Results and interprétation

$\gamma_v = 14.28(13) \times 10^{-3}\ s^{-1}\ Torr^{-1}$

$\gamma_{total} = x_s\gamma_s + x_v\gamma_v$

$\gamma_{glass} = 25.8 \times 10^{-3}\ s^{-1}$

$\gamma_{gold} = 64.8 \times 10^{-3}\ s^{-1}$

$$\gamma = 2\,|V_{\alpha\alpha'}|^2 \frac{\Gamma_{\alpha\alpha'}}{\Gamma_{\alpha\alpha'}^2 + \omega_{\alpha\alpha'}^2}(W_\alpha + W_{\alpha'})$$

Low pressure range ($\Gamma_{\alpha\alpha'} << \omega_{\alpha\alpha'}$)

γ proportional to Γ and pressure

$$\bar{v} \cong 430\ \text{m/s};\quad \lambda = 1\ \text{mm}$$

$$\Rightarrow \Gamma_s = \frac{\bar{v}}{\lambda} = 4.3 \times 10^5\ \text{s}^{-1}$$

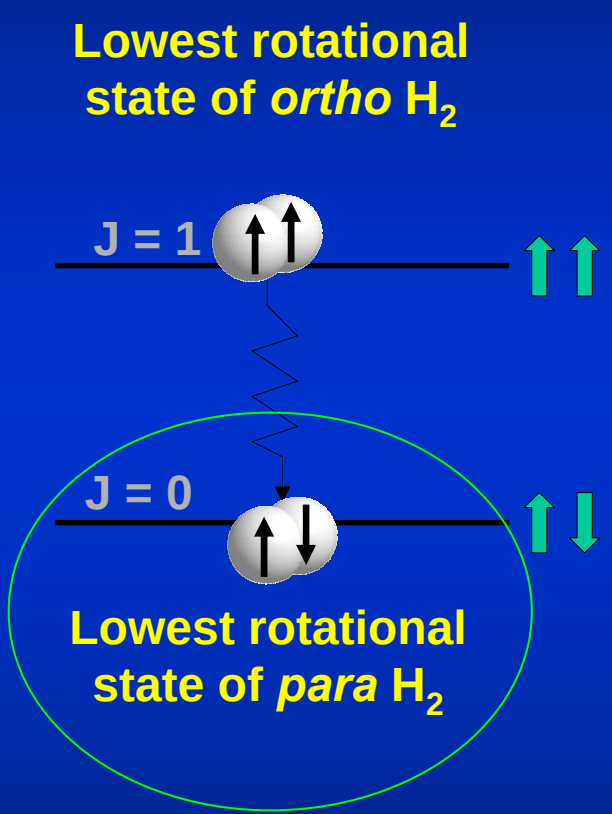
$$\Gamma_s << \Gamma_v\ (= 1.4 \times 10^8\ \text{s}^{-1}\text{Torr}^{-1})$$

