

# Excitation collisionnelle des molécules interstellaires : approches *ab initio*

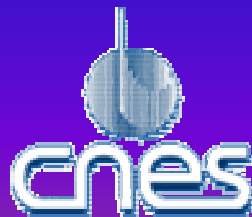
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&

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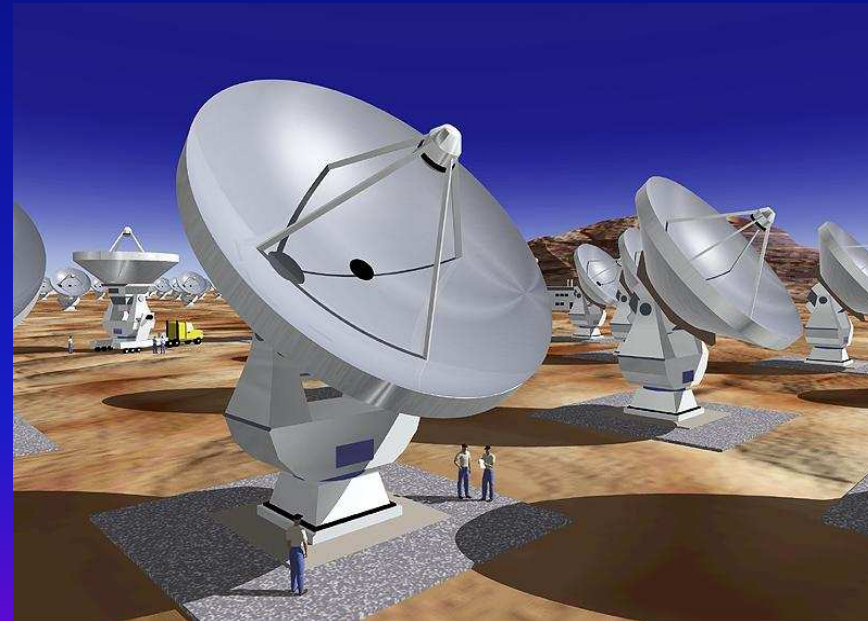
# Plan

- Contexte :  
l'univers moléculaire
- Chimie quantique : PES  $\text{H}_2\text{O}-\text{H}_2$   
Calculs de référence: CC R12  
Echantillonnage 5-D en R12  
Echantillonnage 9-D
- → L'approche grille en 9-D

# Une nouvelle fenêtre sur l'Univers moléculaire : le submillimétrique.

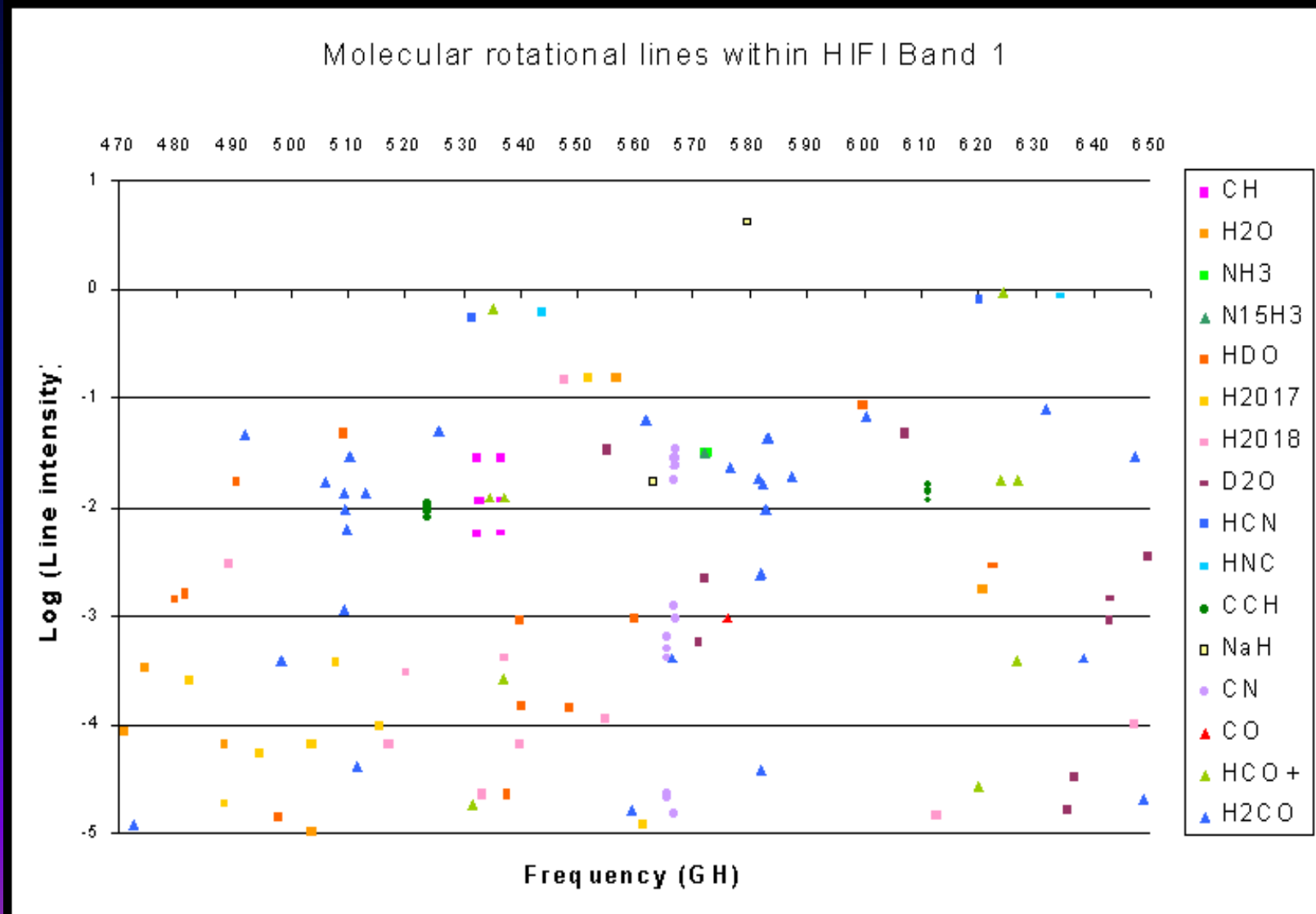


Herschel (2007)  
(490–1910 GHz)



ALMA (2010)  
(30–950 GHz)

# Le spectromètre Herschel-HIFI



# Molécules prioritaires (I)

Molecules	Astrophysical sources	Parameters*	Comments
CH <sup>+</sup>	shocks, PDR		A major question in astrochemistry
H <sub>2</sub> O HDO	Everywhere(?)	n, T	Very important species Very important species
NH <sub>3</sub>	DC, evolved stars	n, T	done ?
CO	Everywhere	n, T	done ?
CN( <sup>2</sup> Σ) CO <sup>+</sup>	PDR, disks PDR	n, B	to be done with CN
HCO <sup>+</sup>	PDR, DC	n, x <sub>e</sub>	OK, except H <sub>2</sub> ortho
HCN HNC	SFR, DC, evolved stars	n, T	
H <sub>3</sub> O <sup>+</sup> N <sub>2</sub> H <sup>+</sup>	DC, SFR	x <sub>e</sub> x <sub>e</sub>	
H <sub>2</sub> CO	evolved stars, SFR	n, T	
SO <sub>2</sub>	SFR, evolved stars	n	needs high T
HC <sub>3</sub> N	DC, evolved stars, SFR	n	done, except for high T ???
(C <sub>4</sub> ) (C <sub>5</sub> ) (C <sub>6</sub> )	PDR		Theoretical chemistry Need for spectroscopic parameters

