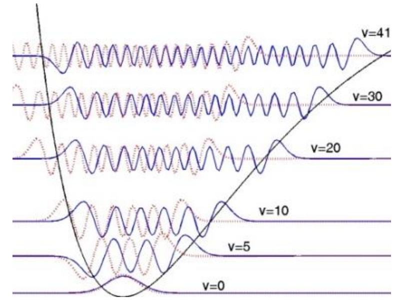
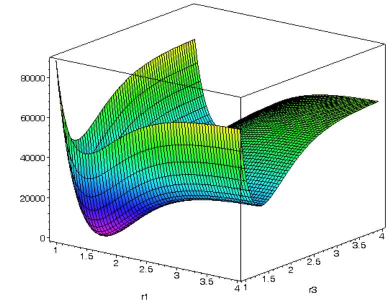
PMT : Physique Moleculaire Theorique, Reims,France
IOA Acad.Sci. & Tomsk State University, Russia





New approach for spectroscopic data reduction using *ab initio* calculations and experimental lines: application to methane

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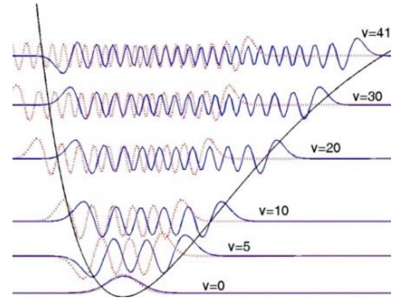

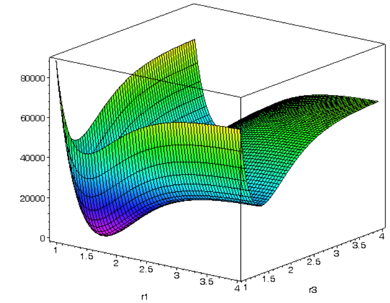

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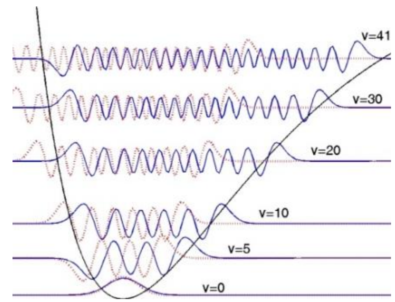

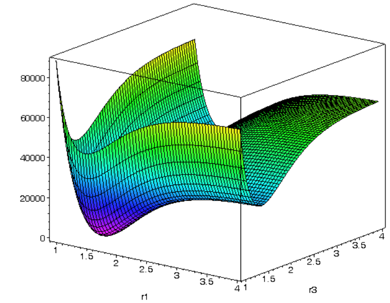

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Data base accuracy issue

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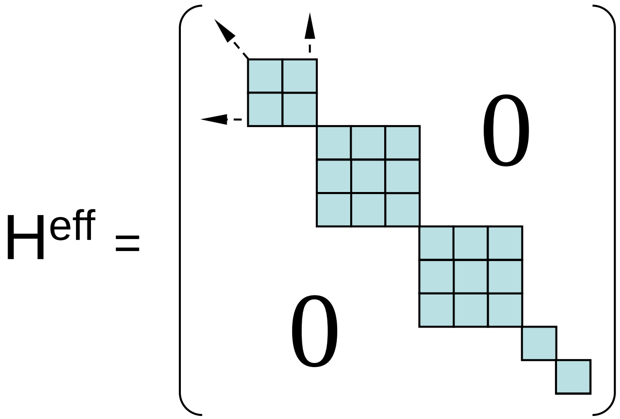
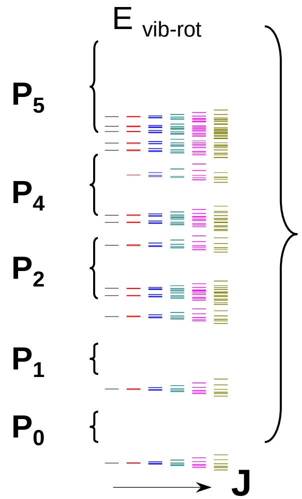
Data base completeness issue

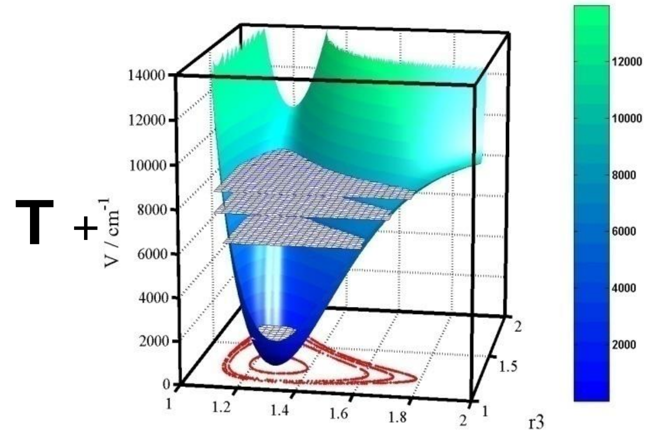
Main theoretical methods for vib-rot data reduction in spectroscopy

Effective models:
polyad Hamiltonians & trans. moments

Variational calculations
from PES & DMS







essentially empirical

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using ab initio

Main theoretical methods for vib-rot data reduction in spectroscopy

Effective models:
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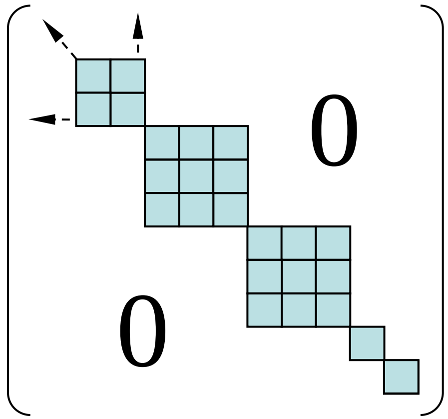
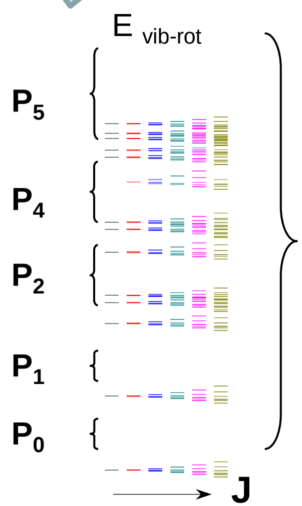
H^{eff} =





Variational calculations
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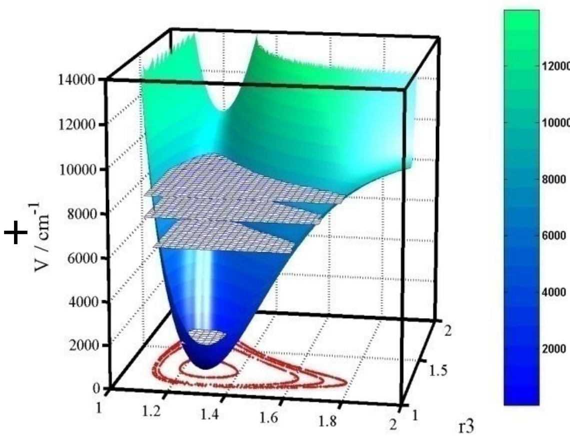
T +



essentially empirical

Complementary approaches

using ab initio

Databases that aim at approaching exp. accuracy

HITRAN / GEISA

S&MPO (ozone) : GSMA / IOA

TDS, STDS, MeCaSDa (methane): Dijon

CDSD (CO_2)

Problems

Non complete

Extrapolations, isotopic effects

Poorly determined parameters

Databases providing a complete set of lines:

(« bird's eye view »)

Partridge&Schwenke, HITEMP , IUPAC (water)

ExoMol (Tennyson,Yurchenko),

Lee, Huang-Schwenke (NH_3,CO_2), Csazar et al,

Reims-Tomsk lists (CH_4 : ApJ 789, 1 (2014))….

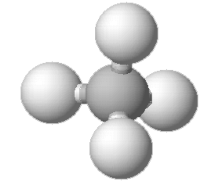
Problems

Accuracy

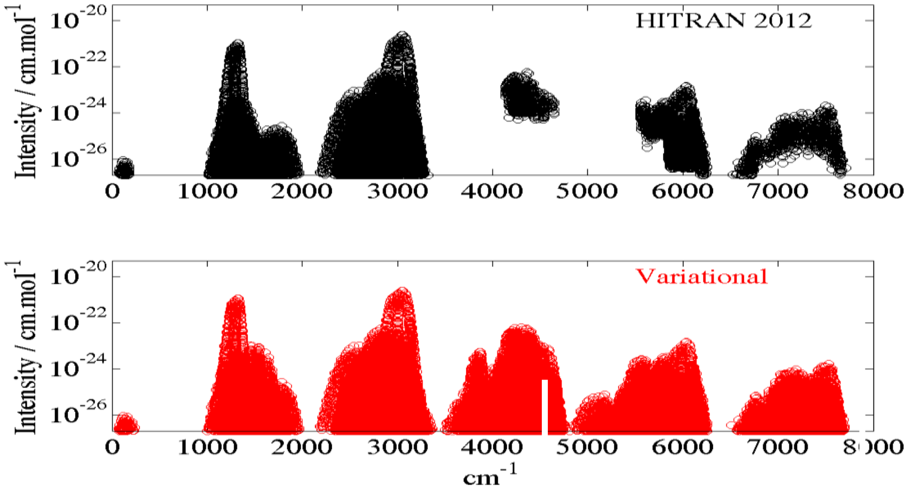
Spectroscopic assignment

Scaling with N (dimension pb)

methane isotopic spectra



Example log scale : example $^{13}CH_4$

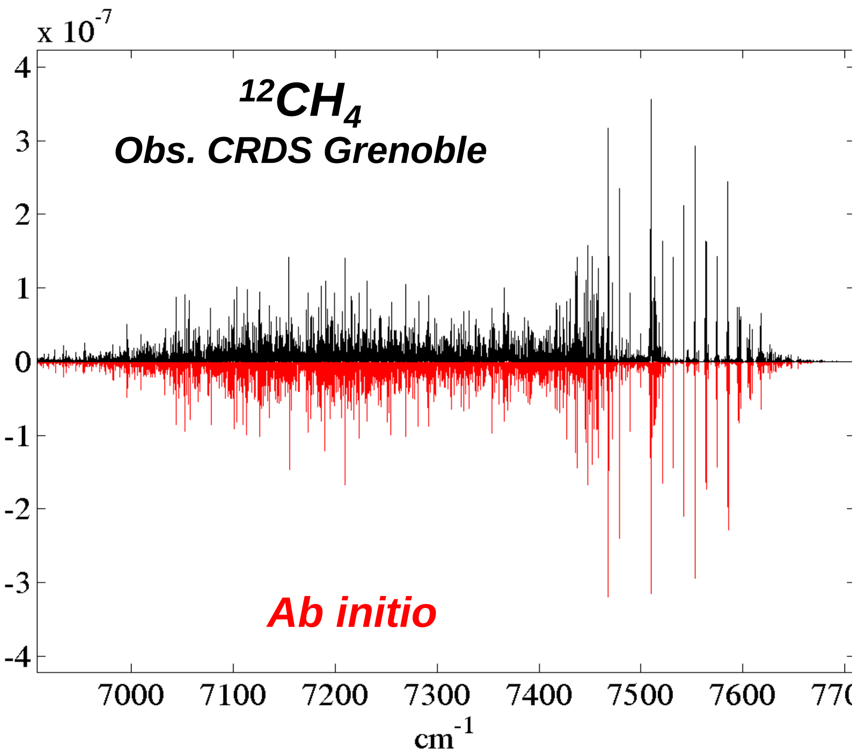


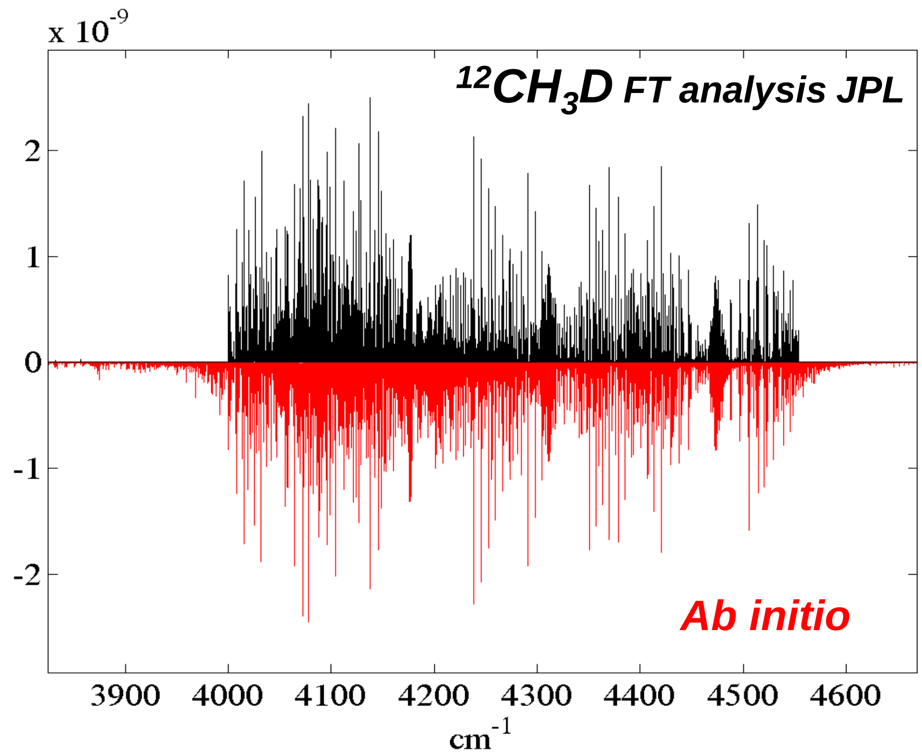
Ab initio PES & DMS :
Nikitin, Rey, Tyuterev, CPL 2011, 565, 5 *(2013)*

variational preds: *Rey, Nikitin, Tyuterev, PCCP 15, 10049 (2013), JCP (2014)*

T=300 K : *2 million lines*

T=2000 K : *20 billion lines :* ApJ 789, 1 (2014).