Conclusion

Quantum relaxation is a marginal process on surface

$\Rightarrow$ Direct mechanisms

Conversion of H_2 on a surface



Cooling

Molecules are on the lowest states,

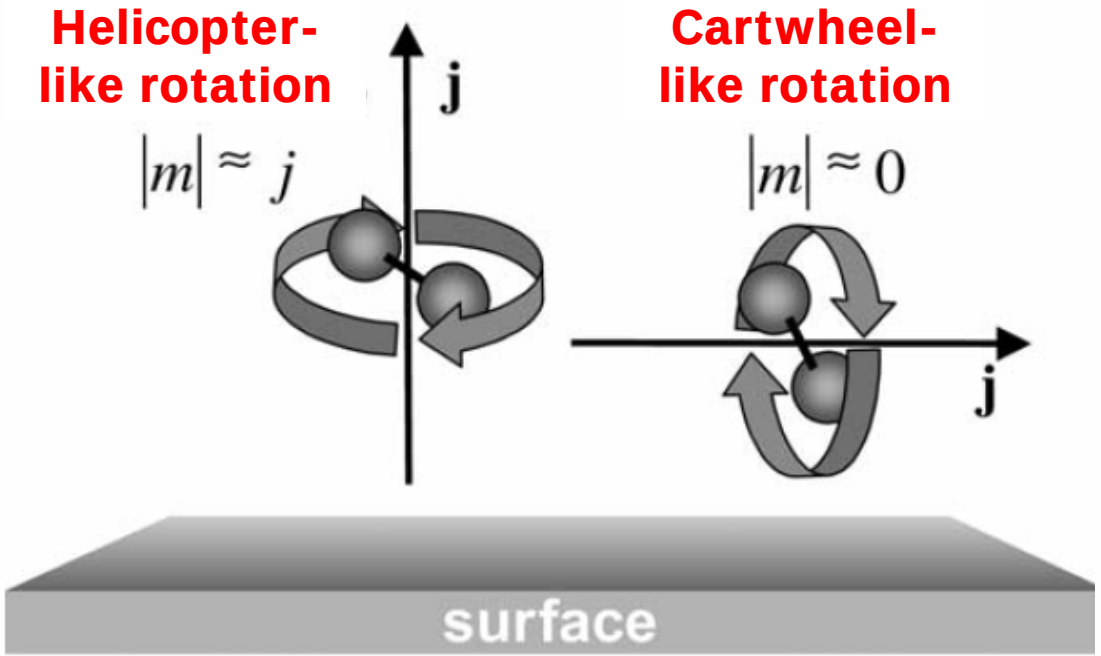
J = 0 and J = 1.

Technique allowing an acceleration of the conversion of *ortho* H_2 in *para* H_2

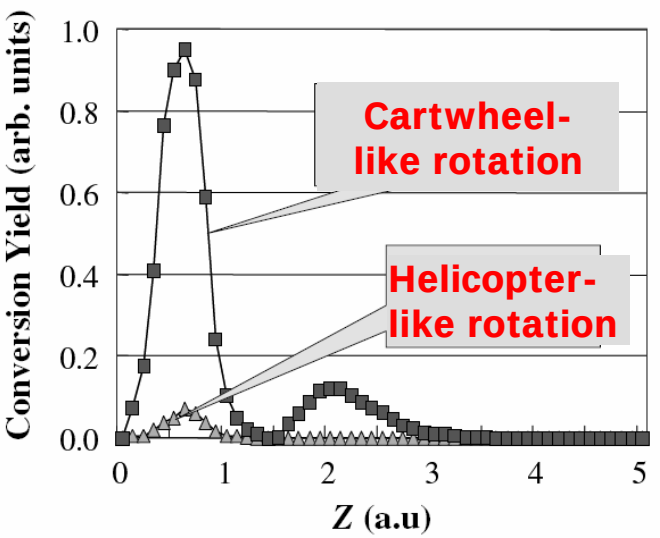
= catalytic surface

Orientation of H_2 with respect to the surface

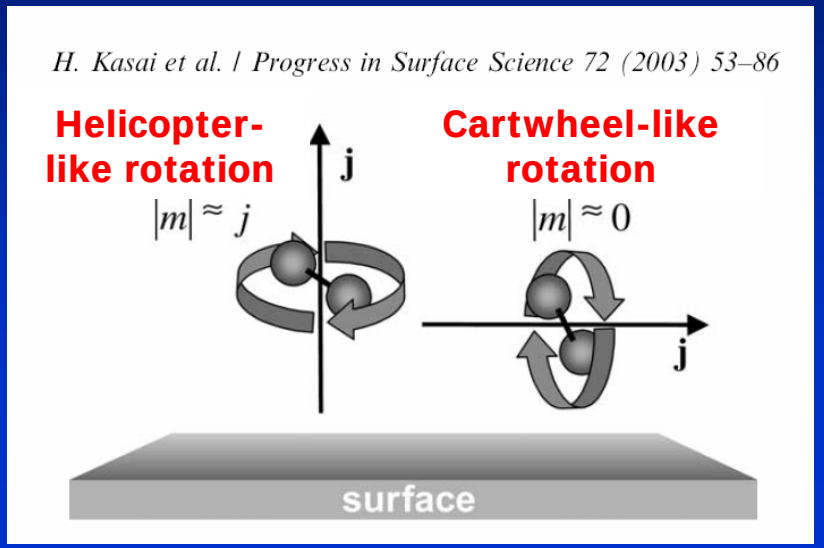
H. Kasai et al. / Progress in Surface Science 72 (2003) 53–86