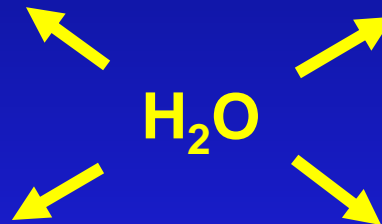
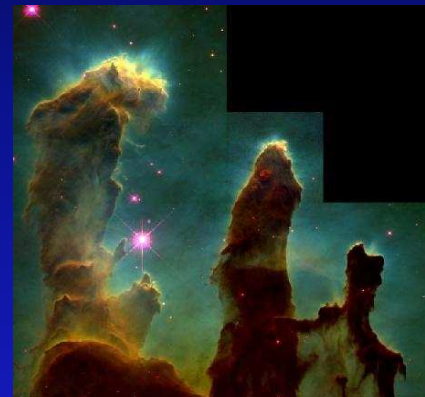
\* n means density, T temperature, x<sub>e</sub> electronic abundance, B magnetic field (through Zeeman effect).

# Molécules prioritaires (II)

Molecules	Astrophysical sources	Parameters*	Comments
CH <sub>3</sub> OH	SFR, comets	T	under study (D. Flower)
CH ( <sup>2</sup> Π)	PDR	n, B	Difficult Quantum chemistry
NH	PDR		Difficult Quantum chemistry
OH( <sup>2</sup> Π)	PDR	B	done ?
H <sub>2</sub> D <sup>+</sup>	DC	x <sub>e</sub>	
H <sub>2</sub> O <sup>+</sup>	PDR, comets		
C <sub>2</sub> (electronic transitions)	PDR	n	done
C <sub>2</sub> H ( <sup>2</sup> Σ)	PDR, SFR	n, B	Difficult Quantum chemistry
H <sub>2</sub> S	shocks, SFR		
CS	DC, SFR, evolved stars	n	done ?
CH <sub>3</sub> CCH	DC	T	
SiO	shocks, evolved stars	n	Maser lines in stars
SO ( <sup>3</sup> Σ)	DC, evolved stars,	n, B	Difficult Quantum chemistry
HeH <sup>+</sup>	XDR, cosmology		

\* n means density, T temperature, x<sub>e</sub> electronic abundance, B magnetic field (through Zeeman effect)

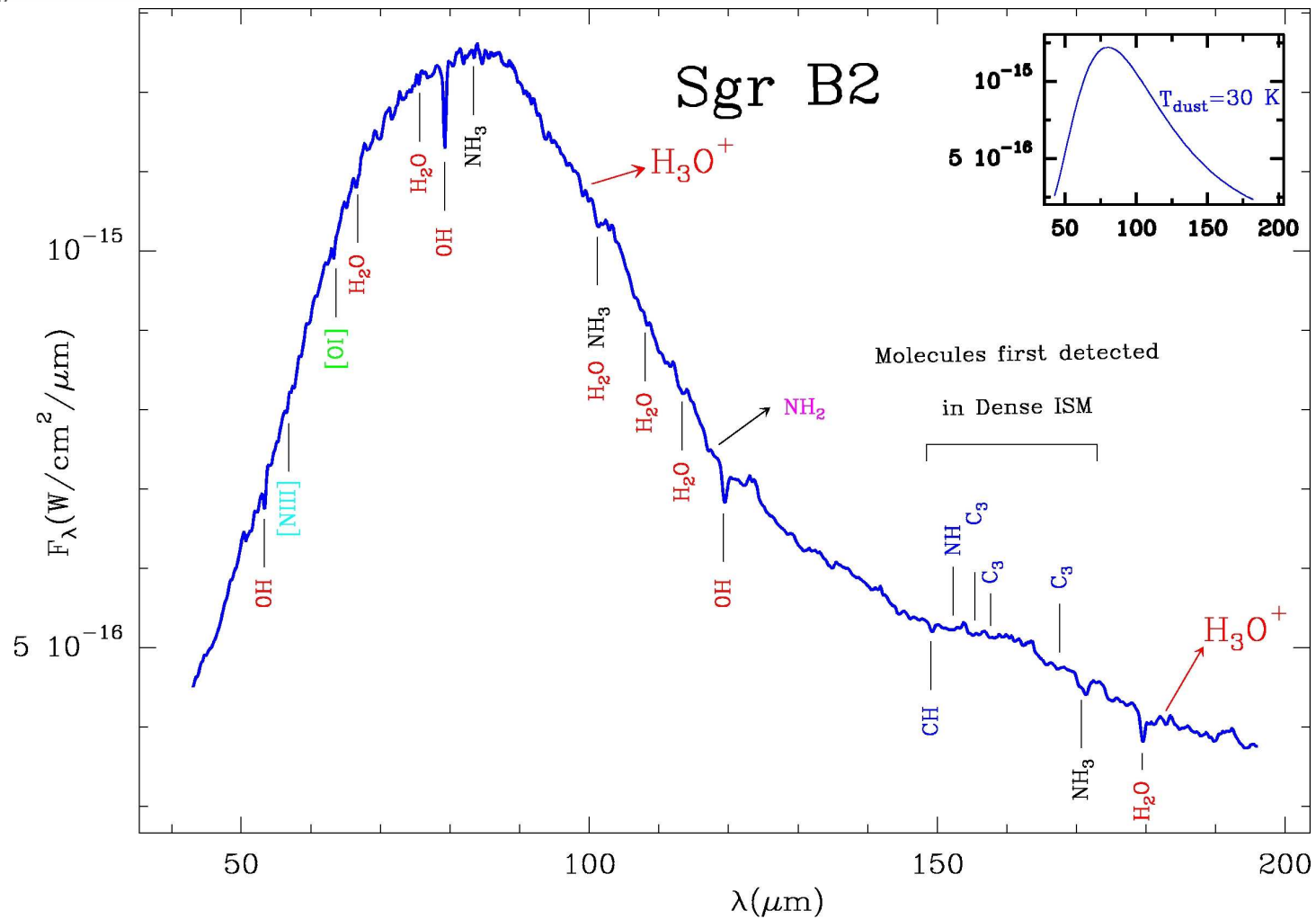
# Observations ISO, SWAS et ODIN : ubiquité de l'eau dans l'Univers