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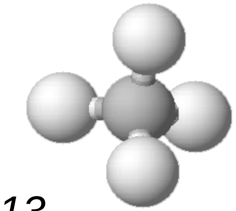

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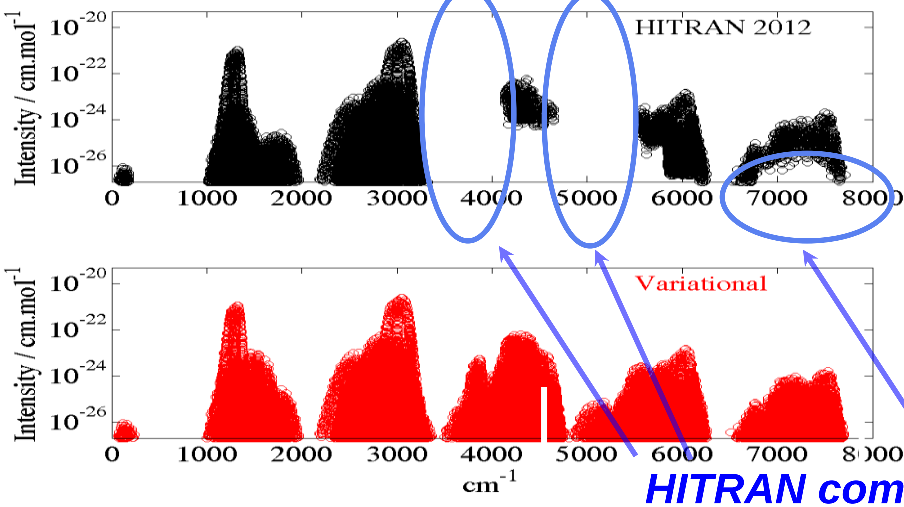

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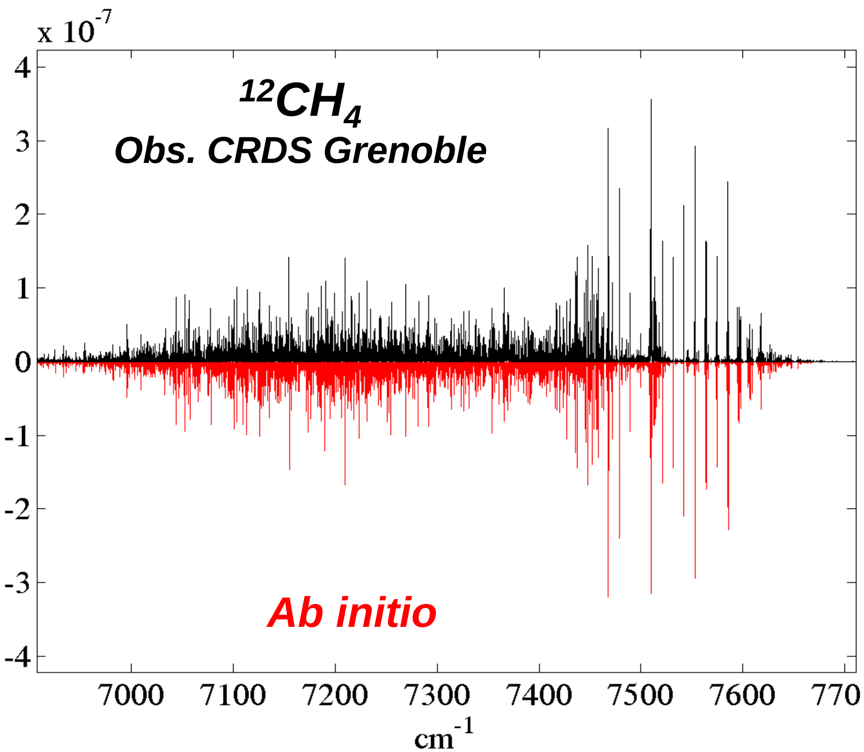
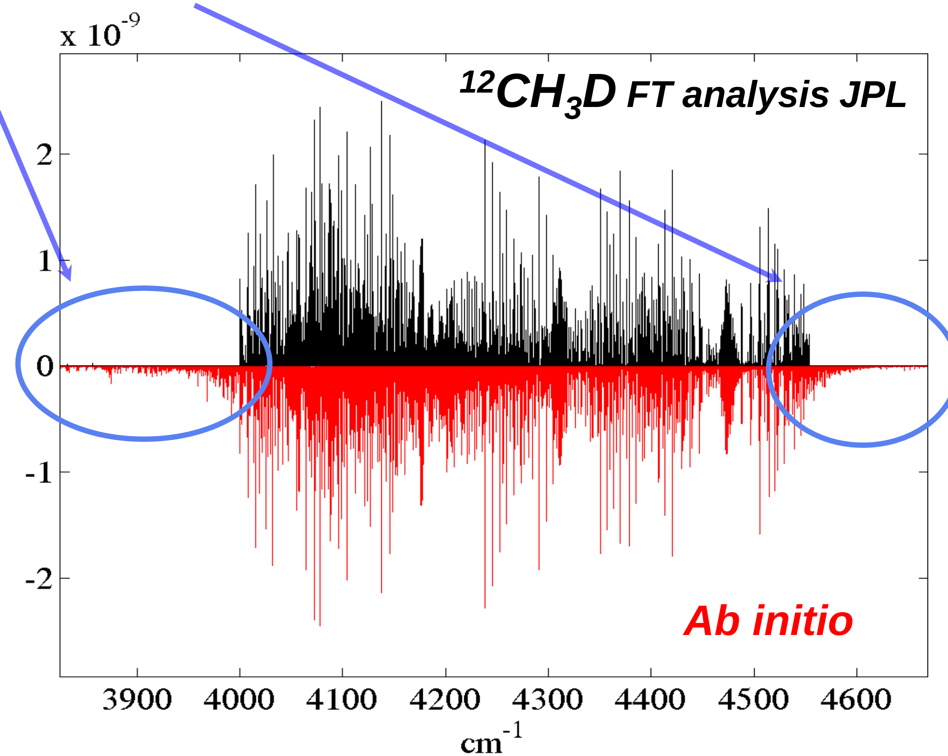
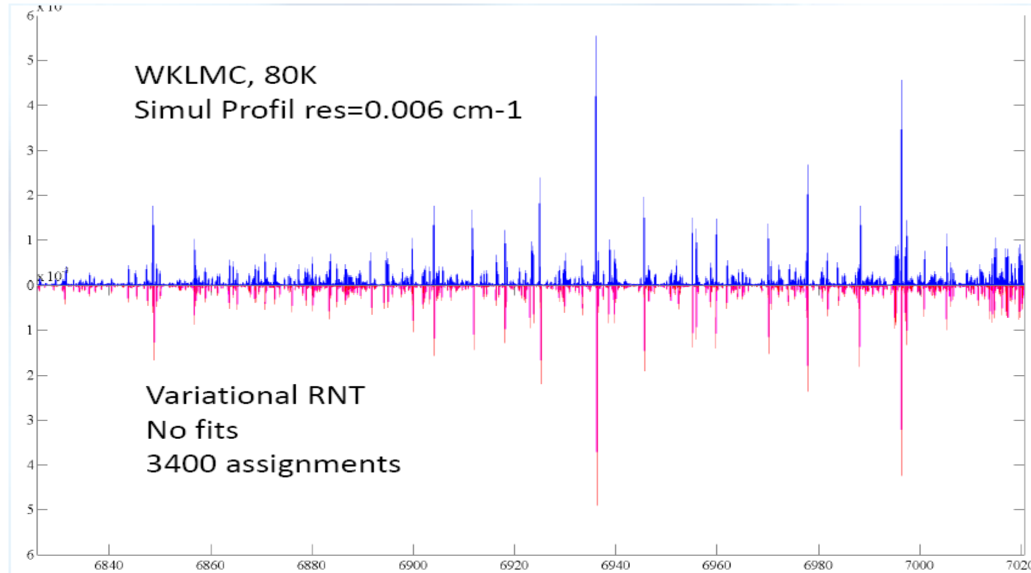
HITRAN completeness issue





Ab initio data base accuracy issues

I_{cutoff}	CB/HB	#Lines	RMS (cm^{-1})	RMS (%)
cm/molecules			Positions†	Intensities
10^{-23}	CB	7912	0.057	4.1
	HB	863	0.016	1.0
10^{-24}	CB	14810	0.070	4.8
	HB	2335	0.026	1.3
10^{-25}	CB	21556	0.087	4.8
	HB	5585	0.039	2.2
10^{-26}	CB	27493	0.10	5.1
	HB	10119	0.06	3.1



Accuracy of our room-temperature predictions (T=296 K) in the range [0 - 5000] cm^{-1} compared to HITRAN for the rotational dependence of line positions and for intensities.

Ab initio variational   Rey, Nikitin, Tyuterev, PCCP (2013)

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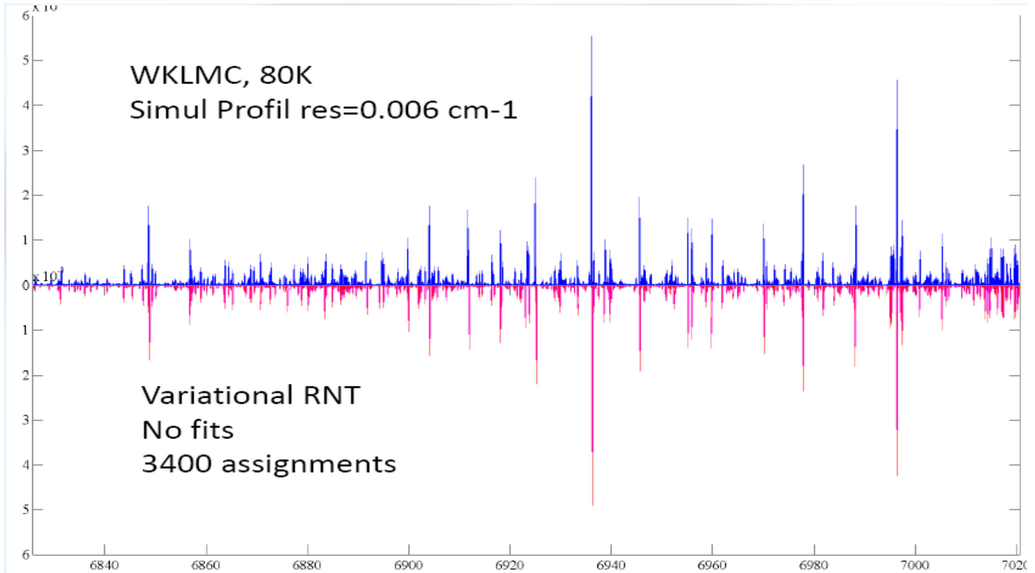

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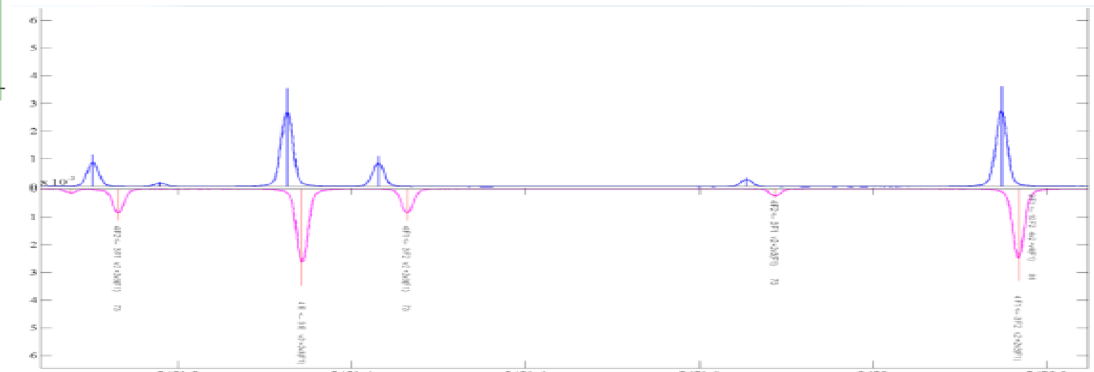
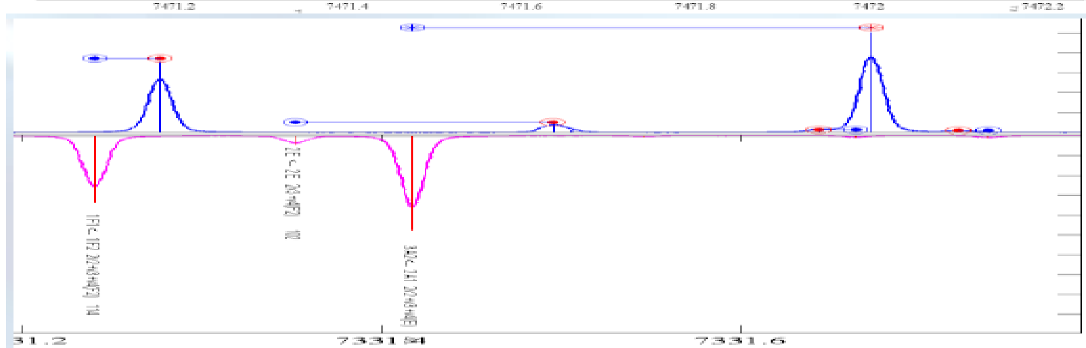


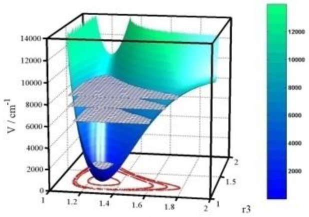


Line position accuracy need to be improved by one or two orders of magnitude !