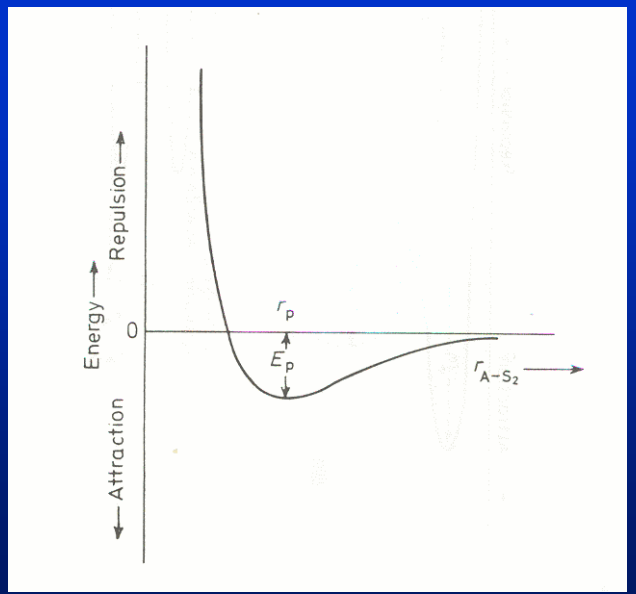


H. Kasai et al. / Progress in Surface Science 72 (2003) 53–86

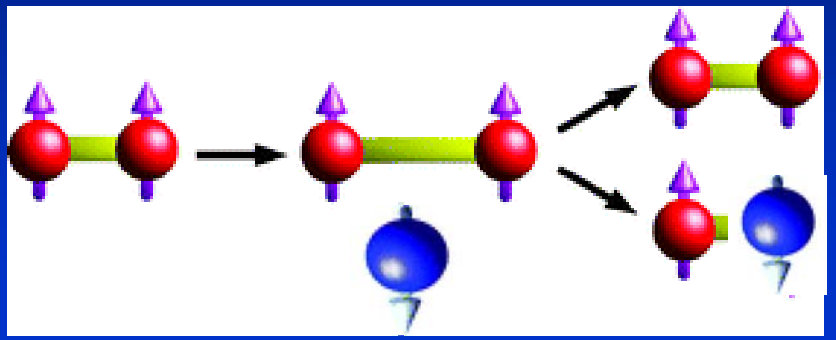


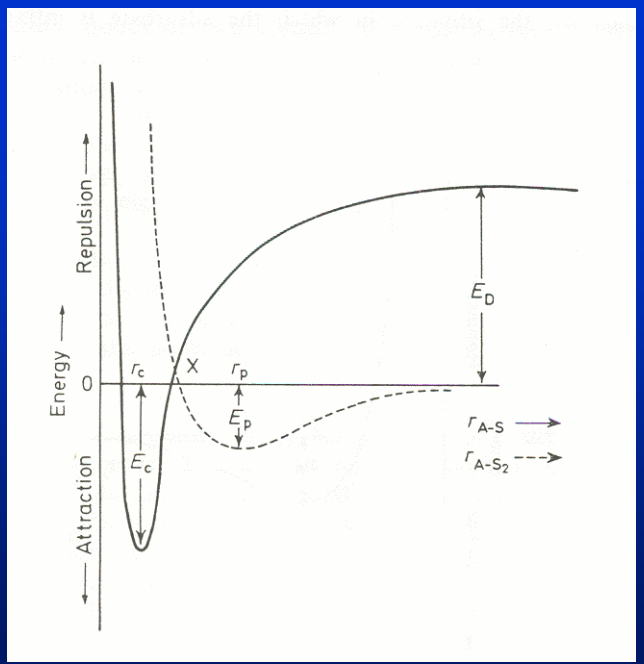
Physisorption

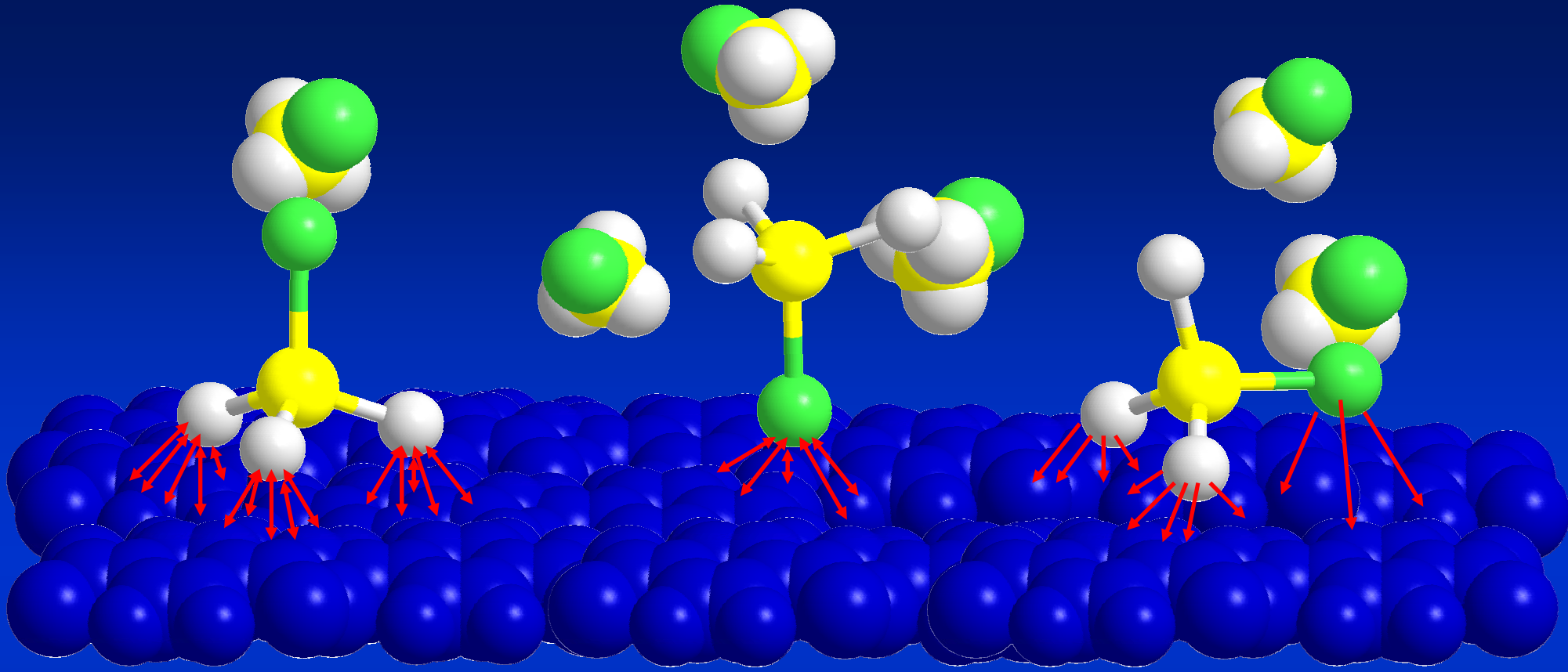




Chemisorption







- contact interaction if H atoms interact with surface (protons are exposed to an inhomogeneous magnetic field inducing a dephasing in the precession of the nuclear spins)

- internal modification of the whole electronic cloud if the F atom interacts.

