0 0 0
-1.708241358E+00 R 2 ( 0, 0A1 ) Pol(0) A1 0 0 0 0 0 0 0 0 0 0 0 0
-1.933653075E-05 R 4 ( 4, 0A1 ) Pol(0) A1 0 0 0 0 0 0 0 0 0 0 0 0
...
1.249094800E+03 R 0 ( 0, 0A1 ) Pol(1) A1 0 0 0 0 0 1 0 0 0 0 0 1
2.429445278E-02 R 2 ( 2, 0A1 ) Pol(1) A1 0 0 0 0 0 1 0 0 0 0 0 1
-1.227980327E-06 R 4 ( 4, 0A1 ) Pol(1) A1 0 0 0 0 0 1 0 0 0 0 0 1
...
3.417615524E+00 R 0 ( 0, 0A1 ) Pol(2) A1 0 0 0 0 0 2 0 0 0 0 0 2
4.705171650E-05 R 2 ( 2, 0A1 ) Pol(2) A1 0 0 0 0 0 2 0 0 0 0 0 2
-2.468795961E-05 R 2 ( 2, 2A1 ) Pol(2) A1 0 0 0 0 0 2 0 0 0 0 0 2
-8.026430213E-08 R 3 ( 3, 3B2 ) Pol(2) B2 0 0 0 0 1 0 0 0 0 0 0 2

```