Empirical corrections:

« unstable lines » issue

Potential $U(r_i)$



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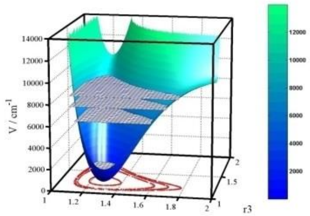

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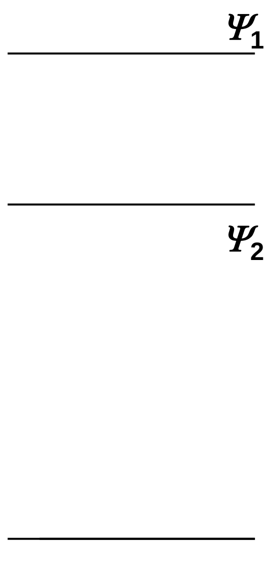

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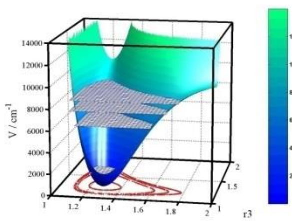
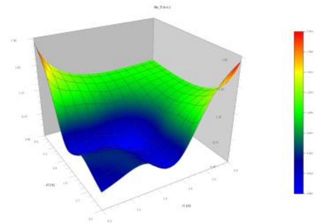


Dipole $D(r_i)$



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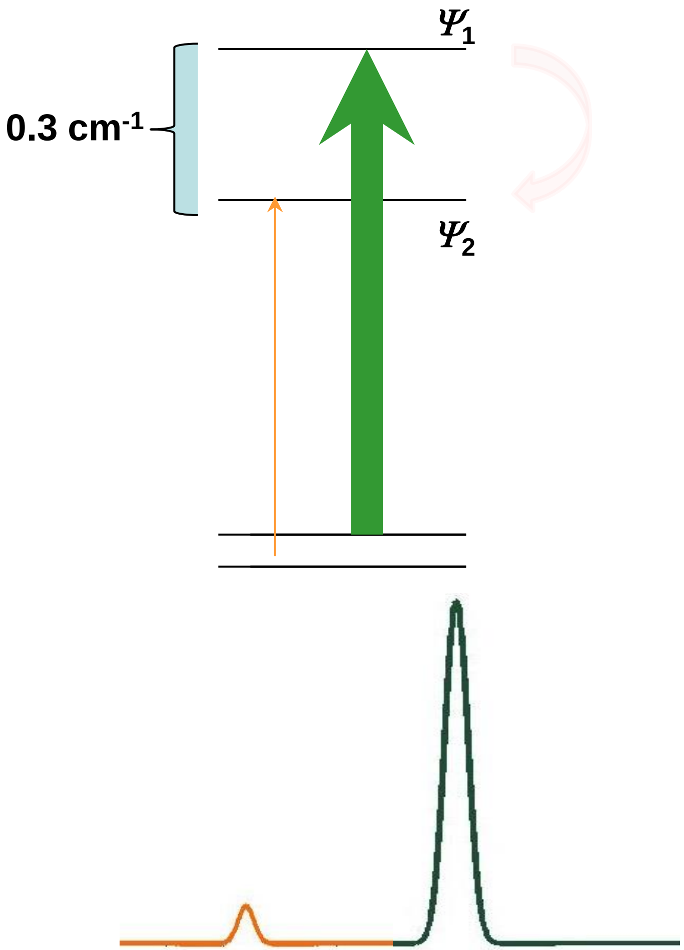

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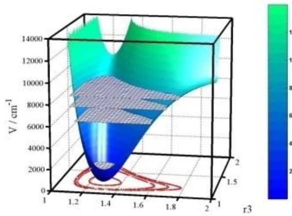

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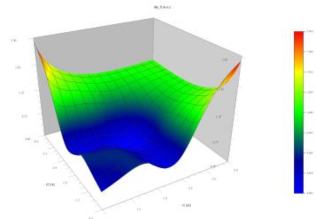

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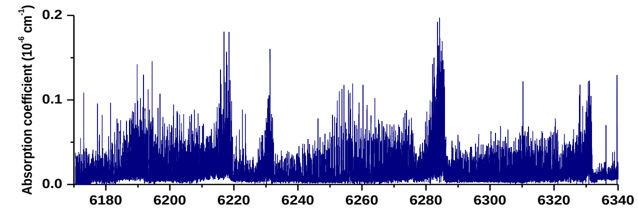

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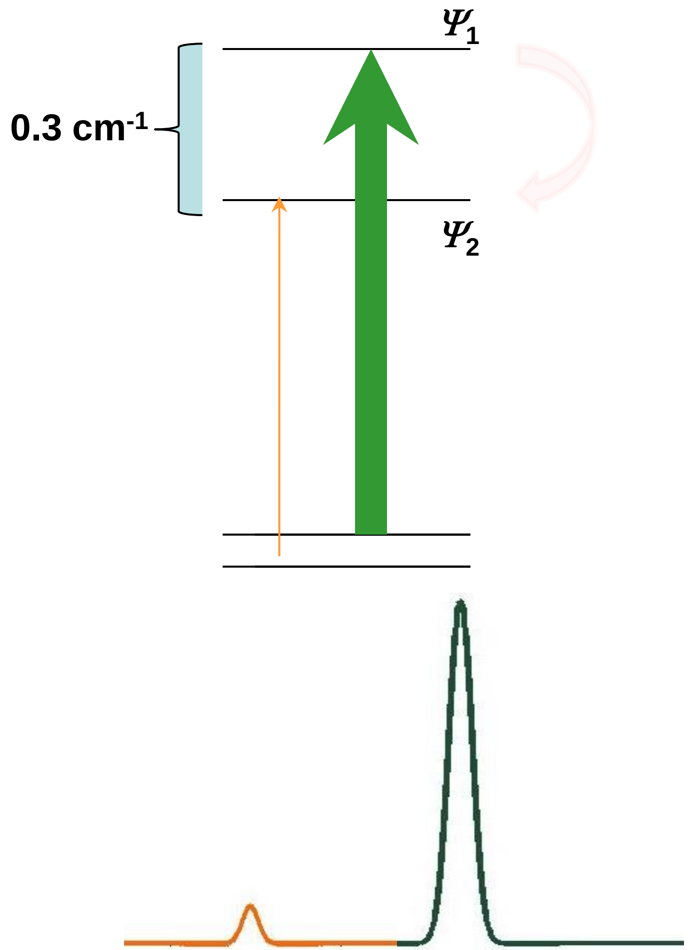

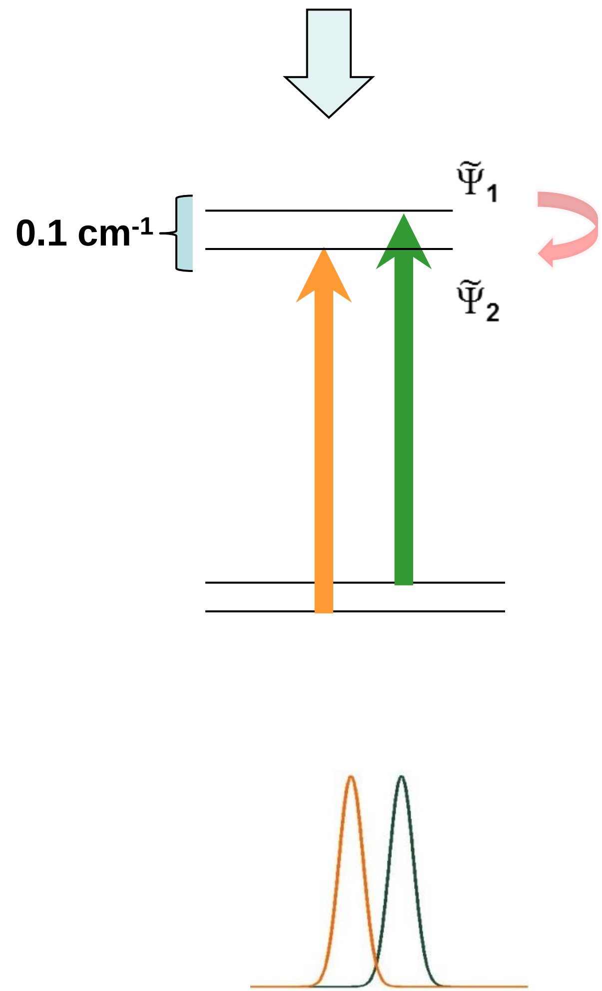

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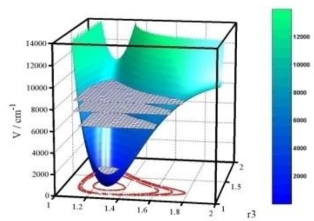

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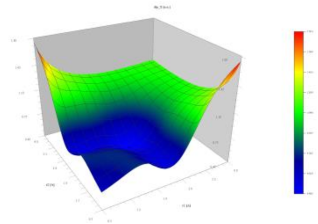

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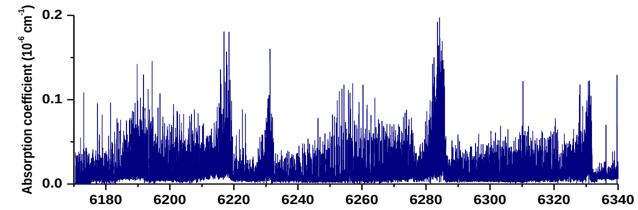

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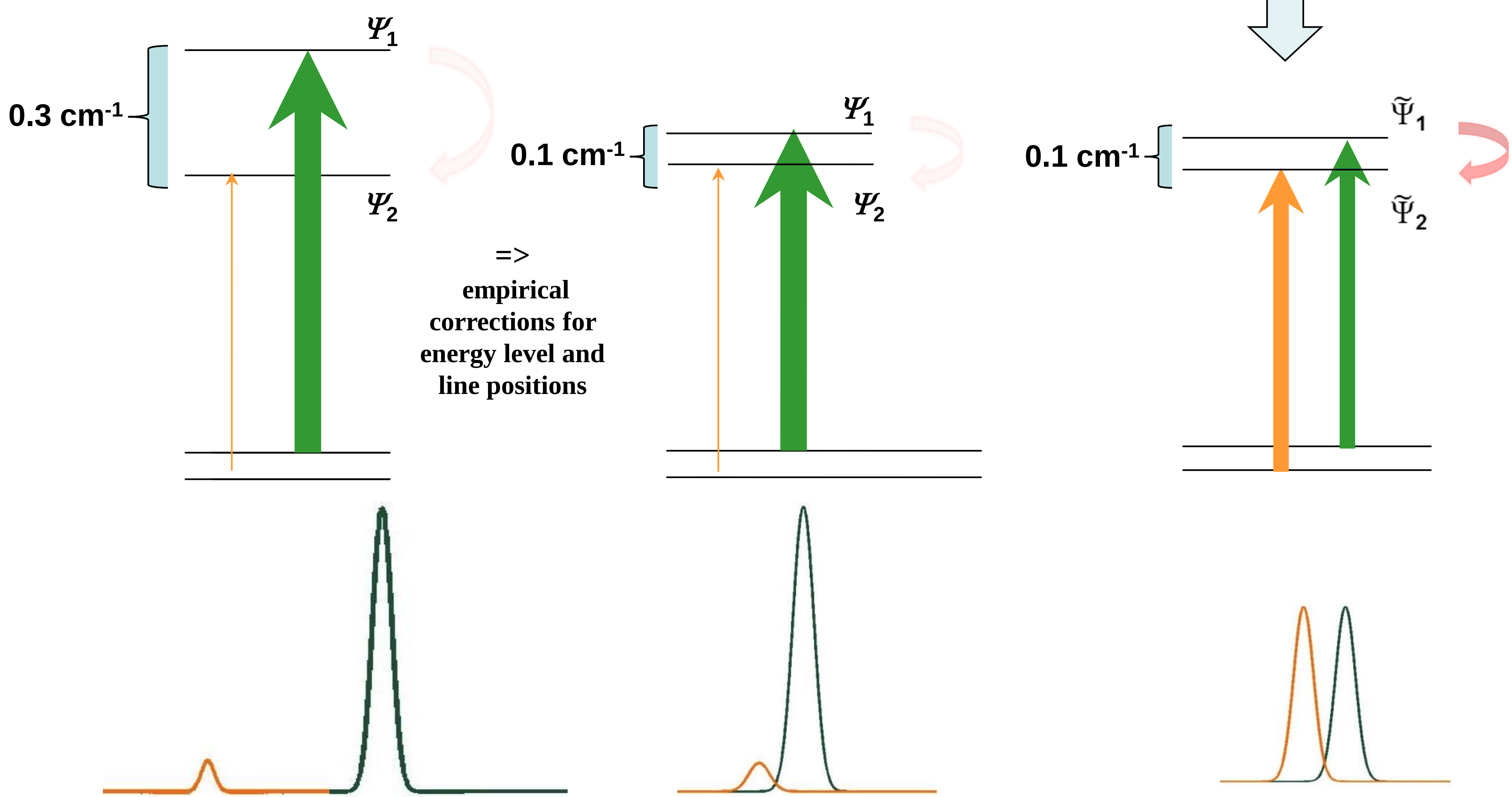

Does this work with effective empirical models ?

$$\widetilde{\Psi}_2 = \Psi_2 + \frac{\langle \Psi_1 | H | \Psi_2 \rangle}{E_1^0 - E_2^0} \Psi_1 + \cdots$$

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Not always !