Letter to the Editor

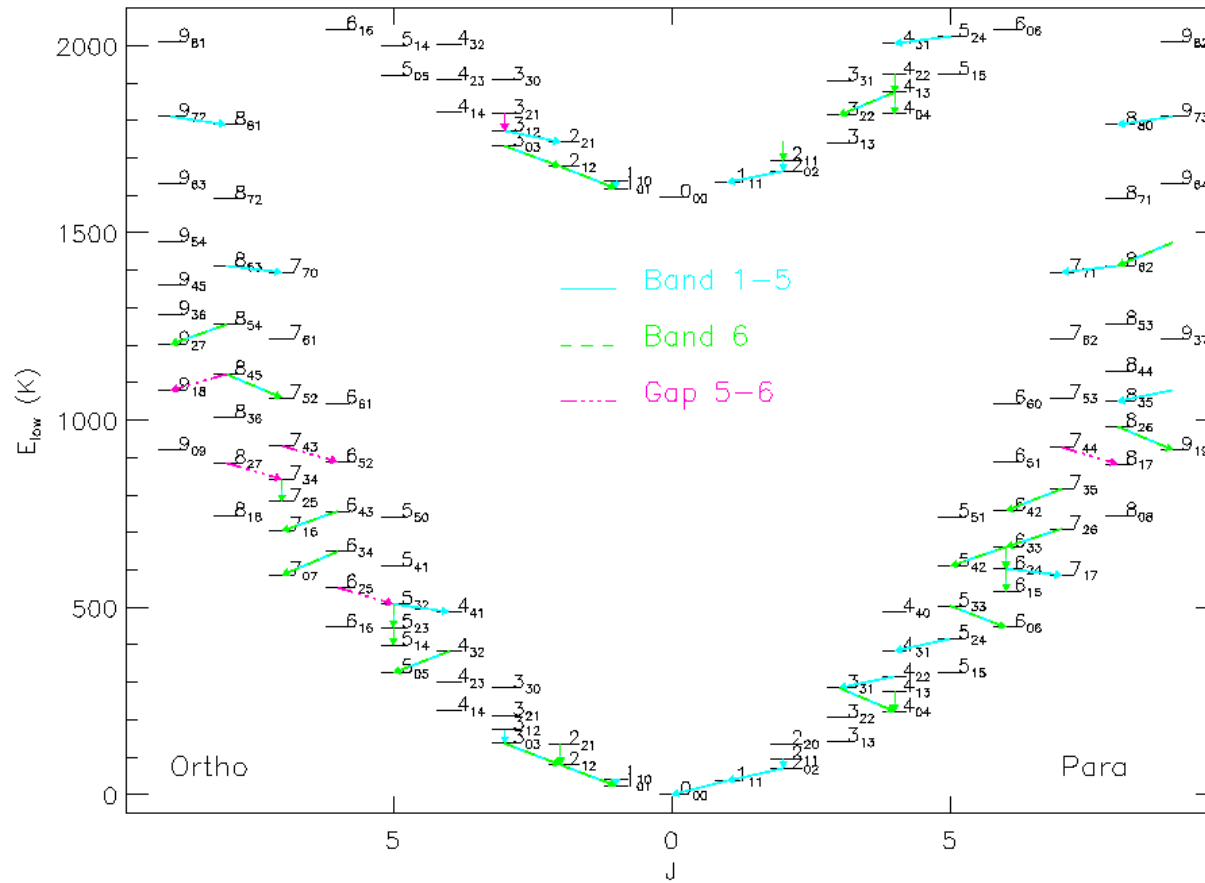
## Widespread water vapour absorption in SgrB2<sup>1</sup>

J. Cernicharo<sup>1</sup>, T. Lim<sup>2</sup>, P. Cox<sup>3</sup>, E. González-Alfonso<sup>4,5</sup>, E. Caux<sup>6</sup>, B.M. Swinyard<sup>7</sup>, J. Martín-Pintado<sup>5</sup>, J.P. Baluteau<sup>8</sup>, and P. Clegg<sup>9</sup>





# HIFI et l'eau



# Quels processus d'excitation collisionnelle ?



PDRs, comètes  
( $T > 100 \text{ K}$ ,  $x_e > 10^{-5}$ )

A. Faure  
J. Gorfinkiel (UCL)  
J. Tennyson (UCL)



Nuages diffus  
( $T > 100 \text{ K}$ )

A. Faure  
P. Valiron  
L. Wiesenfeld  
M.L. Dubernet (Meudon)

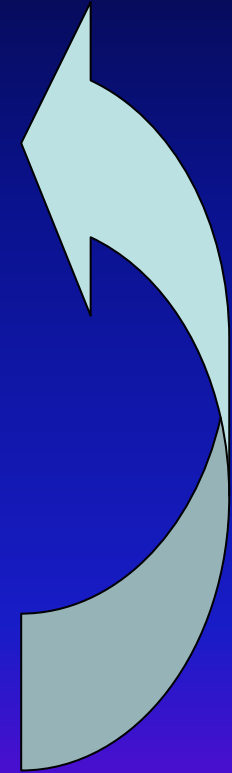
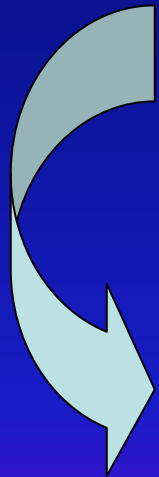


Nuages froids  
( $T < 100 \text{ K}$ )

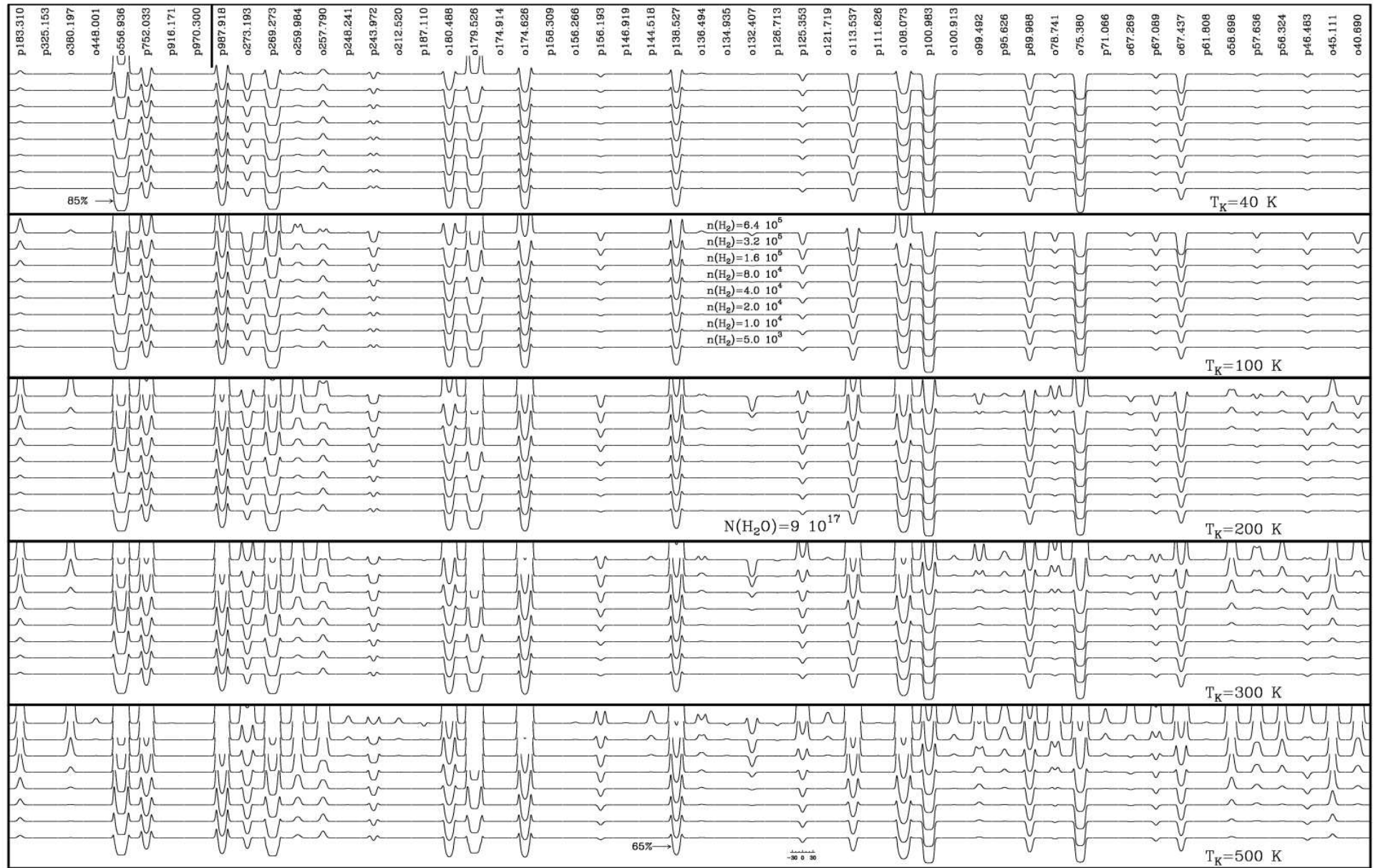
P. Valiron  
M.L. Dubernet (Meudon)  
A. Faure  
L. Wiesenfeld  
M. Wernli