- immobilization $\rightarrow$ $V_{surf} \approx \hbar\omega_{op}$

Current projects

Universality of the QRM with new molecules

Acetylene C_2H_2

Water H_2O

Molecules of higher symmetry NH_3, C_2H_4

Rovibrational spectra
Line profile
Magnetic spin rotation interaction

Information needed !

Current projects

How to improve the enrichment ?

Enrichment is only possible if experimental conditions ensure isomer lifetimes exceeding the characteristic duration of enrichment.

Light-Induced Drift

A vibrational and velocity-selective excitation produces a change of collisional cross section of one isomer species

Selective adsorption

Isomer species flow differently through a chromatography column filled by paramagnetic granules (activated carbon)

simplicity, versatility, adaptability

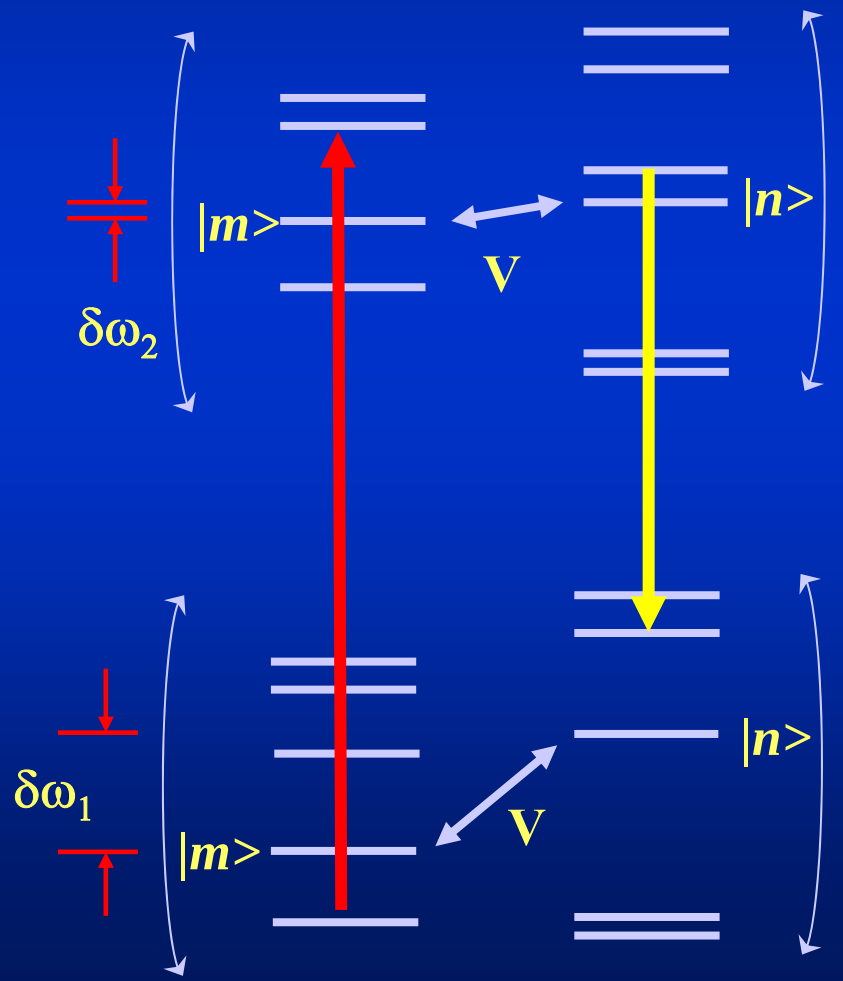
Current projects

Direct enrichment (C_2H_2, NH_3)

Excited Vibrational state

$\delta\omega_1 >> \delta\omega_2$

Ground Vibrational state



Current projects

How to improve the detection ?