**Dipole moment parameters for  $H_2CO$**

```

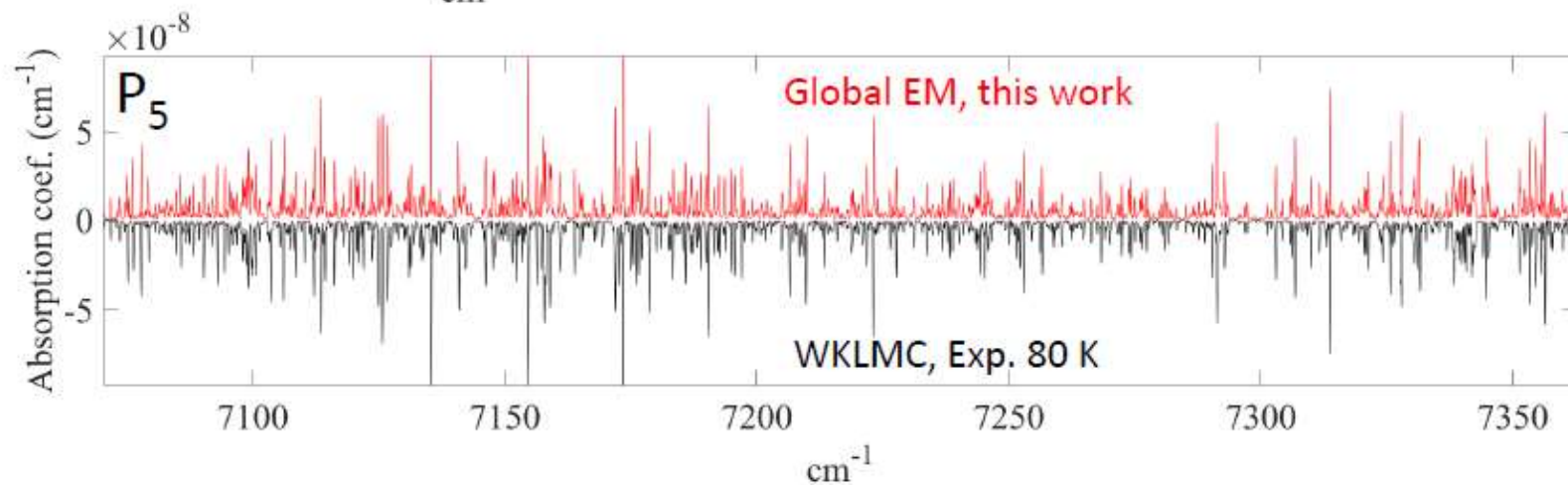
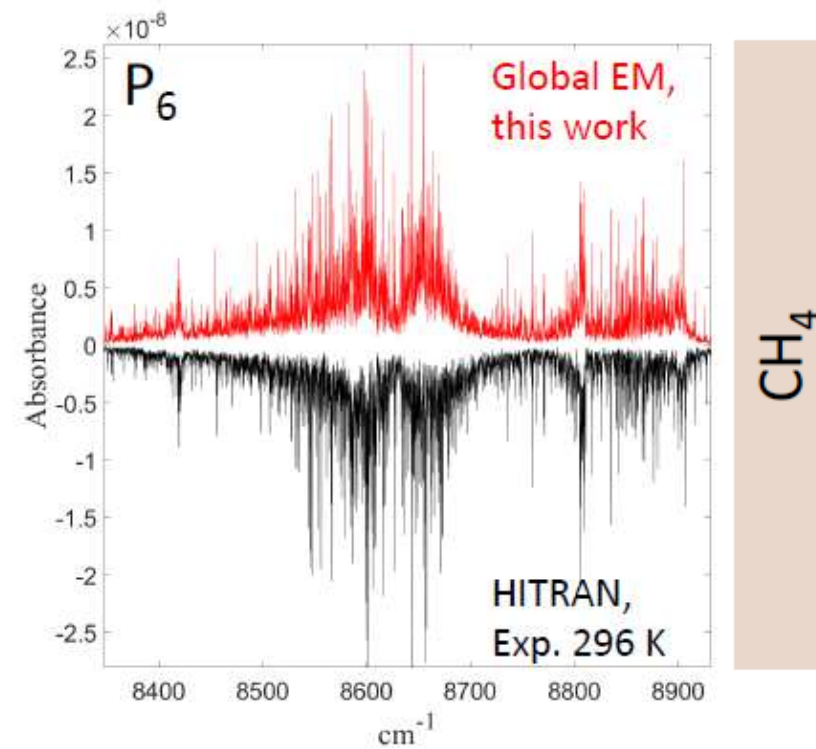
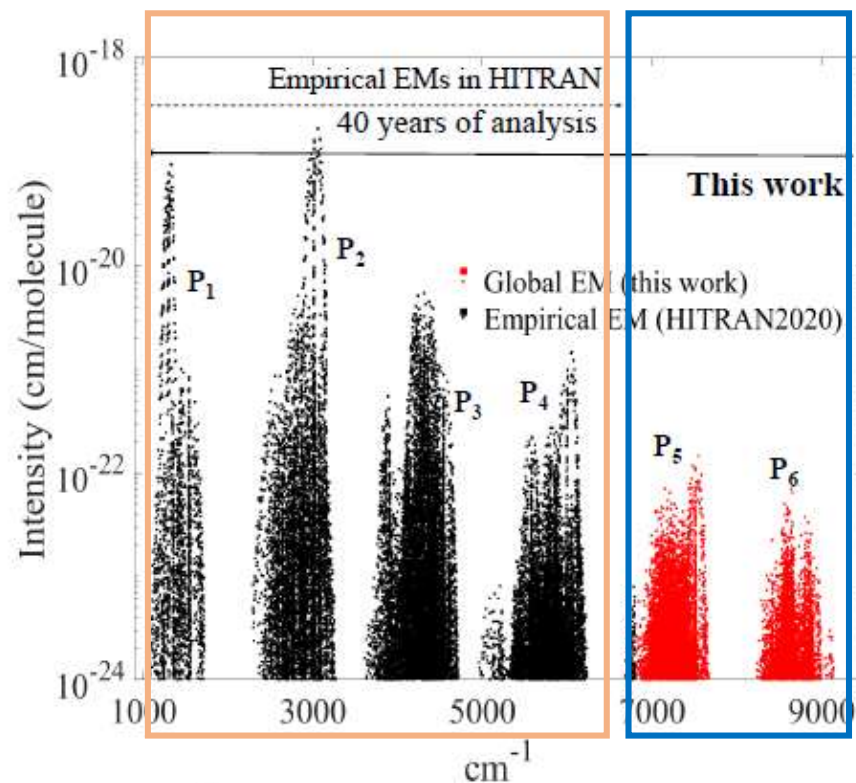
-2.124753007E-05 R 1 ( 1, 1B2 ) Pol(0<-1) B2 0 0 0 0 0 0 0 0 0 0 0 1
1.359724732E-07 R 2 ( 2, 1B2 ) Pol(0<-1) B2 0 0 0 0 0 0 0 0 0 0 0 1
1.138668371E-05 R 1 ( 1, 1B1 ) Pol(0<-1) B1 0 0 0 0 0 0 0 0 0 1 0 0
1.250949908E-08 R 2 ( 2, 1B1 ) Pol(0<-1) B1 0 0 0 0 0 0 0 0 0 1 0 0
...
-2.973674145E-05 R 1 ( 1, 1B2 ) Pol(1<-2) B2 0 0 0 0 0 1 0 0 0 0 0 2
-1.678617860E-03 R 0 ( 0, 0A1 ) Pol(1<-2) A1 0 0 0 0 0 1 0 0 0 0 1 0
1.131876807E-07 R 2 ( 2, 0A1 ) Pol(1<-2) A1 0 0 0 0 0 1 0 0 0 0 1 0
...