# Principe des modèles astrophysiques

- Physique de base (taux de collision)
- Géométrie de l'objet observé
- Transfert radiatif
- Prédiction de raies synthétiques
- Comparaison aux observations
- Recherche de solutions auto-consistantes

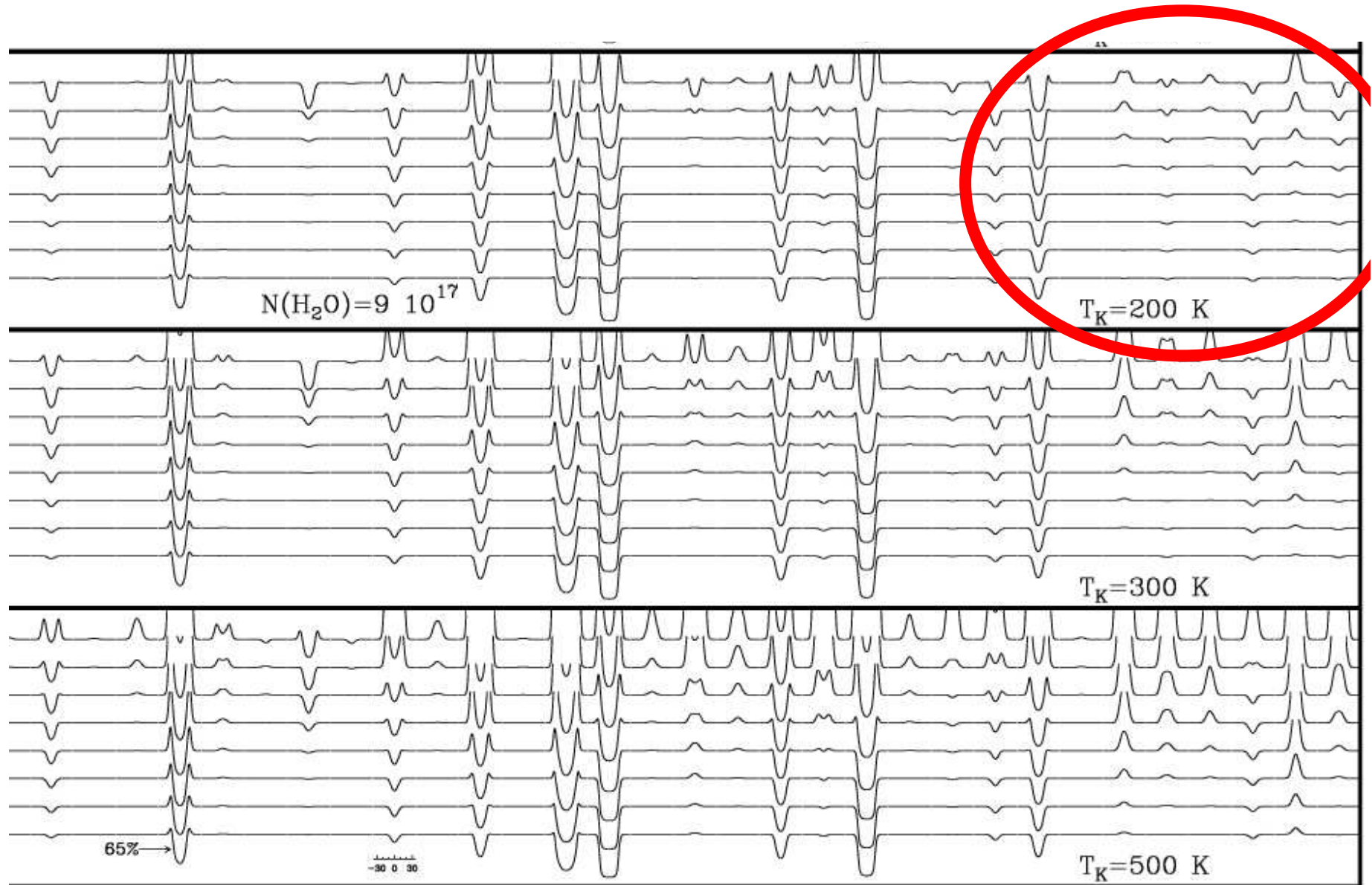


$$N(\text{H}_2\text{O}) = 9 \cdot 10^{17} \text{ cm}^{-2}$$

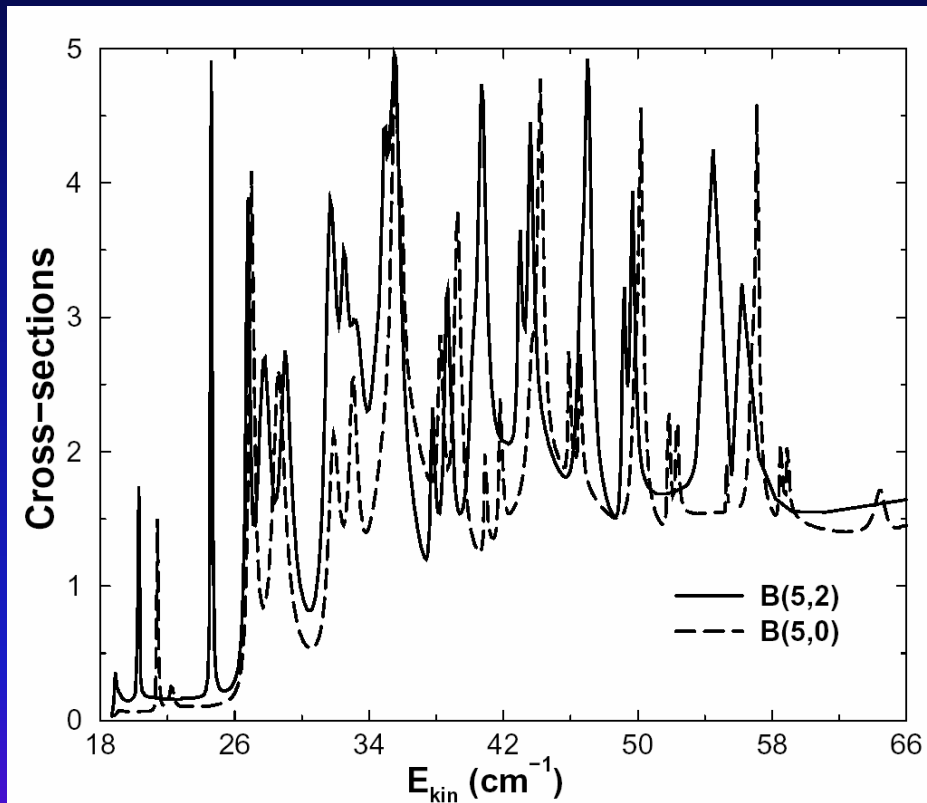


$$N(\text{H}_2\text{O}) = 9 \cdot 10^{17} \text{ cm}^{-2}$$

(détail)...