Monitoring the absorption of one isomer with CO_2 lasers

Constraints:

- **finding a coincidence between the spectrum of the studied molecule and the spectrum of the CO_2 source.**
- **the sample pressure has to be stable as the measurement takes often several minutes**

Recording 1 cm^{-1} of the spectrum in the 1.5 μm region

Most of the molecules have transitions in this domain

Cavity Enhanced Absorption Spectroscopy technique

- **weak absorption (combination bands)**
- **measurements at low pressure**

Conclusion

Provide measurements of
intramolecular magnetic interactions and collisional relaxation properties in molecules having atoms in equivalent positions.

Astrophysics :

In gas phase, no conversion (QRM)

On surfaces, faster conversion ?

Need of experiments in order to derived models of molecular formation in the ISM

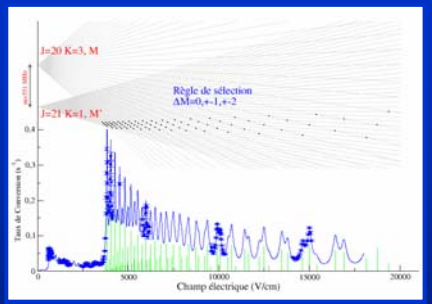
Biology :

Enrichment obtained for the water molecule in gas, liquid and solid phases (Tickonov et Volkov Science 2002). (contradiction with other observations)

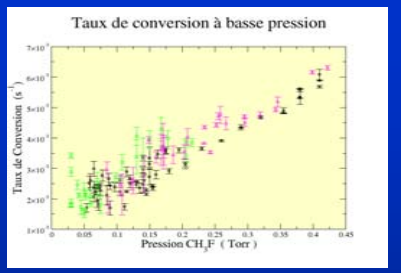
Selective reactivity in biological environment ? (*Spin dependence adsorption of water molecules*, Poteckin, Khusainova, Biophysical Chemistry 118, 2005)