-8.714515646E-04 R 0 ( 0, 0A1 ) Pol(0<-3) A1 0 0 0 0 0 0 0 0 0 0 1 1
2.045201780E-07 R 2 ( 2, 0A1 ) Pol(0<-3) A1 0 0 0 0 0 0 0 0 0 0 1 1
-2.752671683E-09 R 2 ( 2, 2A1 ) Pol(0<-3) A1 0 0 0 0 0 0 0 0 0 0 1 1
-1.323314481E-07 R 2 ( 0, 0A1 ) Pol(0<-3) A1 0 0 0 0 0 0 0 0 0 0 1 1

```

40 years

<1 day

Extension up to 20,000  $\text{cm}^{-1}$  in progress

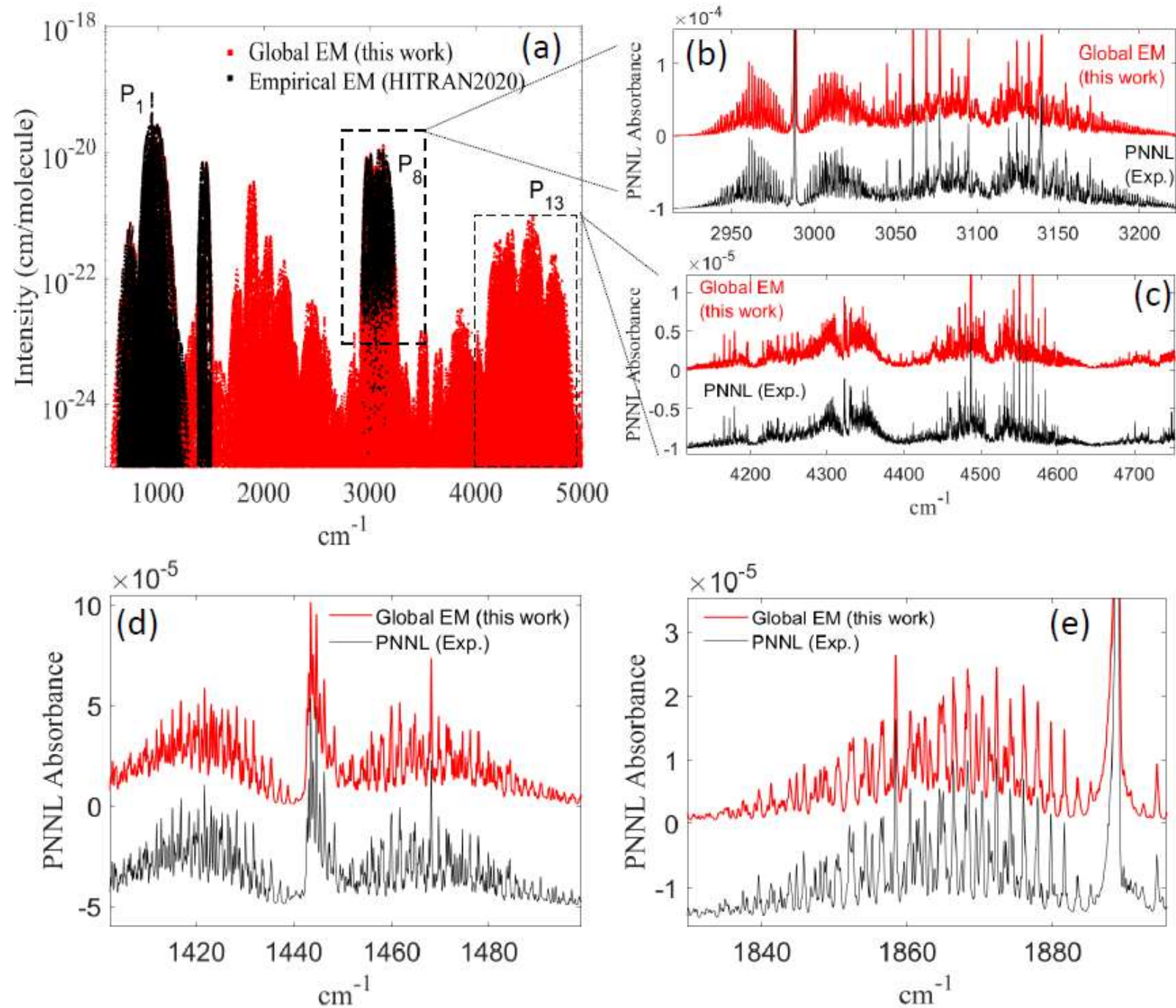




Ex: @ 3 microns

- 4 bands in HITRAN  
(not complete)

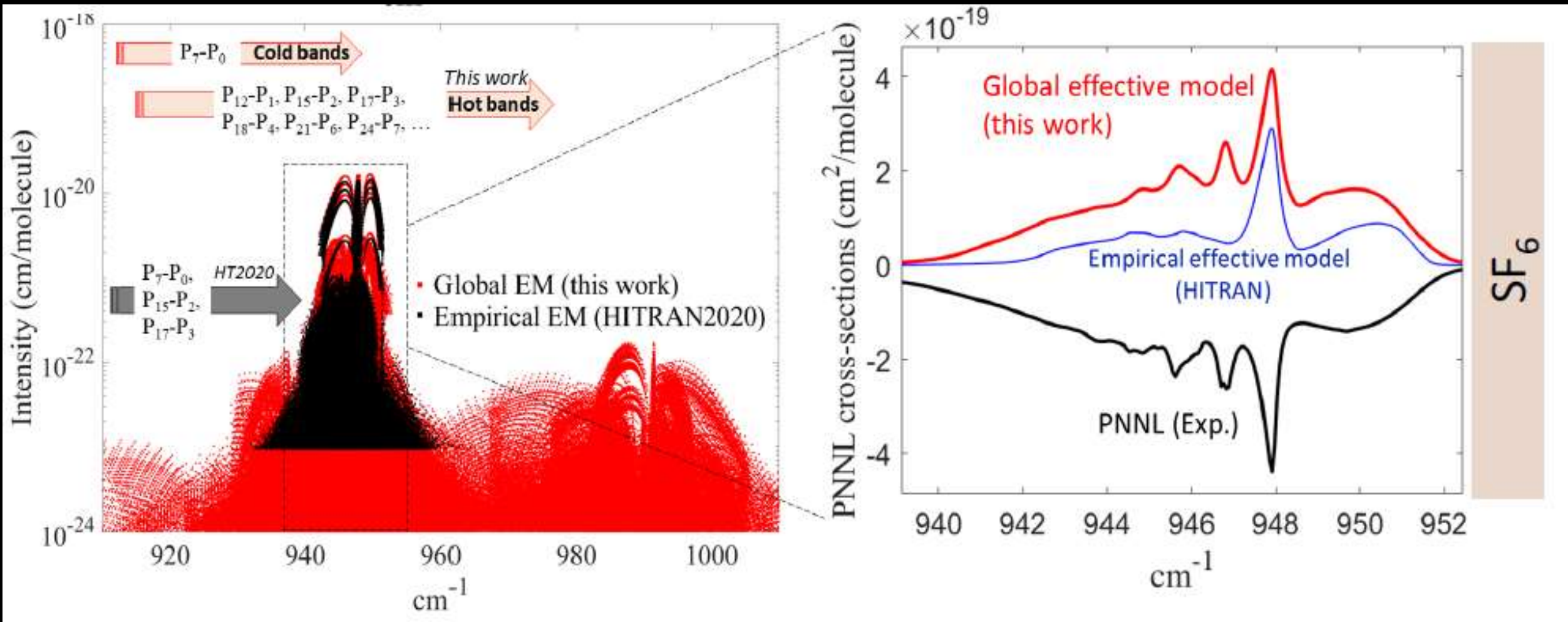
- 52 bands in this work



$\text{C}_2\text{H}_4$

# Towards a change of paradigm in high-resolution spectroscopy?

- Current models: 10-20 bands
- This model: >500 bands with corresponding parameters in few hours



I hope you are now convinced that *ab initio* is useful for the modelling of planetary atmospheres and that the construction of line list is far from being simple...