# Excitation rotationnelle de H<sub>2</sub>O par H<sub>2</sub>



**Fig. 2.** Resonance structures of the CC  $1_{0,1} \rightarrow 1_{1,0}$  cross sections calculated with the  $B(5, 0)$  basis set (dashed line) and with the  $B(5, 2)$  basis set (solid line). Cross sections are in  $\text{\AA}^2$ .

A basse température ( $T < 100\text{K}$ ) importance des **résonances** dont la structure est liée à la topologie de la **surface d'énergie potentielle** à courte-portée.

# Détermination *précise* des interactions moléculaires: l'approche R12

Electron-electron cusp condition (T. Kato, 1975)

$$\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_n) = \left(1 + \frac{1}{2}r_{12}\right)\Psi(\vec{r}_1, \vec{r}_1, \dots, \vec{r}_n) + \mathcal{O}(r_{12}^2)$$

which implies

$$\lim_{r_{12} \rightarrow 0} \left( \frac{\partial \Psi}{\partial r_{12}} \right)_{av} = \frac{1}{2} \Psi(r_{12} = 0).$$

is **not** fulfilled by any conventional CI-like approach.

R12 methods avoid explicitly correlated geminals and corresponding many-electron integrals by introducing an approximate one-electron ansatz (W. Kutzelnigg, 1985).

# La méthode R12 : convergence

Max angular momentum  $L$  on atoms  $\rightarrow$  truncation error

$(L+1)^{-3}$  for any conventional CI-type expansions

$(L+1)^{-7}$  for R12-type methods

R12 corrects for basis set angular incompleteness and (mostly) for basis set superposition error (BSSE).

Référence :

Noga J., Valiron P., « Explicitly Correlated Coupled Cluster R12 Calculations », *Computational Chemistry: Reviews of Current Trends Vol. 7*, 2002, 131, edited by J. Leszczynski, World Scientific, Singapore, New Jersey, London, Hong Kong.



# Energies moléculaires

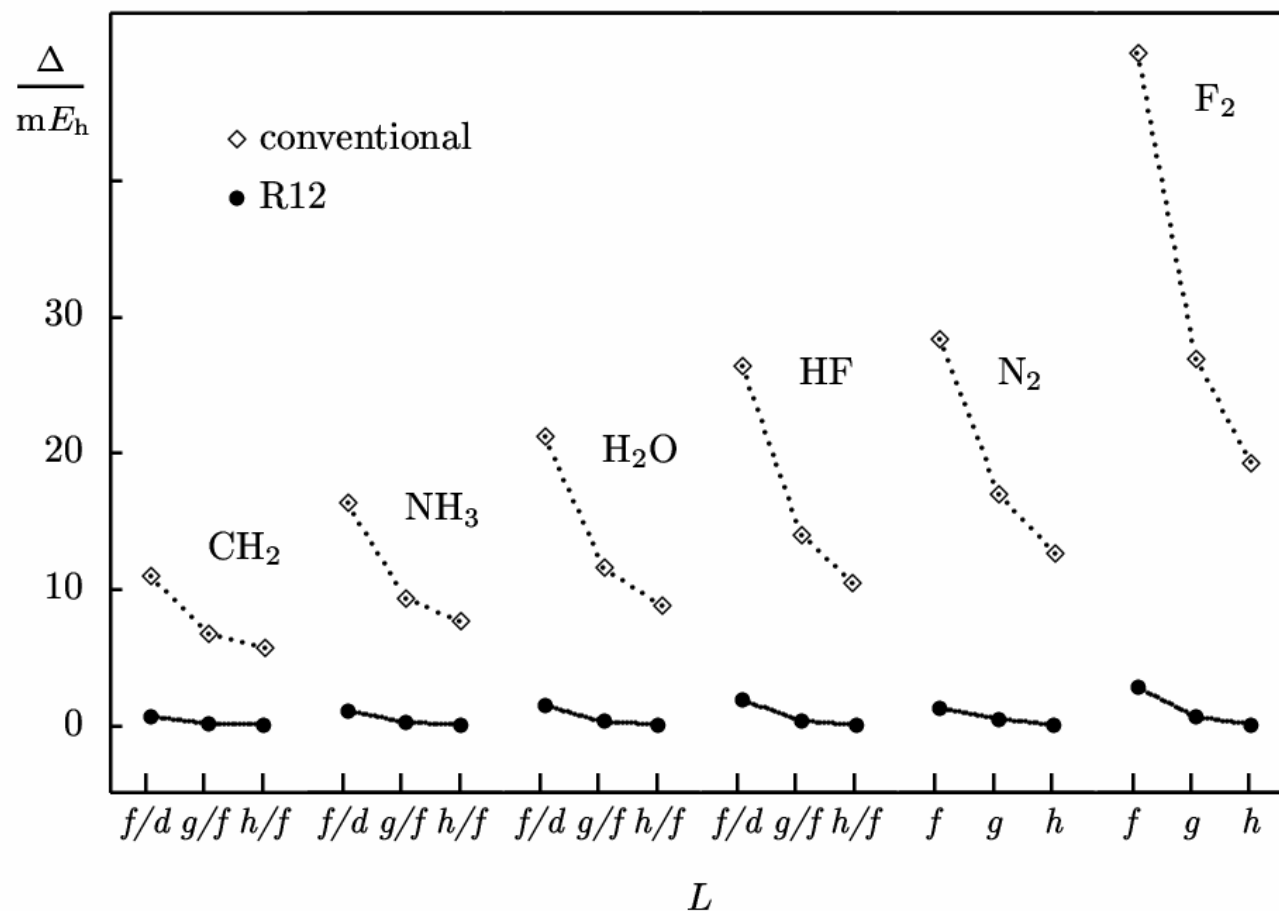


Fig. 2 Errors ( $\Delta$ ) of the CCSD(T)-R12 molecular energies with increasing angular momentum ( $L$ ) functions included in the basis. Subsets of  $9s6p4d3f$  basis for hydrogen and  $19s14p8d6f4g3h$  for other atoms were used. The conventional values are approximated by taking the cusp correction contributions from MBPT(2)-R12. For details see the text.

# Le prix à payer pour R12

Large basis sets to fulfill the « standard approximation » for the closure relation of the R12 ansatz:

- saturated s set for H, He, Li and Be;
- saturated *spdf* sets from B to Ca.

Conventional basis sets need adjustments to fulfill above conditions and might induce numerical instabilities of the R12 amplitudes.

→ **development of « R12 suited » basis sets** (done for H→Ne).

## Références :

Valiron P., Kedzuch S. and Noga J., « Avoiding numerical instabilities in R12 calculations through universal R12 consistent basis sets », *Chem. Phys. Lett.*, **2002**, 367, 723-729.

Noga J. and Valiron P., « Towards universal R12 consistent basis sets », *Collect. Czech. Chem. Commun.*, **2002**, accepted.