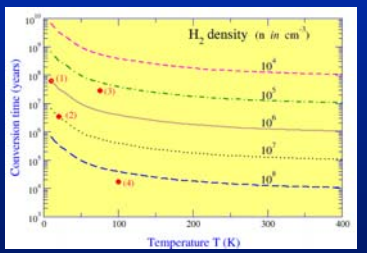
Patrice Cacciani

Mohamed Khelkhal



Julien Lecointre





Marcela Tudorie

Thanks to Petr,

The Academy of Sciences

And all of you for your attention

Selection rules for ortho – para couplings in C_{3v} molecules

Spin-spin interaction
$\Delta J \leq 2,\ \Delta k \leq 2$

Spin-rotation interaction
$\Delta J \leq 1,\ \Delta k \leq 2$

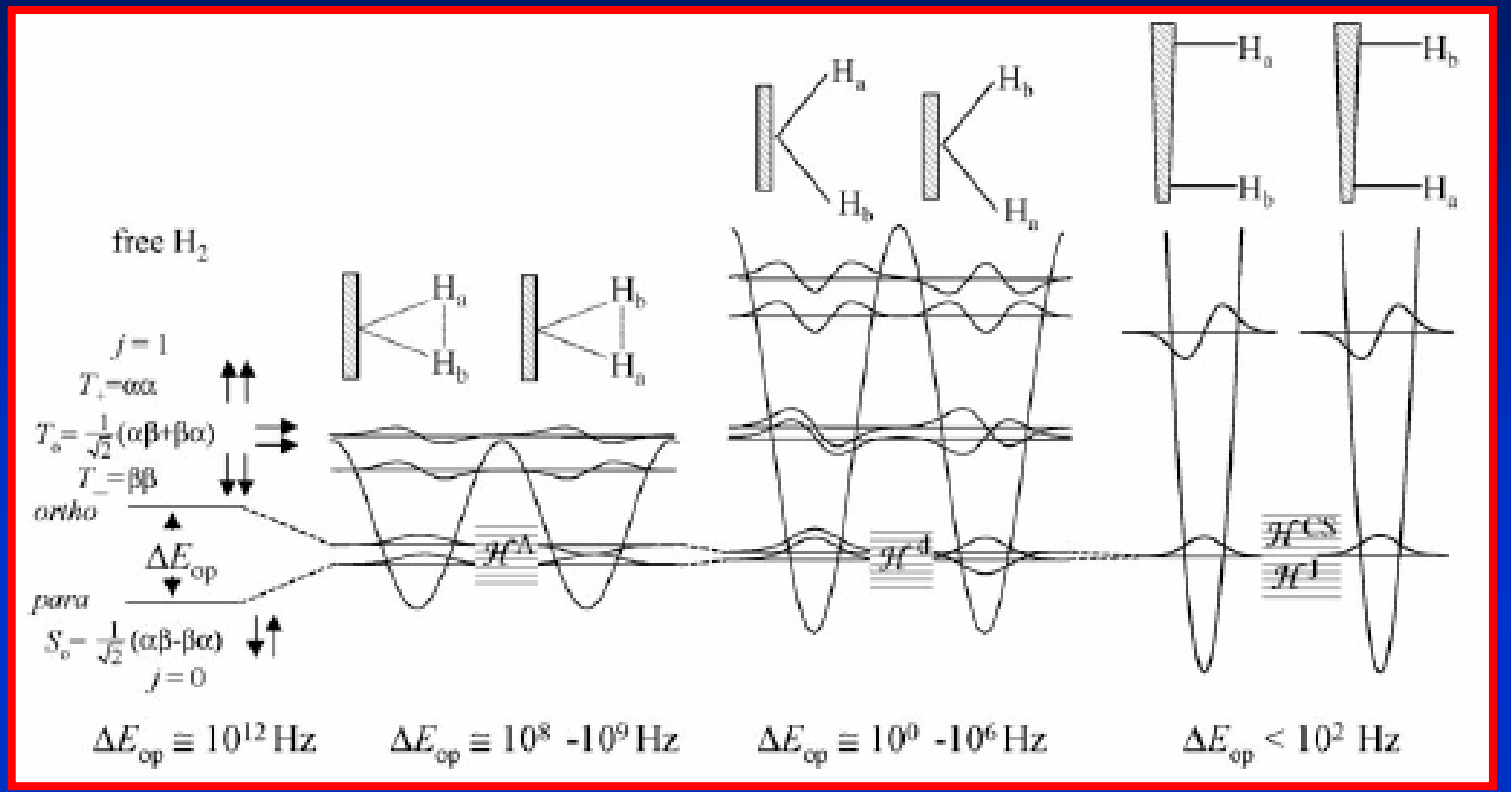
Characteristics of $^{13}CH_3F$

Ortho – para $(J_o,K_o) – (J_p, K_p)$ pairs	ħω (MHz)	W (10^{-5})	interaction
(9,3) – (11,1)	130	3.8922	spin-spin
(20,3) – (21,1)	350	1.0263	spin-spin and spin-rotation

Characteristics of $^{12}CH_3F$

Ortho – para $(J_o,K_o) – (J_p, K_p)$ pairs	ħω (MHz)	W (10^{-5})	interaction
(50,6) – (51,4)	41	0.0002	spin-spin and spin-rotation
(27,6) – (28,5)	1189	0.2839	spin-spin and spin-rotation
(17,6) – (15,7)	1746	1.8301	spin-spin
(10, 0) – (9,2)	8591	8.8187	spin-spin and spin-rotation