« Blind » fit : mathematically ill-defined inverse problem !!!

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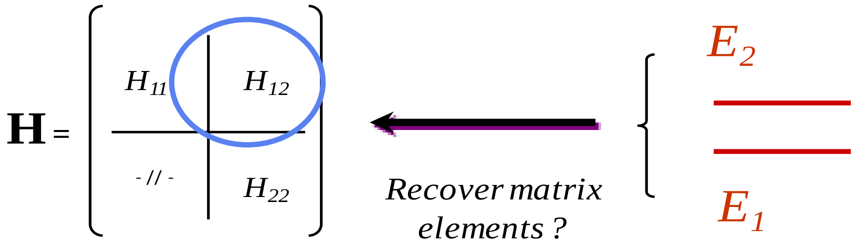
<u>"Inverse problem"</u> for a 2×2 matrix:

determine parameters of a matrix H from experimental energies



Poorly defined problem:

3 parameters H_{11} , H_{22} , H_{12} ← *no unique solution* ← $N_{data} = 2$

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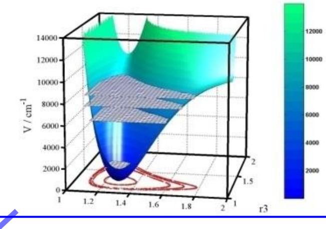
Key of the new data reduction approache: accurately compute the coupling from ab initio PES



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$$\mathbf{H} = \begin{pmatrix} H_{11} & H_{12} \\ \text{- // -} & H_{22} \end{pmatrix} \longleftarrow \left\{ E_2, E_1 \right.$$

Recover matrix elements ?

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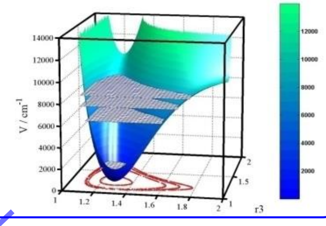

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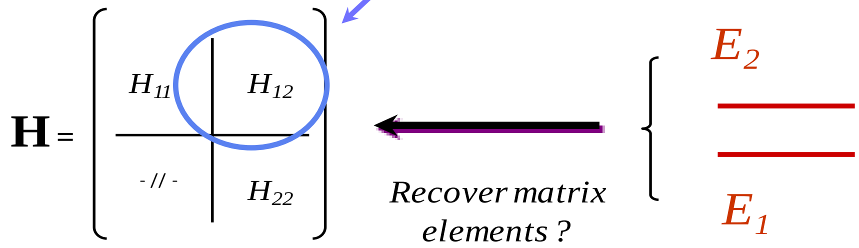

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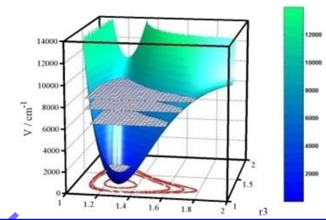

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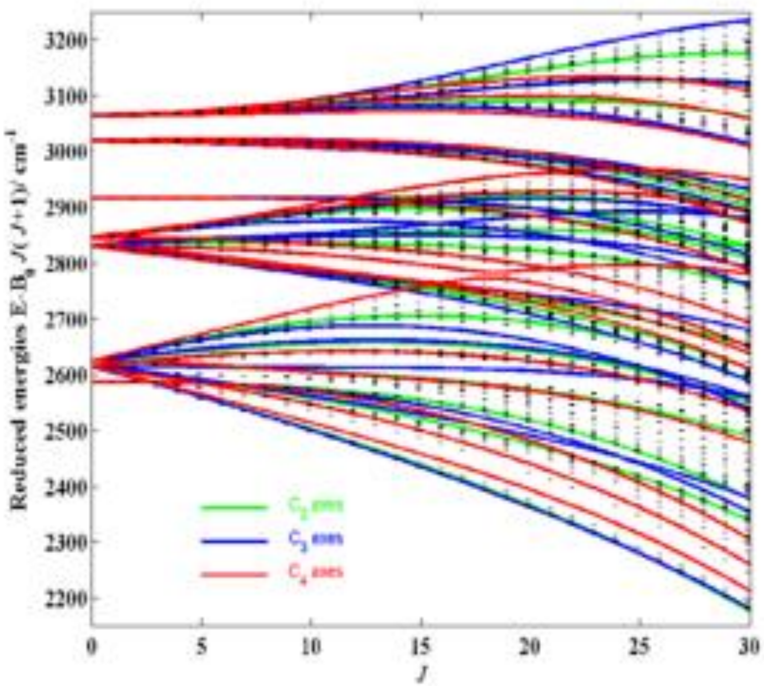
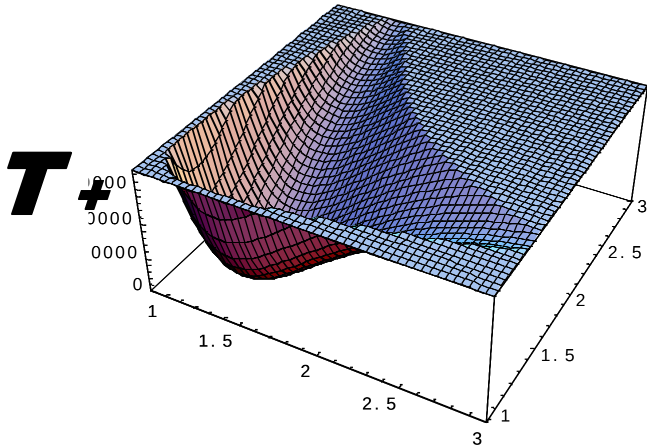


“Global” (variational) and “local”(effective) calculation in spectroscopy

$E_{n_s}^{ob}$

PES = ab initio potential energy surface



Direct global calculations

Infinite dimension ,

« integro-differential » technique

(methodes : variationnal, DVR,…)

« Locale » methods:

Finite dimension ,

talgebraic techniques

H_2^{eff}

H_1^{eff}

Effective Hamiltonians

Ajustable parameters = Spectroscopic Constants

polyades of closely lying states

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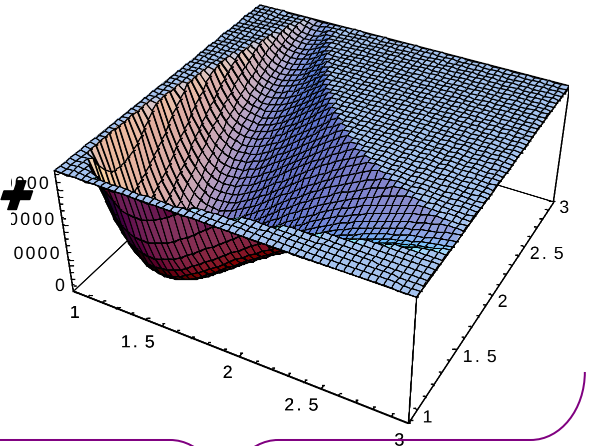
T +



Direct global calculations

Infinite dimension ,
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(methodes : variationnal, DVR,…)

« Locale » methods:
Finite dimension ,
talgebraic techniques

H_2^{eff}

H_1^{eff}

Globale-to-local « bridge »:

Contact Transformations (CT)

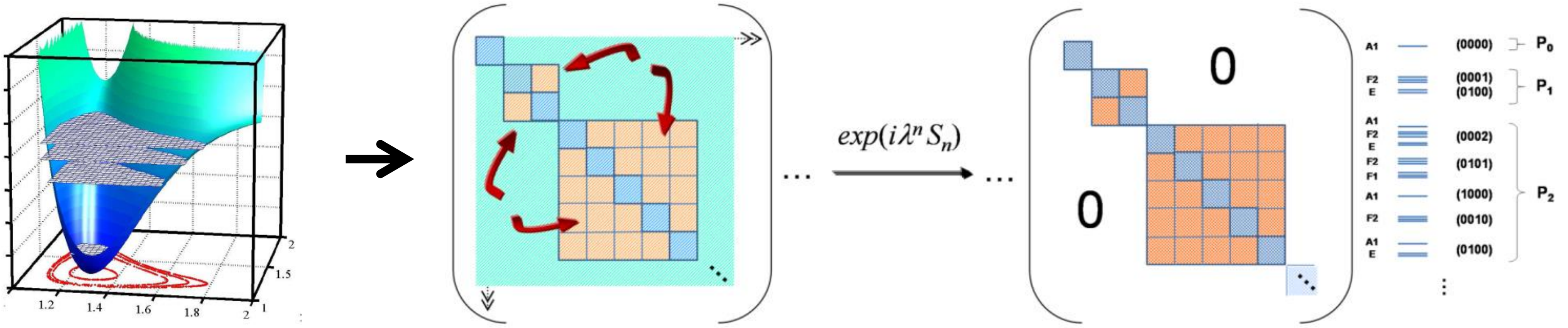
MOL_CT code

$$\tilde{H} = \ldots e^{iS_2} e^{iS_1} H e^{-iS_1} e^{-iS_2} \ldots$$

Effective Hamiltonians
Ajustable parameters = Spectroscopic Constants

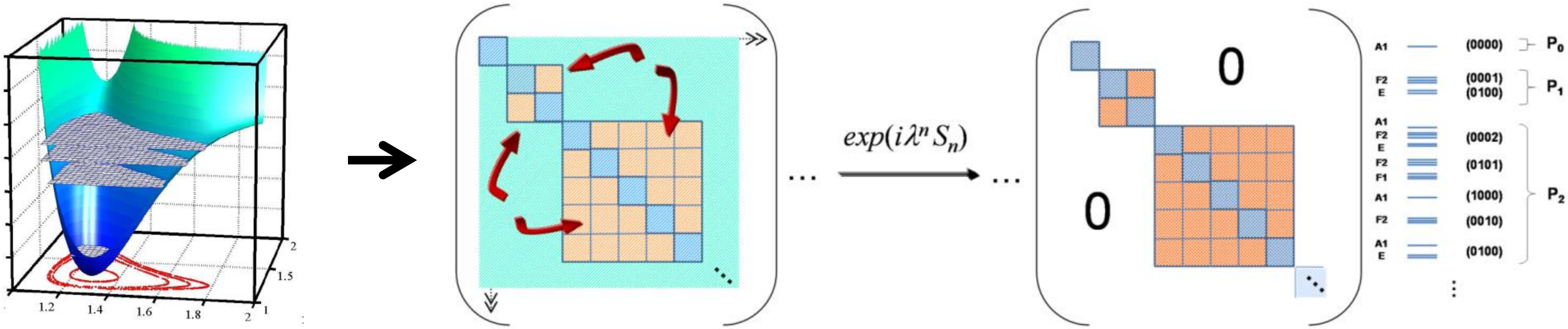
polyades
of closely
lying states

New combined model: «CT-polyads / ab initio » (Tyuterev et al JCPA 139, 134307 (2013)



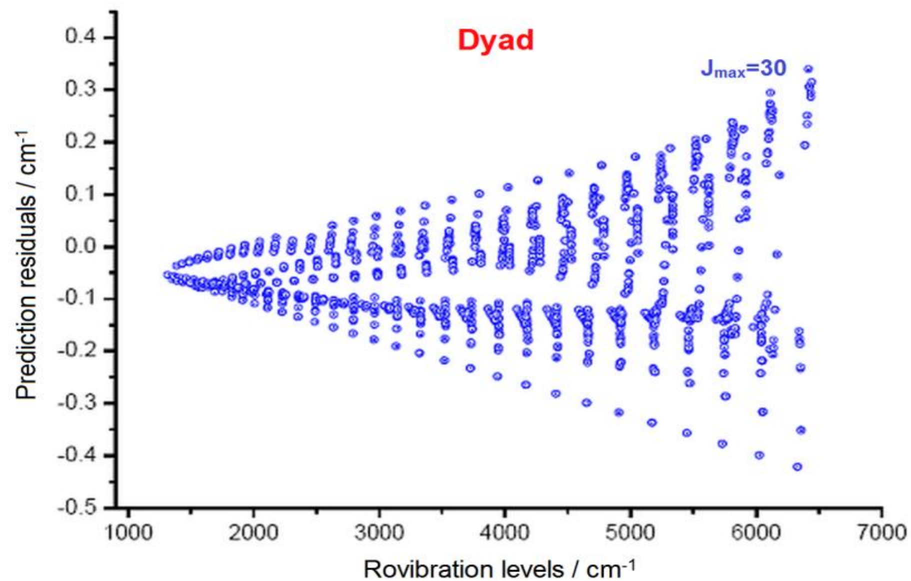
Direct MOL_CT calculations for methane:

New combined model: «CT-polyads / ab initio » (Tyuterev et al JCPA 139, 134307 (2013)



P	vib	S	E	Emp - CT
Dyad			cm-1	cm-1
1	0001	F2	1310.81	-0.05
1	0100	E	1533.41	-0.08
Pentad				
2	0002	A1	2587.28	-0.24
2	0002	F2	2614.31	-0.05
2	0002	E	2624.81	-0.20
2	0101	F2	2830.64	-0.32
2	0101	F1	2846.20	-0.13
2	1000	A1	2916.38	0.11
2	0010	F2	3019.47	0.03
2	0200	A1	3064.00	-0.35
2	0200	E	3065.35	-0.20
…				
Icosad				
5	0005	E	6507.77	-0.38
5	0005	F2	6508.02	-0.47
5	0005	F1	6530.34	-0.56
5	0005	F2	6539.91	-0.73
5	1011	F2	7158.22	-1.49
5	0120	F2	7511.10	-0.13
Triacontad				
6	1012	F2	8421.60	-0.60
6	0030	F2	8907.77	-0.47
6	0030	F2	**9046.6**7	-0.71
RMS / cm^{-1}				0.74

Direct MOL_CT calculations for methane:

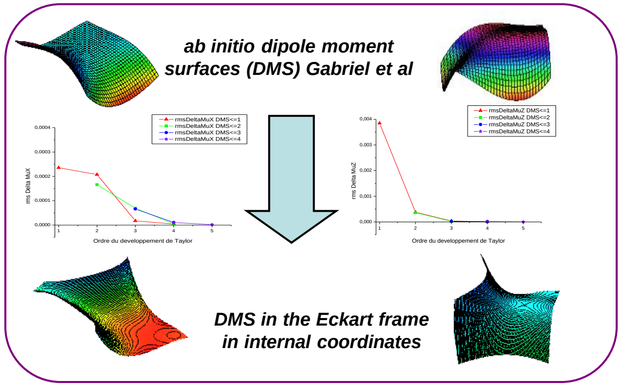


For all experimentally assigned bands centres up to 9050 cm^{-1}

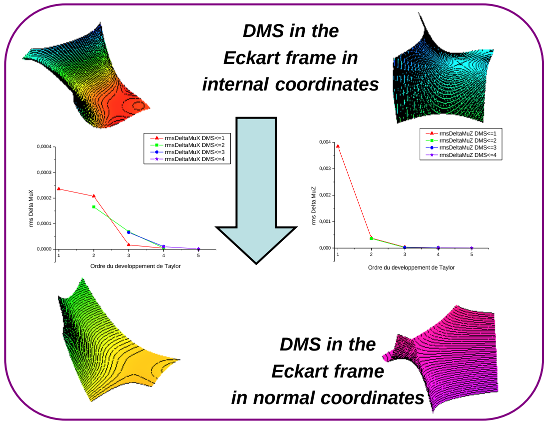
RMS vib-rot (Dyad) = 0.06 cm^{-1}

Ab initio dipole moment surface (DMS) transformations:

(a) axes rotation: from Bisector frame to Eckart frame



(b) from internal to normal coordinates



Intensity CT calculations for band dipole transition parameters

$$\widetilde{\mu_n}^{(n)} = \widetilde{\mu_n}^{(n-1)} + [S_n, \mu_0]$$

$$\widetilde{\mu_n}^{(k)} = \sum_{m=0}^{[[n/k]]} \frac{1}{m!} \underbrace{[S_k, \ldots [S_k, \widetilde{\mu_n}_{n-km}^{(k-1)}] \ldots]}_{m}$$

$$^{vv'}\mu = \langle v | \tilde{\mu} | v' \rangle = \sum_{nml} {}^{\kappa}d^{\theta}_{nml} \, {}^{\kappa}\Re^{\theta}_{nml}$$

Julien Lamouroux:

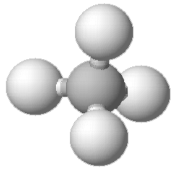
PhD thesis (Reims)

Non-empirical predictions

$$W_{ab} = \left| \sum_{nml\kappa\theta} \sum_{vv'} \sum_{KK'} {}^{\kappa}d^{\theta}_{nml} (C^{v}_{JK\gamma})^{*} \, C^{v'}_{J'K'\gamma'} \langle JK\gamma | {}^{\kappa}\Re^{\theta}_{nml} | J'K'\gamma' \rangle \right|^{2}$$

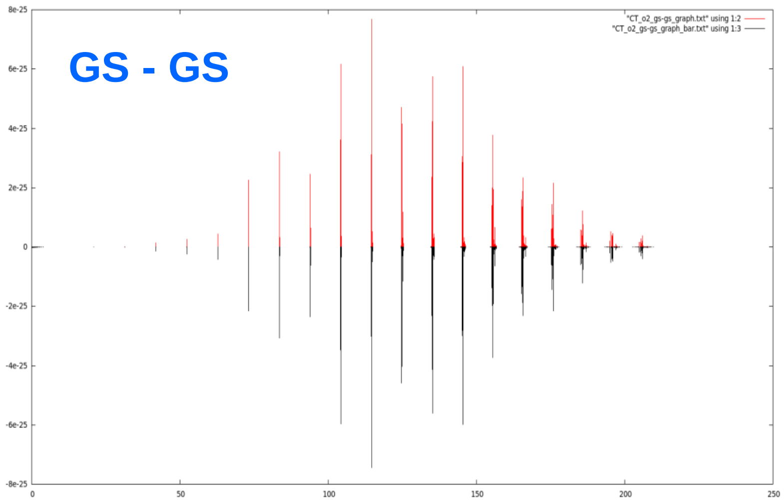
V.Tyuterev, S.Tashkun, H.Seghir SPIE Proc. 5311, 165 (2004)
J.Lamouroux, S.Tashkun, V.Tyuterev, CPL, 452, 225 (2008) } *triatomics*

T.Delahaye, M.Rey, A.Nikitin, V.Tyuterev, in progress (2014) } *5 and 6 atomics ; CH4, C2H4*

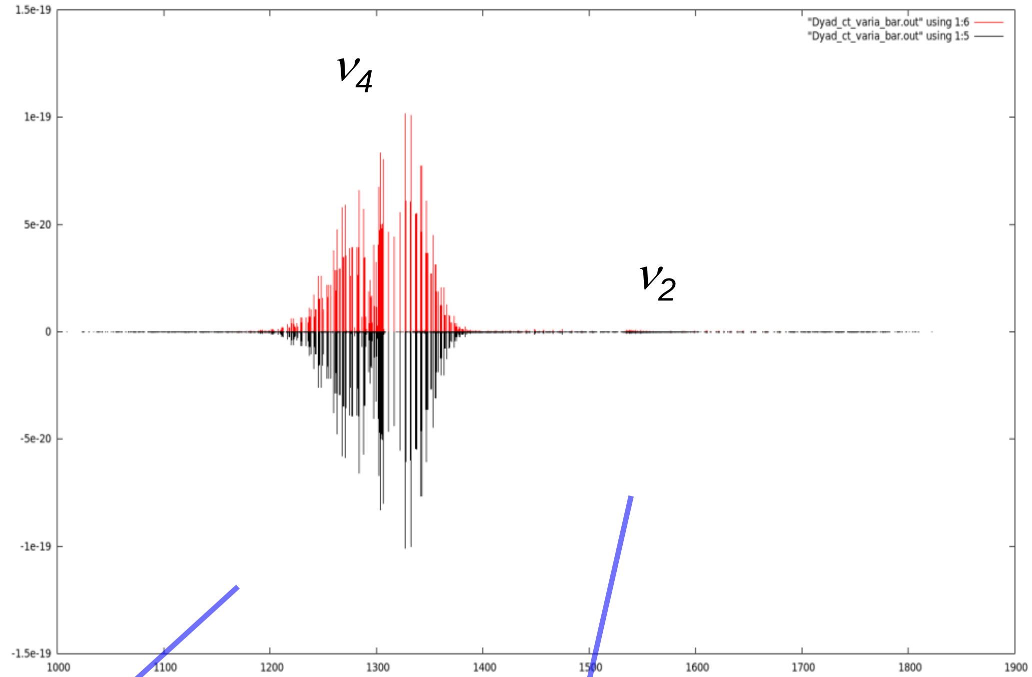


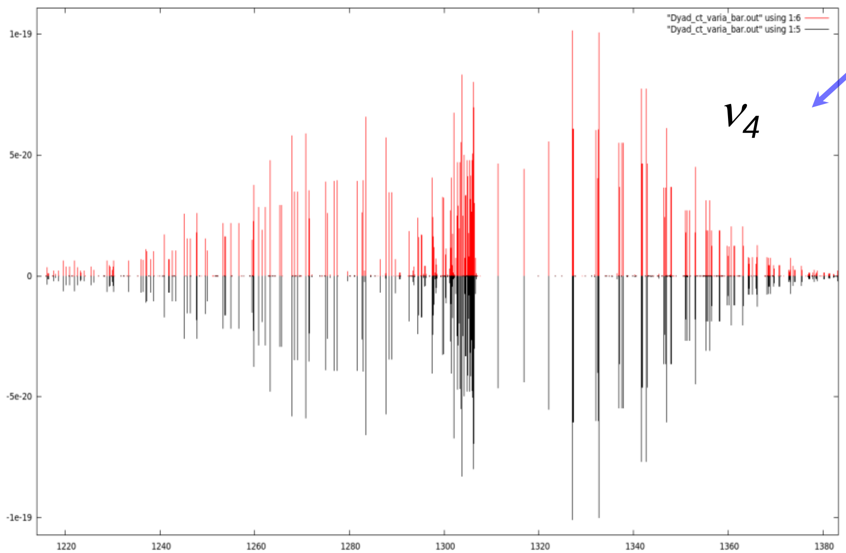
Methane

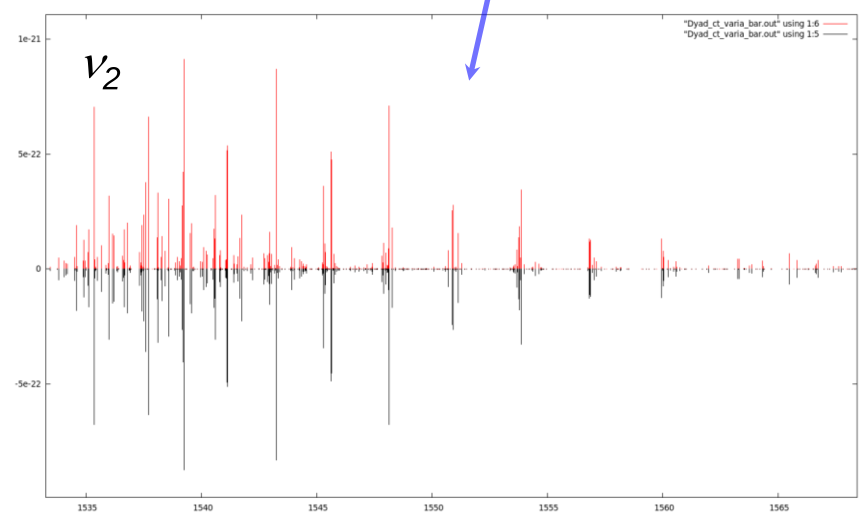
Ab initio => CT / ***Hitran***

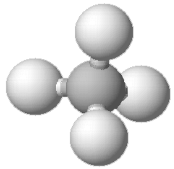


Dyad range (1000-1800 cm^{-1})