# Approche 5-D pour H<sub>2</sub>O-H<sub>2</sub>

- Approximation de rotateurs rigides
- 1 distance, 4 angles → PES 5-D
- Calculs CCSD(T)-R12
- 1000 géométries (SCCI, CINES, IDRIS)
  - précision « spectroscopique » mais...
  - ~ 45 h CPU sur SP3, 15 h sur SP4 (no sym)
  - 1 GB RAM, 70 GB de scratch et 1 TB d'E/S
  - limitation: saturation E/S centres nationaux
  - dével. méthodes // directes (Europe, COST-D26)
- 16000 h SP3 CINES+IDRIS, 5000 h zahir  
+ ~ 10000 h sur le SCCI/OSUG/CIMENT

# Convergence des calculs H<sub>2</sub>O-H<sub>2</sub>

Table 8: Monitoring H<sub>2</sub> -H<sub>2</sub>O PES (in cm<sup>-1</sup>)

$R$	$\theta$	$\phi$	$\theta'$	$\phi'$	Phillips et al	CCSD(T)-R12 <sup>a</sup>	CCSD(T)-R12 <sup>b</sup>	(T)-[T] <sup>a</sup>
5.0	0	0	0	0	69.6	-12.6	-11.0	0.6
5.0	180	0	180	0	771.9	712.3	713.6	-2.1
6.0	0	0	0	0	-198.4	-220.9	-219.6	0.2
6.0	180	0	180	0	73.48	63.5	65.3	-1.2

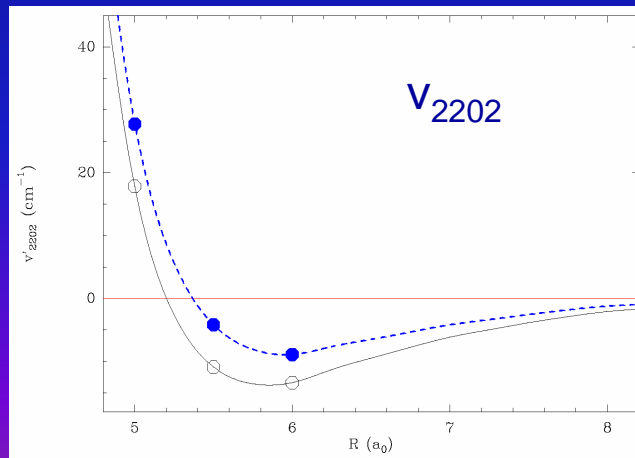
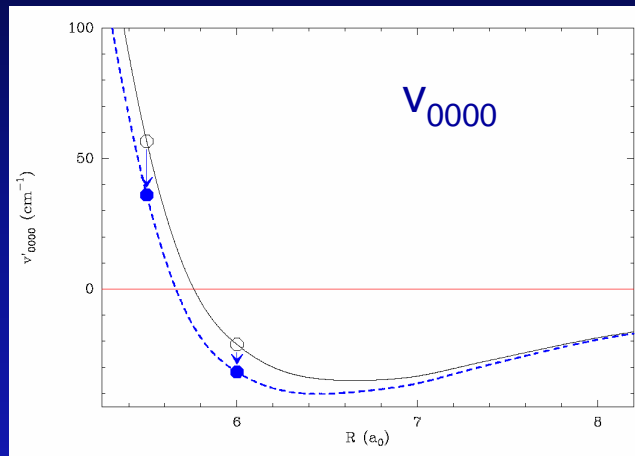
<sup>a</sup> using the R12-suited basis set truncated to 19s14p8d6f and 9s6p4d for O and H, respectively.

<sup>b</sup> using the R12-suited full basis set of 19s14p8d6f4g3h and 9s6p4d3f size for O and H, respectively. These results are expected to be converged better than their difference with previous column, leading to an accuracy of about 1 cm<sup>-1</sup> with respect to the basis set.

<sup>c</sup> the difference between CCSD[T]-R12 and CCSD(T)-R12 indicates the importance of higher order diagrams towards the full CI, and thus provide an estimator of the method accuracy. Non dynamical and relativistic corrections are not included.

Précision de l'ordre du cm<sup>-1</sup>, sans calcul de contreponds.

# Correction R12 pour H<sub>2</sub>O-H<sub>2</sub>



$$V(R, \theta, \varphi, \theta', \varphi') = \sum v_{p_1 q_1 p_2 p}(R) t_{p_1 q_1 p_2 p}(\theta, \varphi, \theta', \varphi'), \quad (7)$$

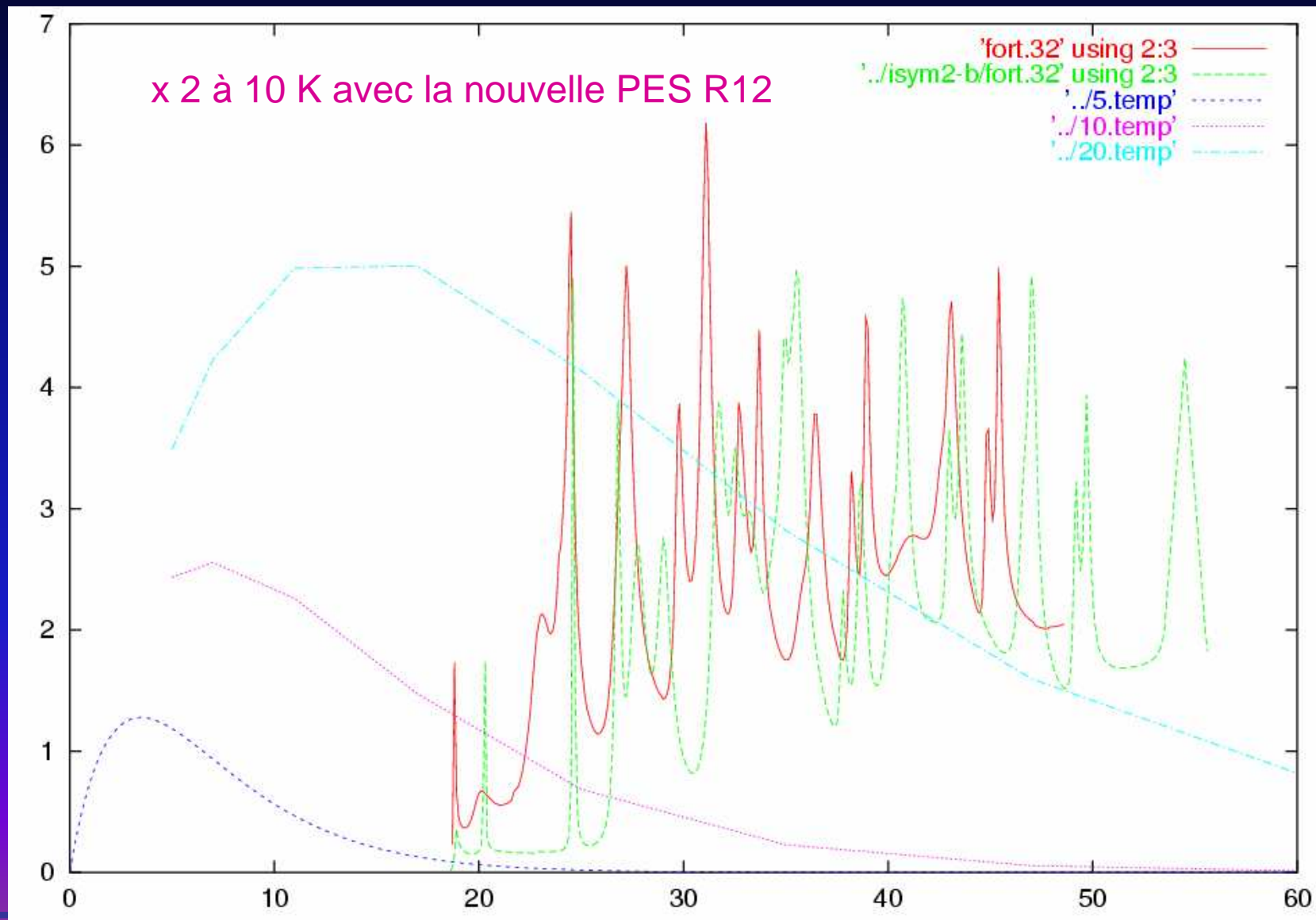
where

$$t_{p_1 q_1 p_2 p}(\theta, \varphi, \theta', \varphi') = (1 + \delta_{q_1 0})^{-1} \sum \begin{pmatrix} p_1 & p_2 & p \\ r_1 & r_2 & r \end{pmatrix} Y_{p_2 r_2}(\theta', \varphi') Y_{p r}(\theta, \varphi) \times [\delta_{q_1 r_1} + (-1)^{p_1 + q_1 + p_2 + p} \delta_{-q_1 r_1}], \quad (8)$$

and the sum is again over  $r_1, r_2, r$ .