# Many molecular lists can be now calculated

Please suggest me other molecules

- ✓  $\text{CH}_4$ ,  $\text{C}_2\text{H}_4$ ,  $\text{PH}_3$ ,  $\text{H}_2\text{CO}$ ,  $\text{SF}_6$
- ✓  $\text{CH}_3\text{D}$ ,  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_3\text{F}$ ,  $\text{CH}_3\text{Br}$ ,  $\text{CH}_3\text{I}$
- ✓  $\text{CH}_2$ ,  $\text{CH}_3$ ,  $\text{NH}_3$ ,  $\text{C}_2\text{H}_6$  (nonrigid)
- ✓  $\text{SiH}_4$ ,  $\text{GeH}_4$ ,  $\text{CCl}_4$ ,  $\text{CF}_4$ ,  $\text{CClF}_3$ ,  $\text{NF}_3$
- ✓  $\text{C}_3\text{H}_4$ ,  $\text{SiF}_4$ , etc.
- ✓  $\text{C}_6\text{H}_6$  ?  $\text{C}_4\text{H}_4\text{O}_2\text{N}_2$  (uracil) ?  $\text{C}_8\text{H}_{10}$  (naphthalene) ?
- ✓  $\text{C}_2\text{H}$ ,  $\text{C}_2\text{H}_2$  (*PES OK, codes to be adapted to linear molecules*)
- ✓  $\text{C}_2\text{H}_4\text{O}$  (no DMS)
- ✓ + all isotopologues