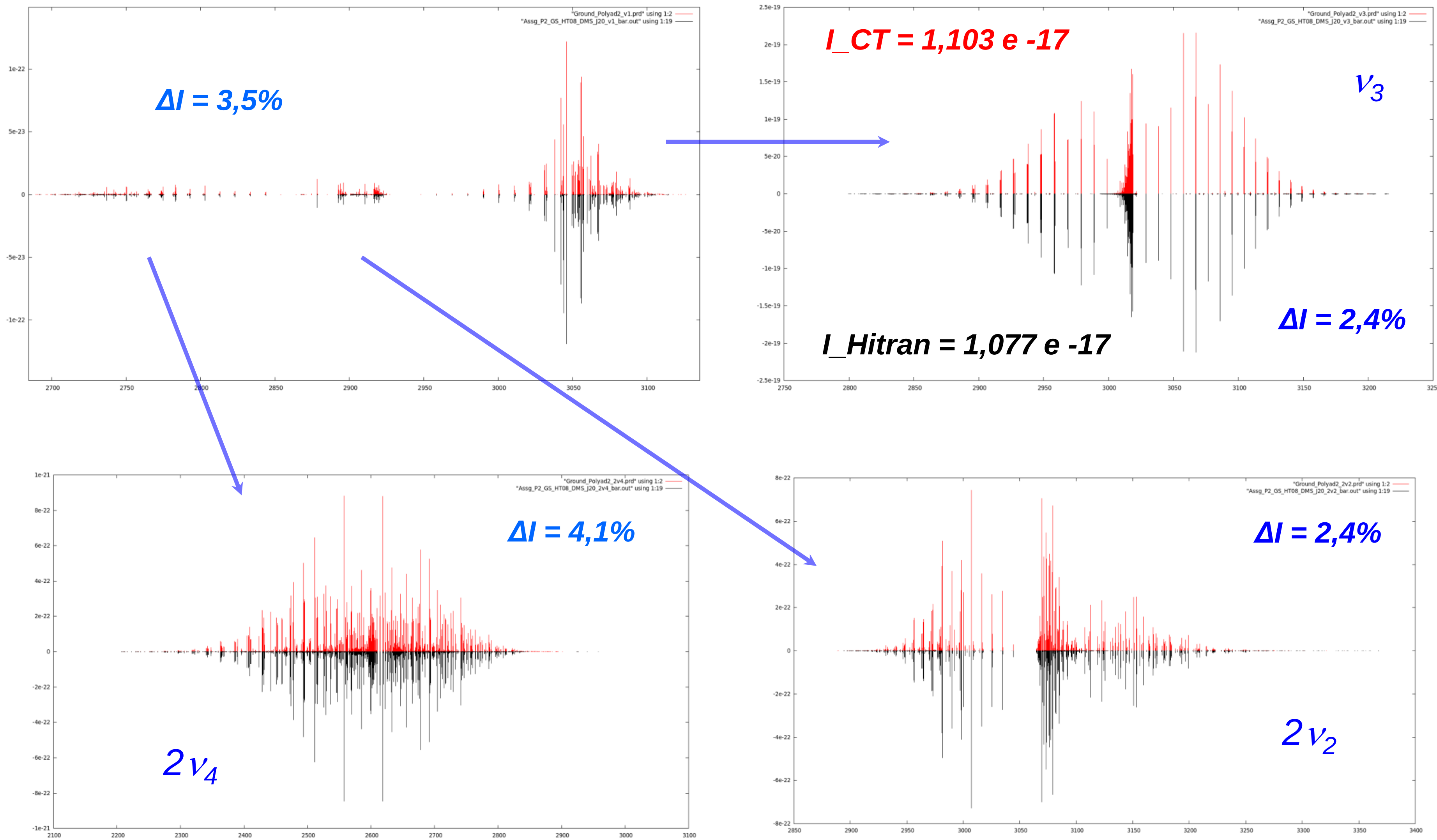


Methane

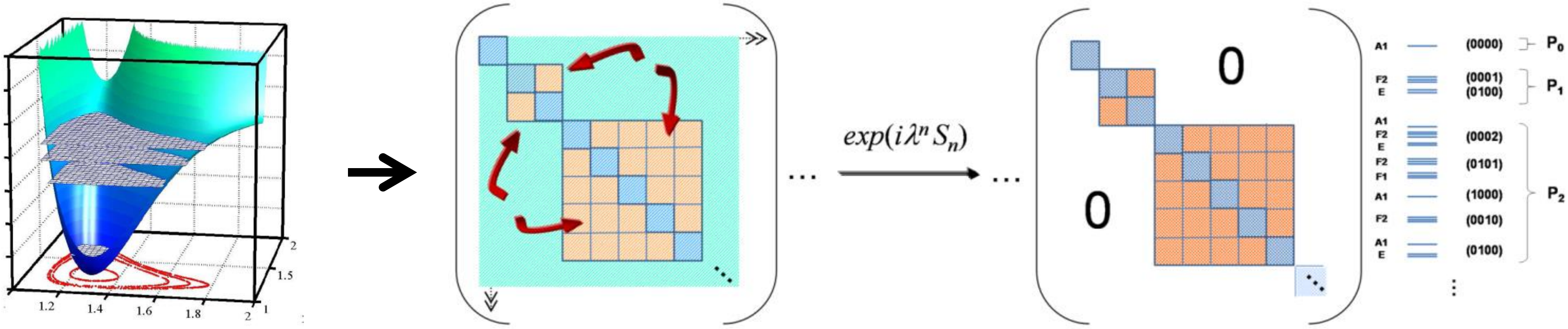
Pentad range (2300-3200 cm^{-1})

Ab initio => CT

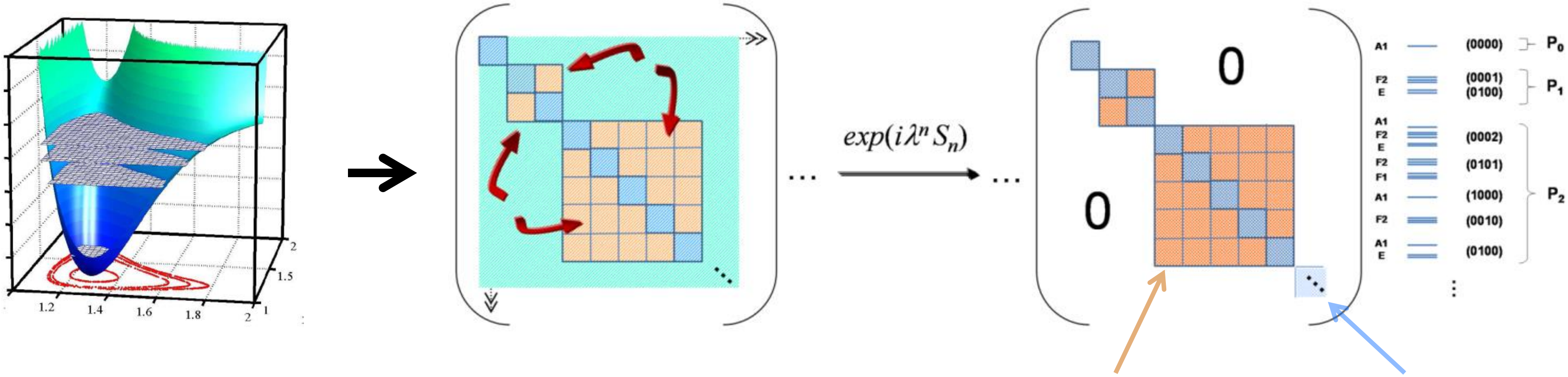
Hitran 08



New combined model: «CT-polyads / ab initio » (Tyuterev et al JCPA 139, 134307 (2013)



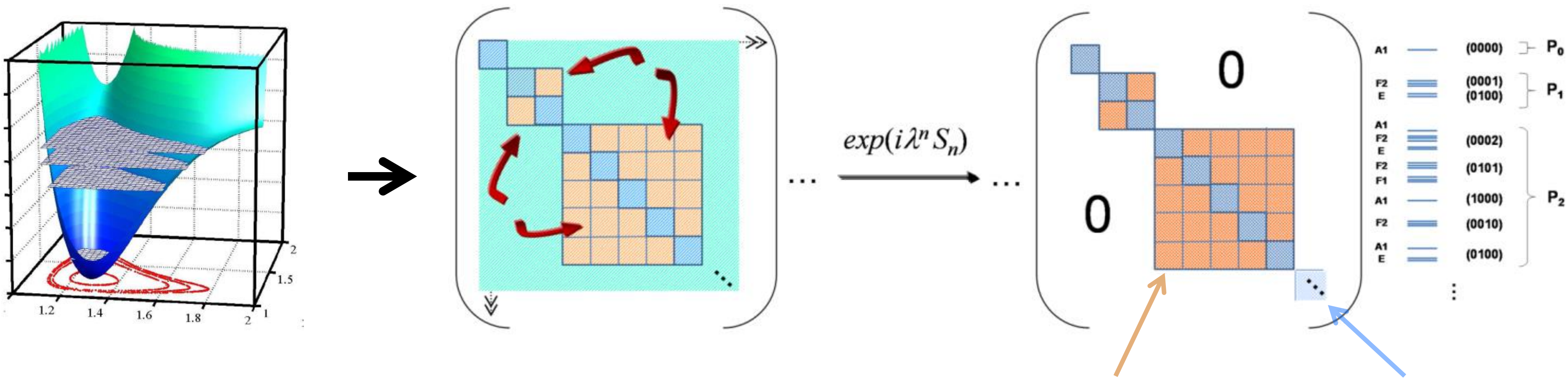
New combined model: «CT-polyads / ab initio » (Tyuterev et al JCPA 139, 134307 (2013)



Resonance coupling terms: fixed to ab initio

Diagonal parameters (ν, B,D, …): fitted to obs lines

New combined model: «CT-polyads / ab initio » (Tyuterev et al JCPA 139, 134307 (2013)



Resonance coupling terms: fixed to ab initio

Diagonal parameters (ν, B,D, …): fitted to obs lines

	vib	Γ	N obs lines a	J_{max}	d_{RMS} / cm^{-1}	σ
			DYAD			
1	0100	E	354	19	0.00011	0.67
2	0001	F2	1109	23	0.00016	0.77
Total			1463	23	0.00015	**0.74**
			PENTAD			
1	1000	A1	186	18	0.00112	1.04
2	0200	E	215	16	0.00061	0.71
3	0200	A1	170	17	0.00063	0.68
4	0101	F1	617	18	0.00056	0.64
5	0101	F2	720	19	0.00052	0.61
6	0010	F2	597	23	0.00059	0.62
7	0002	A1	244	19	0.00041	0.53
8	0002	E	630	20	0.00048	0.57
9	0002	F2	785	21	0.00046	0.58
Total			**4164**	**23**	**0.00058**	**0.63**

Statistics for the line positions fit with resonance coupling parameters held fixed to ab initio CT-values

Line position error in new model:

Dyad:

~0.00015 cm^{-1}

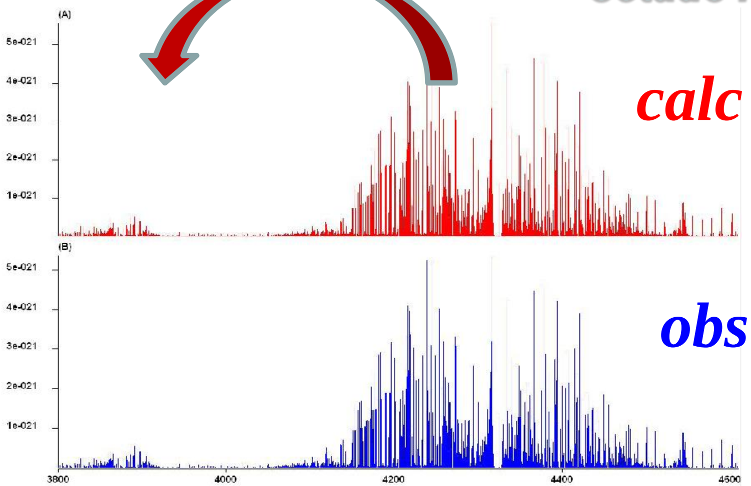
Pentad:

~0.0005 cm^{-1}

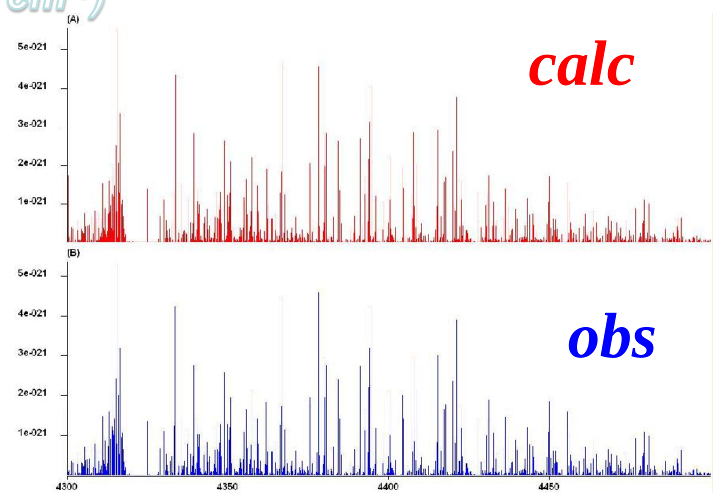
Fixed: all resonance coupling parameters computed by CT from PES

Fitted: 128 diagonal polyad parameters up to Octad + tr. mom parameters

octade range (3900-4500 cm^{-1})



CH_4



- Octad (2–3 μm) : 8 vibrational levels, 24 vibrational sublevels

$$\nu_1 + \nu_2/\nu_1 + \nu_4/\nu_2 + \nu_3/\nu_3 + \nu_4/3\nu_2/3\nu_4/2\nu_2 + \nu_4/\nu_2 + 2\nu_4,$$

Criteria of improvement of resonance couplings and wave-functions:

RMS fit of Octade intensities, 3500 lines :

11.2 % (with pure empirical H^{eff}) => 7.5% (with ab initio couplings)