La correction R12 affecte principalement le **potentiel isotrope** et un petit nombre de **termes anisotropes de bas degré**.

# Taux de collision p-H<sub>2</sub>O + p-H<sub>2</sub>



# PES 9-D

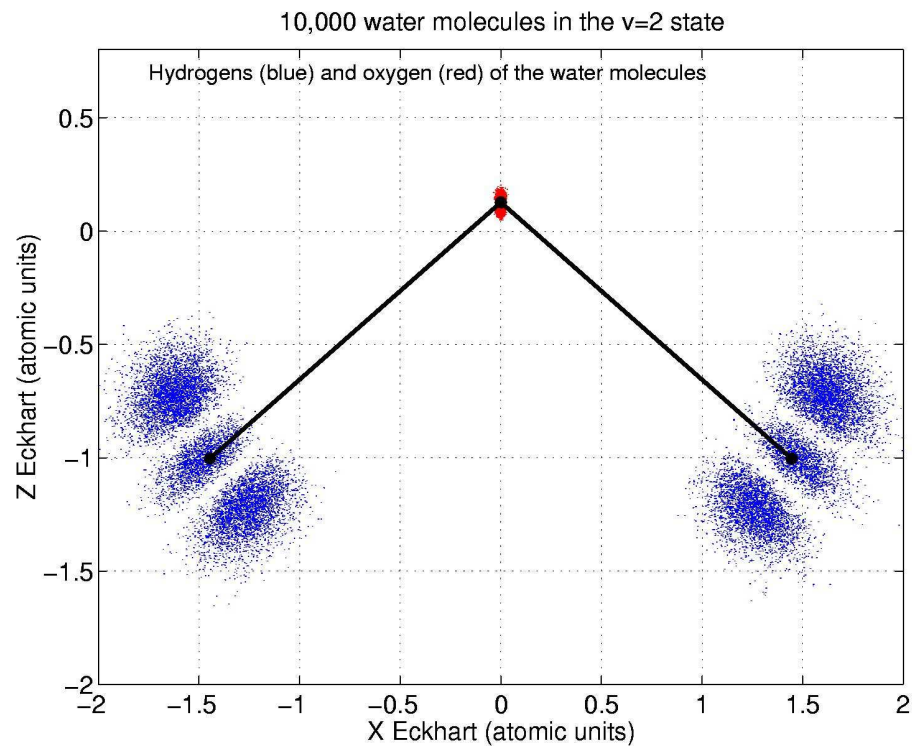
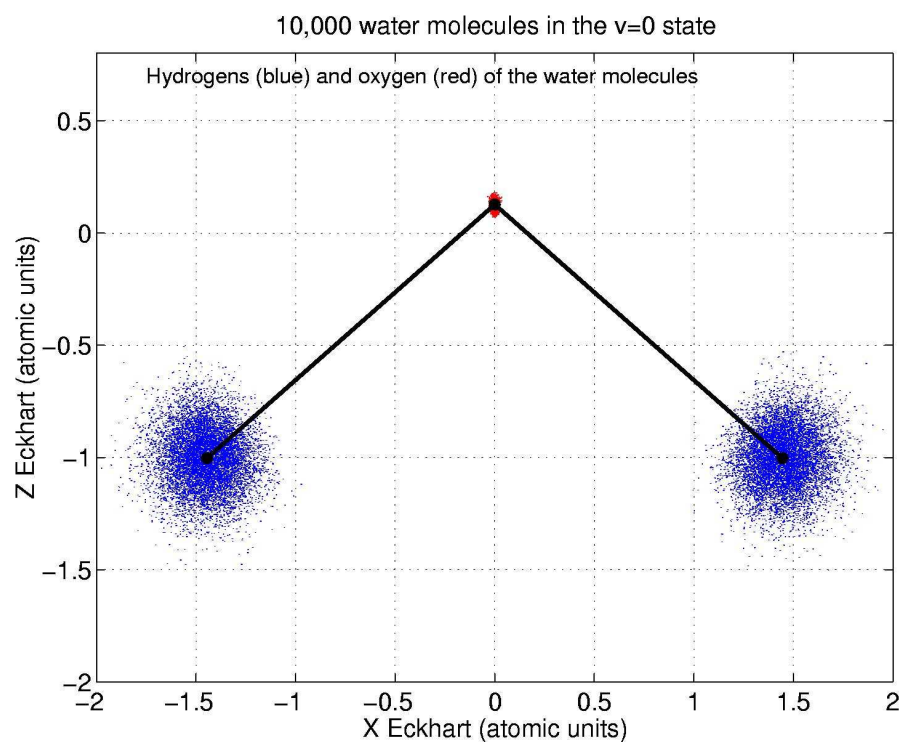
- La dynamique intra-moléculaire induit une délocalisation des positions des noyaux
- Limitation de l'approximation de rotateurs rigides

→ passage d'une PES 5-D à une PES 9-D

# Dynamique intra-moléculaire de l'eau : Délocalisation importante des hydrogènes

$$V=(0,0,0)$$

$$V=(0,2,0)$$





# Eckart conditions

Eckart rotation is defined as follows [6]:

$$\sum_i m_i \mathbf{r}_i^e \times \mathbf{r}_i = 0.$$

[6] P.R. Bunker, *Molecular Symmetry and Spectroscopy*, Academic Press, 1979.