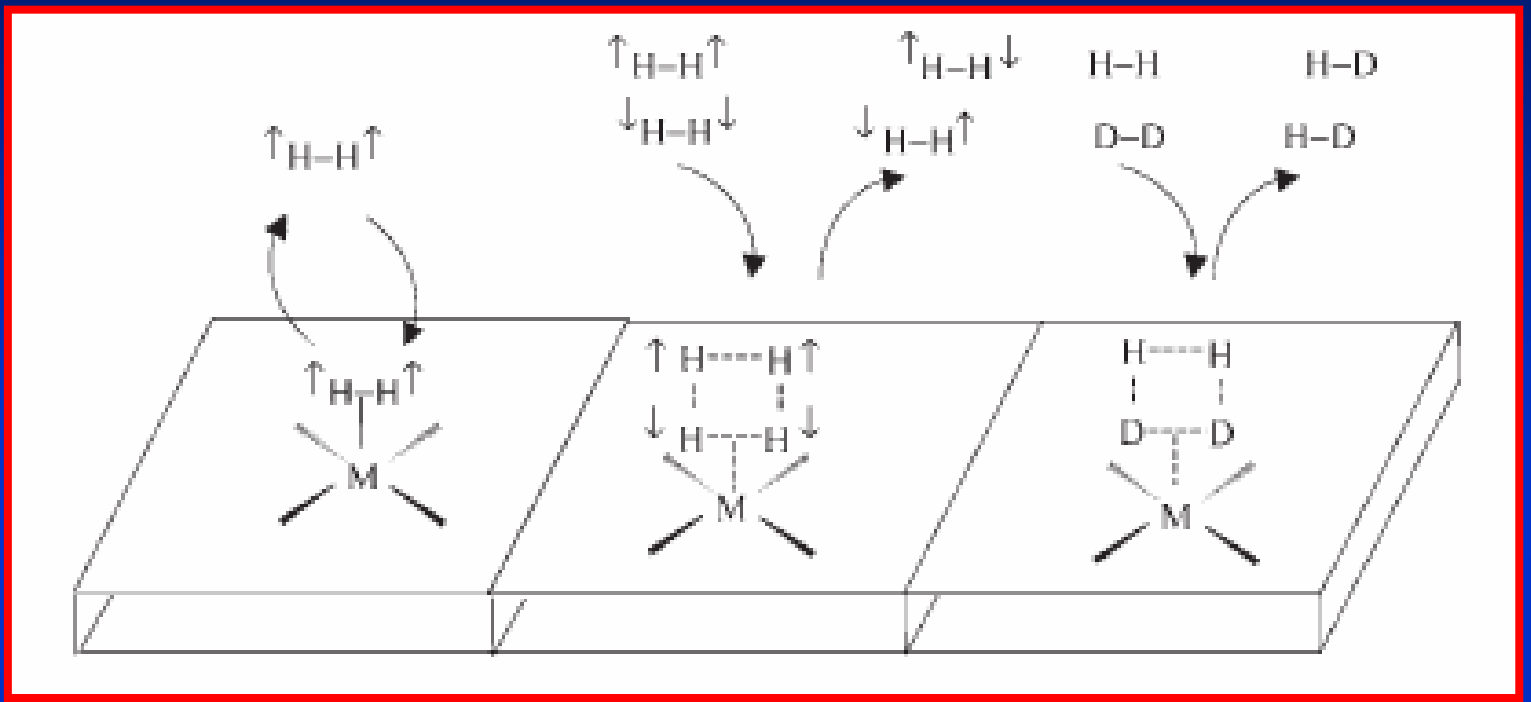
H.-H. Limbach et al., ChemPhysChem 2006, 7, 551 – 554



The quantum rotation is not immediately quenched but converted into a “rotational tunneling splitting”

An efficient catalyst of the magnetic spin conversion not only provides a suitable magnetic interaction, but also reduces the value of ΔE_{op} of the dihydrogen pair by elongation of the HH bond length.

H.-H. Limbach et al., ChemPhysChem 2006, 7, 551 – 554



The magnetic spin conversion is suppressed (left) because of a large value of ΔE_{op} associated with short H···H distances in a dihydrogen complex.

At least two dihydrogen molecules are necessary for the chemical spin conversion that is associated with the corresponding isotope scrambling reaction.