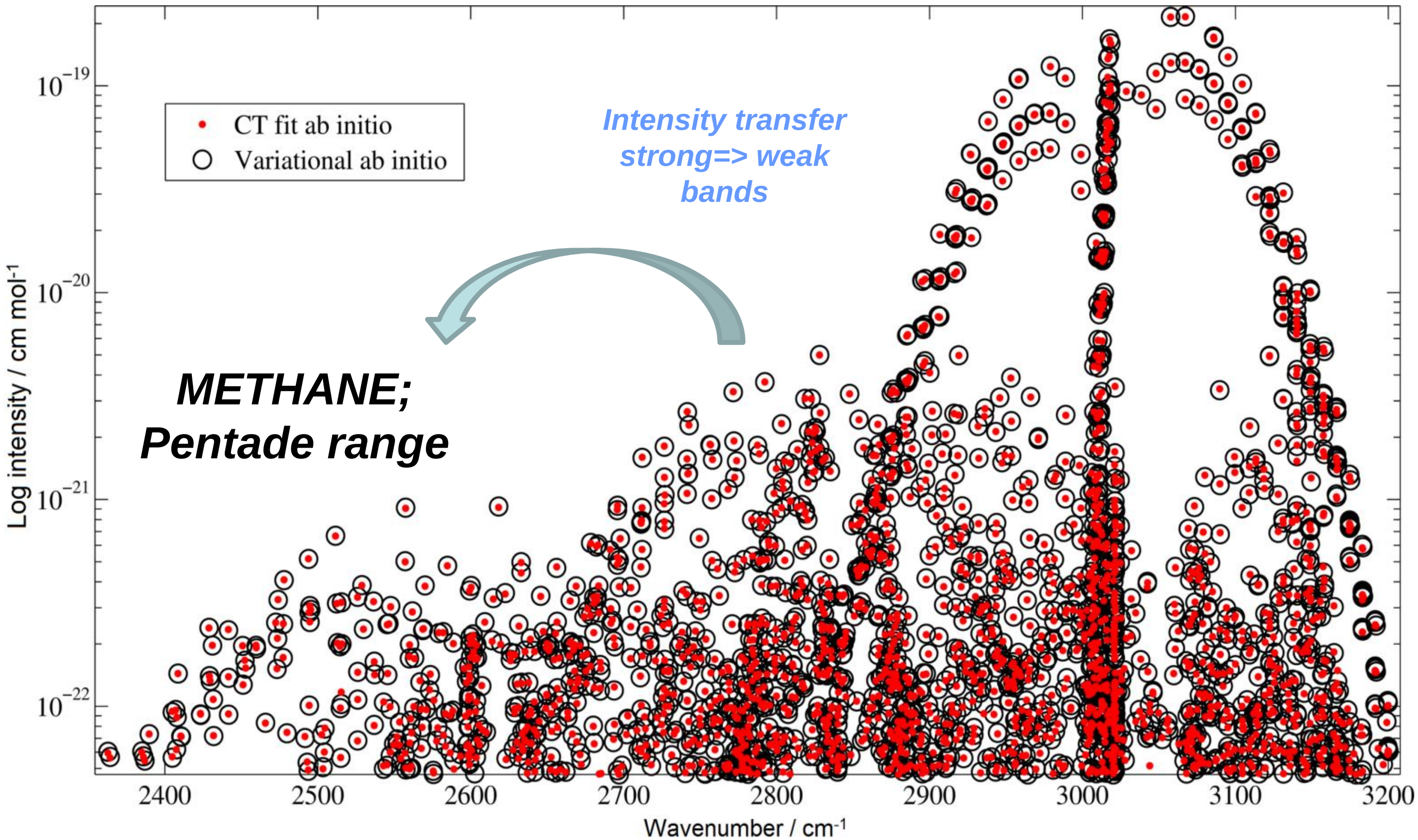
~ 600 res parameters fitted

No res parameters fitted

Better wave functions => better model for intensity borrowing

New combined model: «CT-polyads / ab initio » (Tyuterev et al JCPA 139, 134307 (2013))

Another option: fit with this model variational ab initio intensities



Line position error in new model:

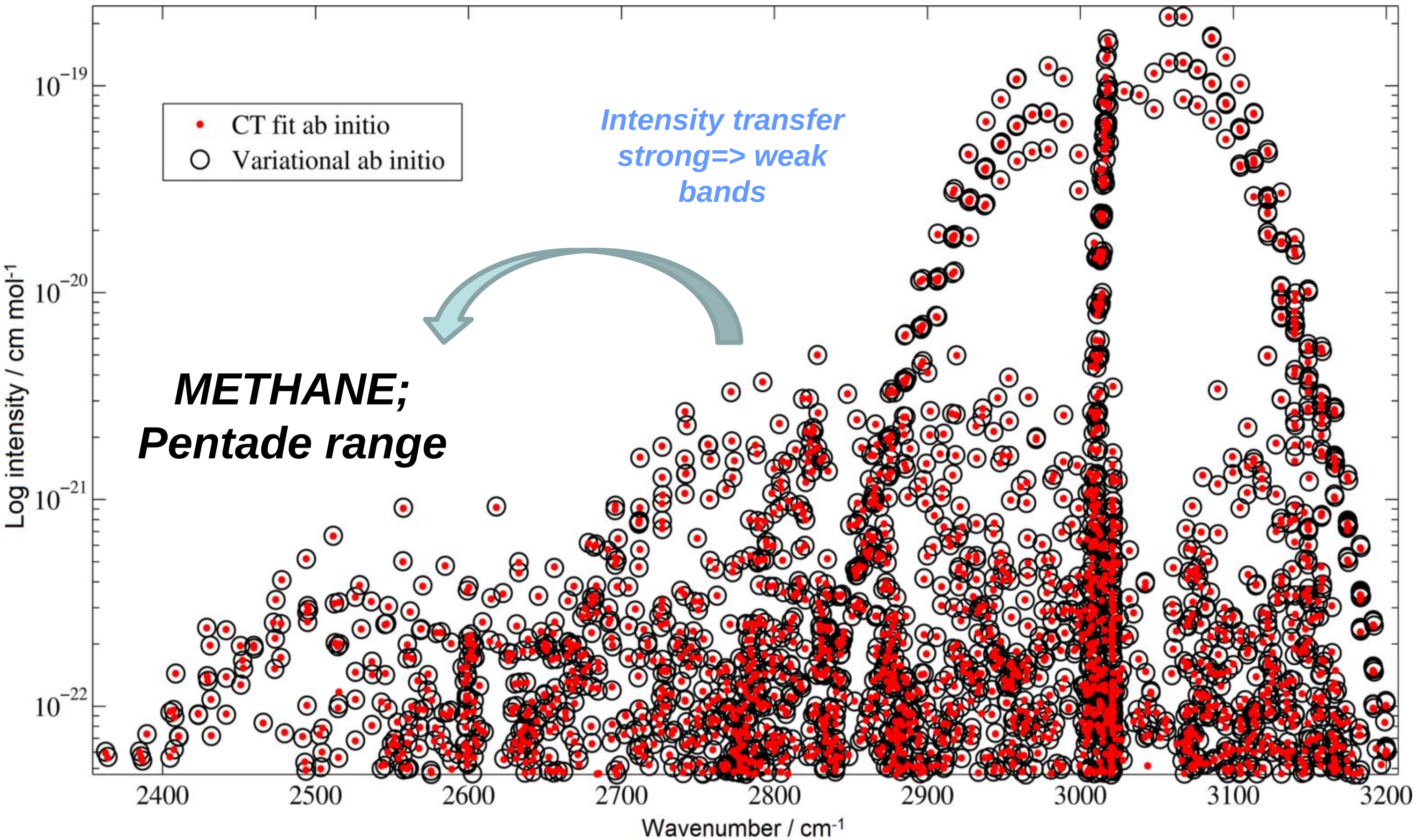
Dyad: ~0.00015 cm-1

Pentad: ~0.0005 cm-1

Output: line lists with line positions to experimental precision
With ab initio intensities sitting on them

New combined model: «CT-polyads / ab initio » (Tyuterev et al JCPA 139, 134307 (2013))

Another option: fit with this model variational ab initio intensities



Line position error in new model:

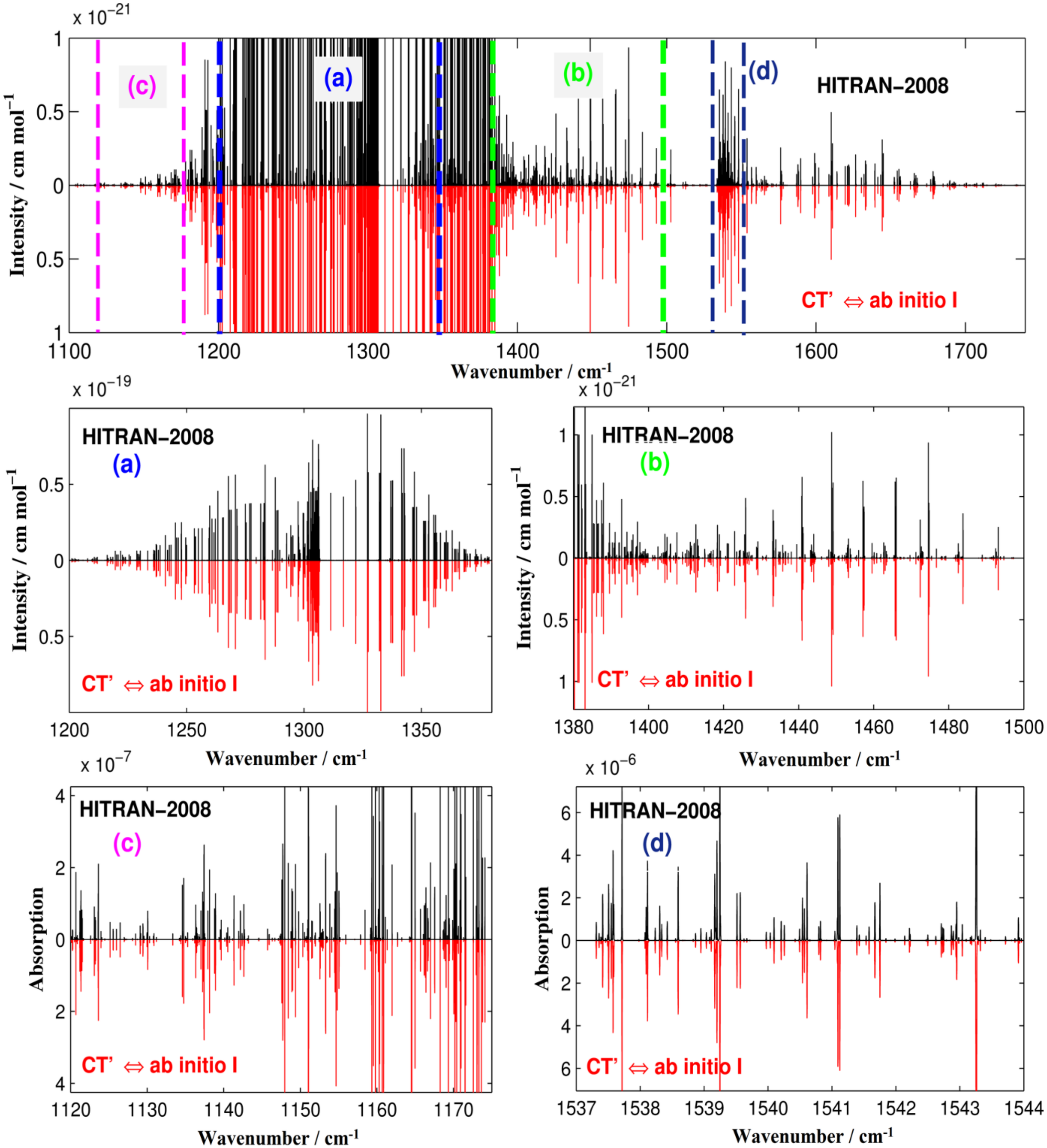
Dyad: **~0.00015 cm^{-1}**

Pentad: **~0.0005 cm^{-1}**

Output: line lists with line positions to experimental precision With ab initio intensities sitting on them

Do we want databases with such lists ?