# Délocalisation comparable pour $H_2$ ( $v=0$ )

$H_2$  Morse wavefunction

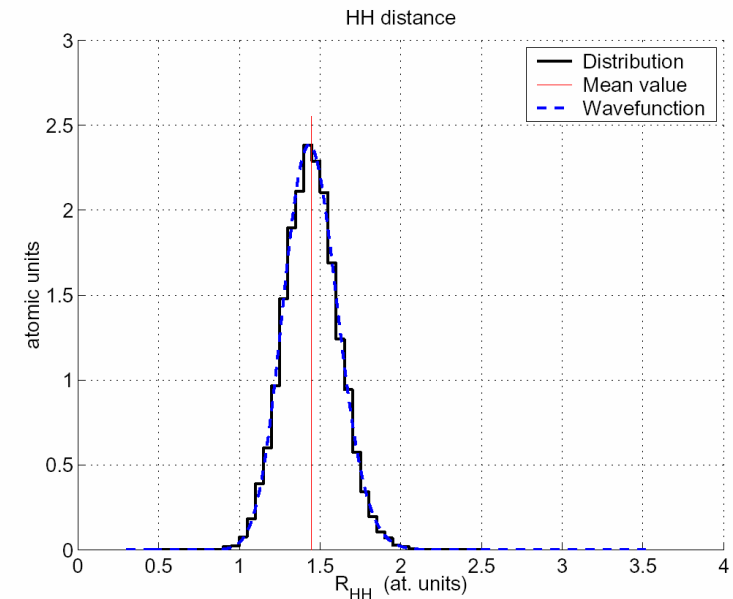
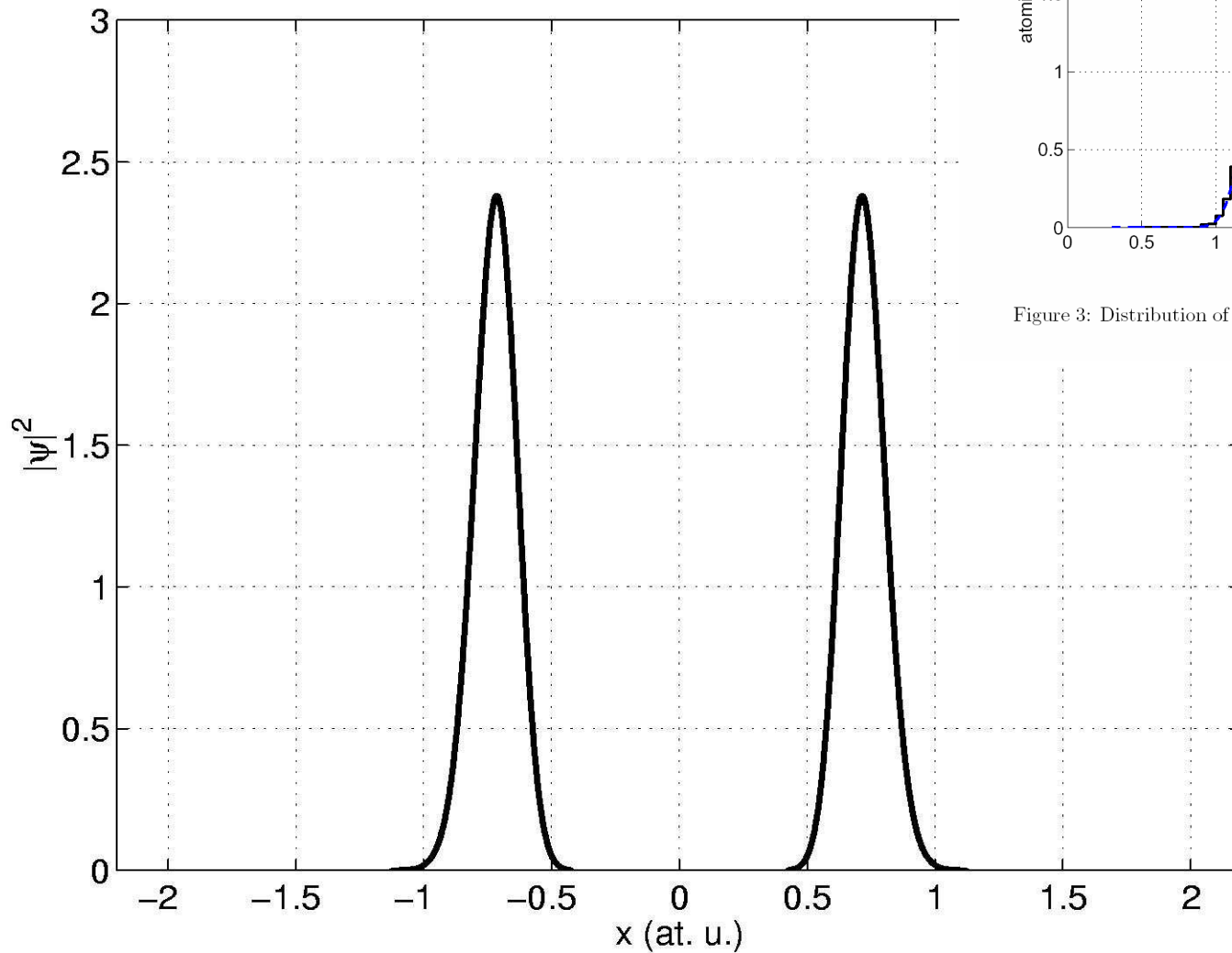
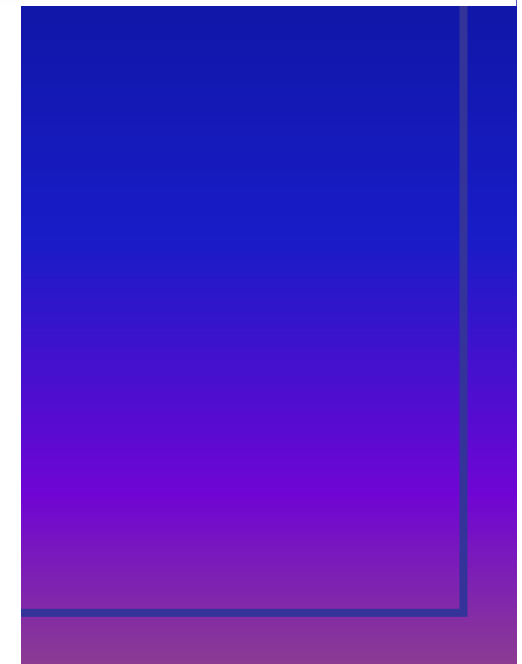


Figure 3: Distribution of the  $r_{HH}$  distance, compared to the exact wavefunction



# PES 9-D : Quelle stratégie ?

- Grille Monte Carlo 9-D par « importance sampling » sur les fonctions vibrationnelles  $\text{H}_2\text{O}$  et  $\text{H}_2$
- Grille 5-D en référence
- Double contreponds
- Base Aug-CC adaptée (mix DZV et TZV)
- CCSD(T) nécessaire
  - ¼ h par géométrie 5-D ou 9-D

# PES 9-D sur la grille...

- PES=funct(R, 4  $\alpha$  inter, hOh, 3 bonds)
- Contrepoids  $\rightarrow$  3 calculs ab-initio / géométrie
- E/S importantes (transformation, triples)
- ¼ h par géométrie sur icluster, production scalable car E/S distribuées
- Mode « artisanal » jusqu'à Noël, envoi manuel de 230000 géométries sur icluster, Phynum, SCCI  $\rightarrow$  ~ 60000 h CPU
- Distribution des calculs par pbs + prun
- Gestion des erreurs disque par « blacklist » semi-automatique, 18 disques cassés...
- Retour et validation manuelle des résultats

# Perspectives

- Modulation de la surface d'énergie potentielle par la dynamique intra-moléculaire (SEP à 9-D)
  - ➔ interpolation 9-D (en cours)
- H<sub>2</sub>O-H<sub>2</sub> : Identification des symétries brisées et des couplages induits par la dynamique intra-moléculaire.
- HDO-H<sub>2</sub> : prise en compte fonctions vibrationnelles et brisure de symétrie via l'interpolation 9-D de la PES.
- Systèmes homologues ( H<sub>2</sub>S )
- NH<sub>3</sub>-H<sub>2</sub> : PES 12-D (7 degrés de liberté intra-moléculaires).
- Mise en place d'outils grille conviviaux (gestion des erreurs, retour des résultats...) pour distribuer les calculs légers en tâche de fond (via CIGRI).
- Gros calculs R12 « directs » parallélisés sur clusters d'itaniums et distribués sur des grilles plus lourdes...