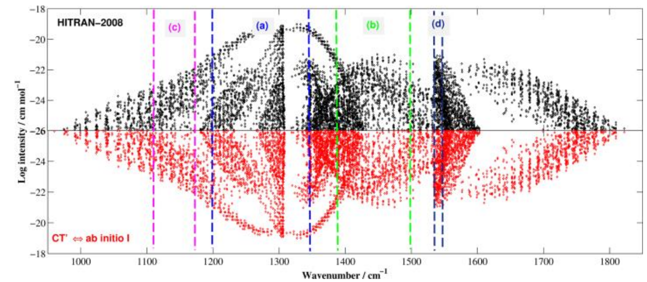
Combined «CT-polyads / abinitio » model , Dyad range



Methane:

HITRAN / CT ⇔ ab initio

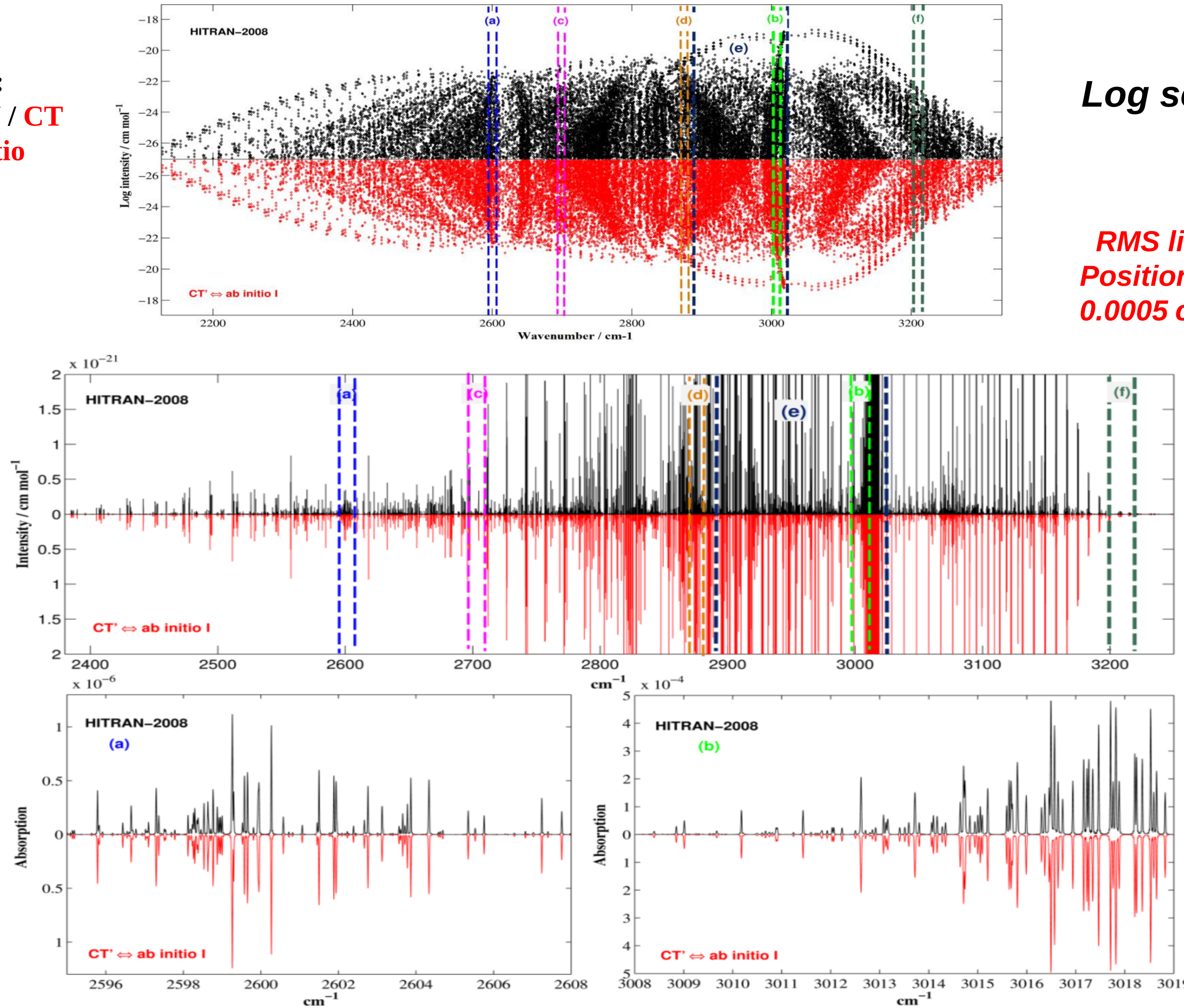
Log scale



RMS line Positions = $0.0001\ cm^{-1}$

Combined «CT-polyads / abinitio » model , Pentad range

Methane:
HITRAN / CT ⇔ ab initio

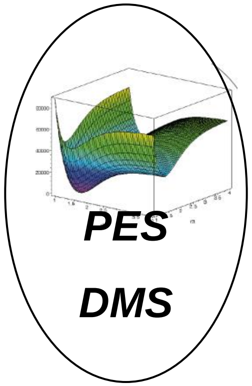


Log scale

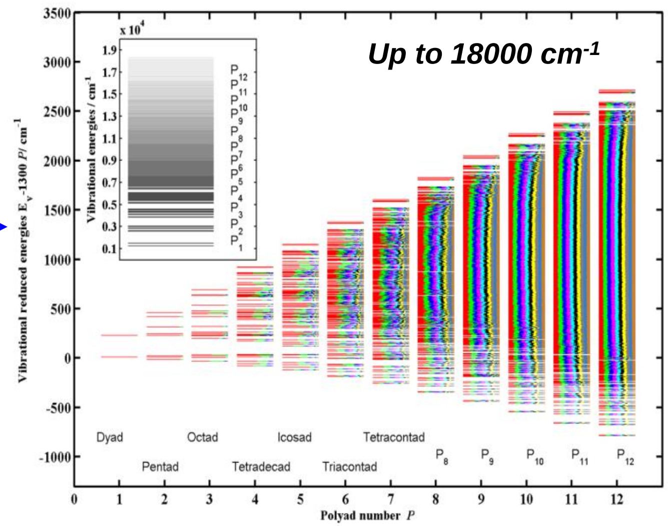
RMS line Positions = 0.0005 cm^{-1}

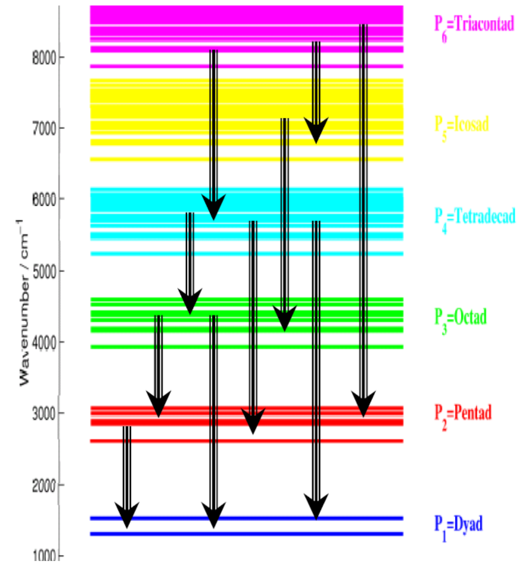
Further work, applications ⇔ astro ⇔ planeto

High energies / hot bands



New CT: Spectr. Models





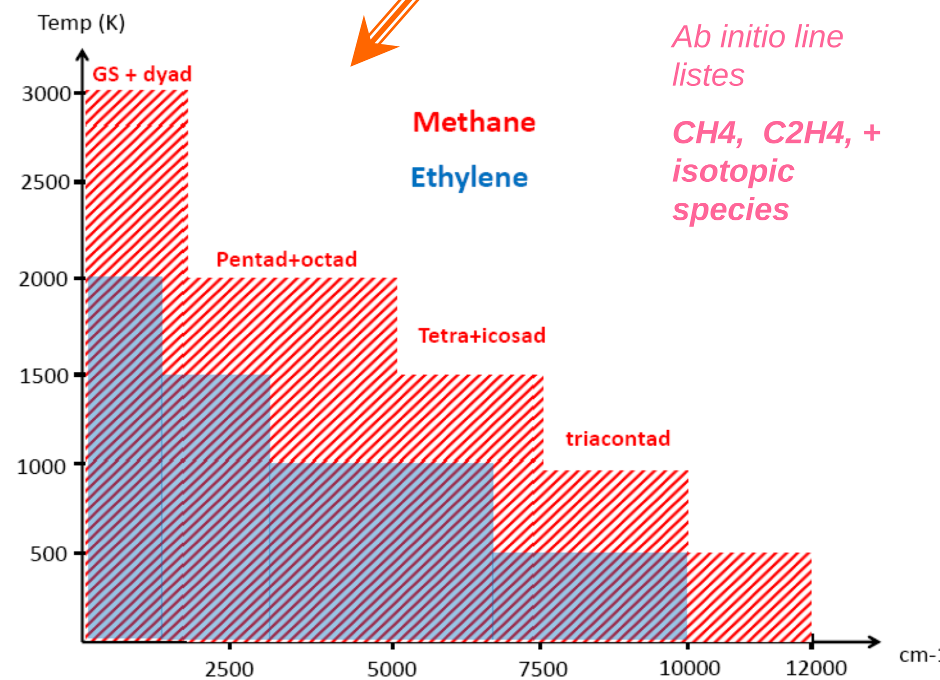
Conclusions / Prospectives:

- Line positions corrected to experimental precision via ab initio ⇔ Heff optimisation

- Some inconsistency found in HTIRAN and the empirical databases

- ***Empirical line position corrections to complete DB up to T=2000 K (11.5 billion lines, ApJ 789, 1 (2014))***

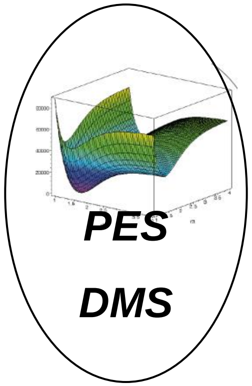
???



Ab initio line listes

CH4, C2H4, + isotopic species

Do we need such lists for higher E, T and other molecules?



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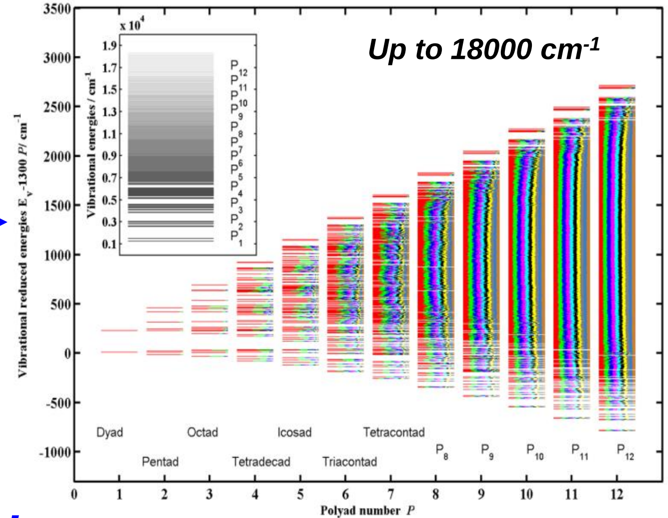
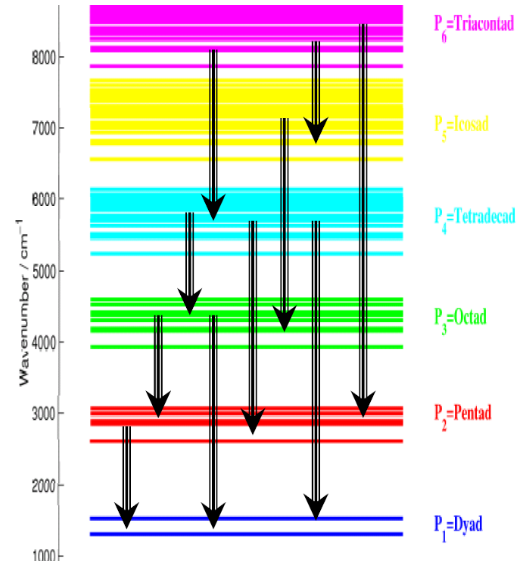
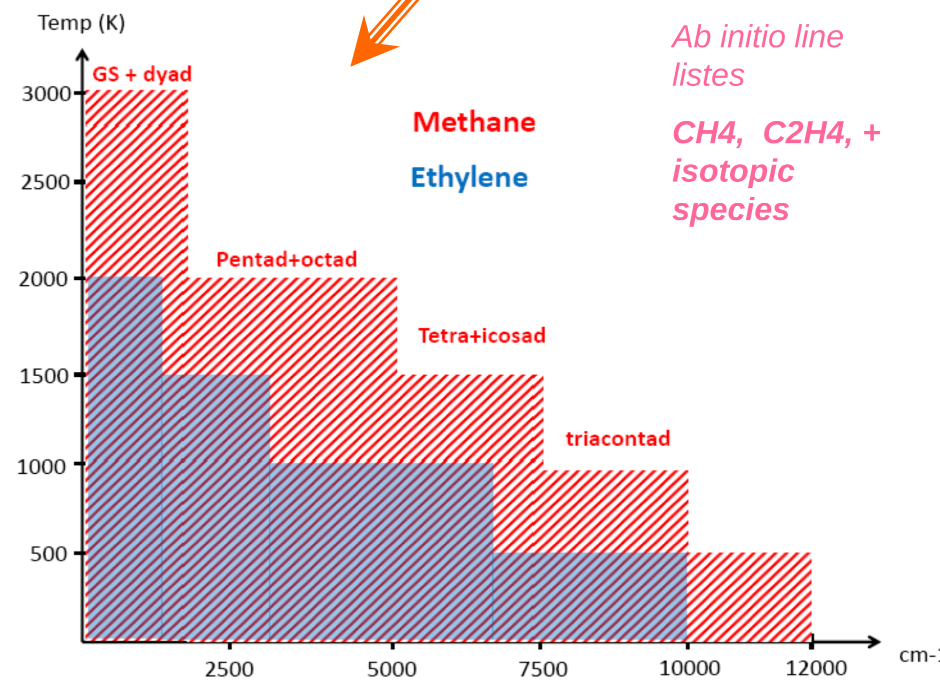


High energies / hot bands



Networking project !



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???

Collaborations:

ab initio:
P.Szalay (Budapest)

Methane analyses / databases:
V.Boudon, C.Wenger, J.P.Champion (Dijon)

CRDS spectroscopic experiments:
A.Campargue, S.Kassi, D.Mondelain, Grenoble University
FT spectroscopic experiments for methane:
L.Brown (NASA) , X.Thomas, L.Daumont, L.Regalia, Reims University

High-T methane spectra:
R.Georges, Rennes University

Applications planeto / astro:
B.Bezard, A.Coustenis (Obs Meudon), P.Rannou (Reims), A.Kutepov (Washington)

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