

Nuclear Spin Conversion in Gas Phase

Recent developments

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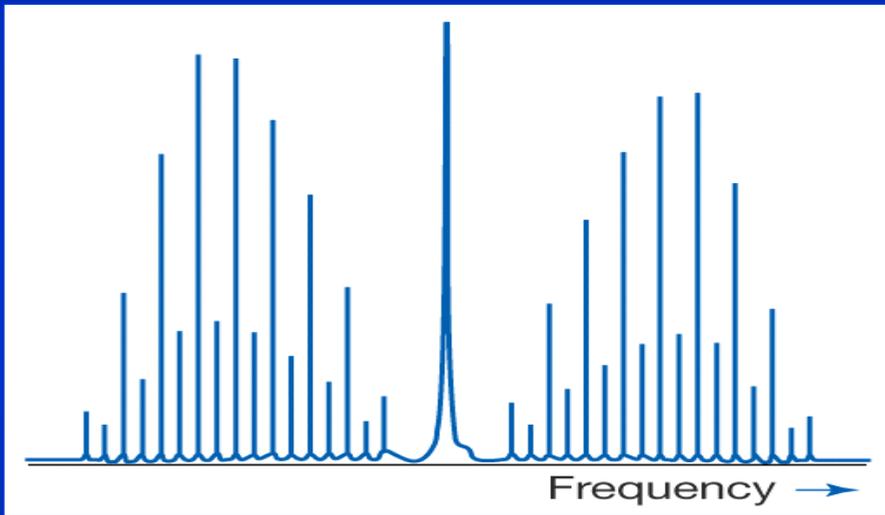
Prague, March 10th 2007

Nuclear spin

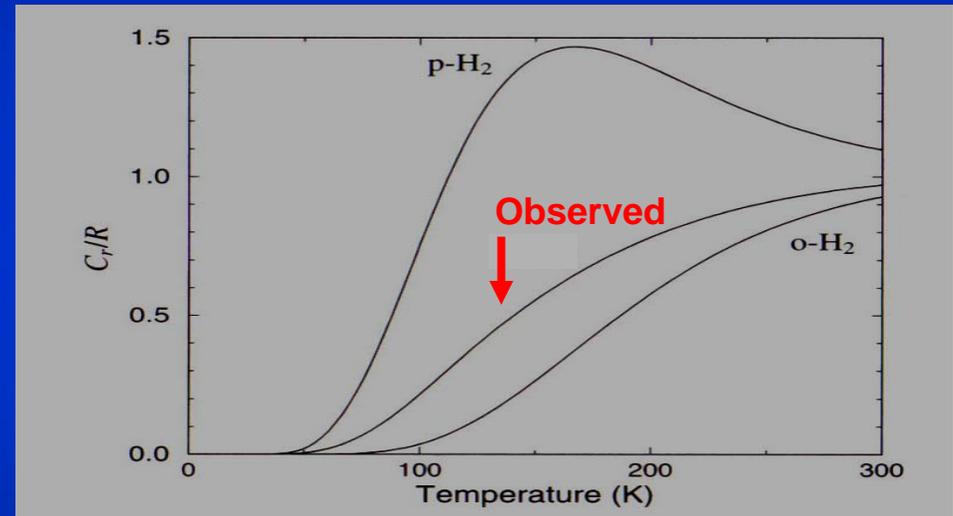
Electron spin : fine structure of hydrogen atom and Stern-Gerlach experiment

G.E. Uhlenbeck and S. Goudsmit, Naturwissenschaften 47 (1925) 953.

Unexplained experimental data for H₂ molecule :



Intensity alternation



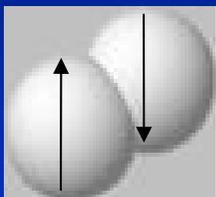
Anormal Rotational Specific Heat

By similarity with the interpretation of the Helium spectrum involving electron spin, Dennison proposed an interpretation of the abnormal specific heat of H₂ introducing the proton nuclear spin.

David M. Dennison Am. J. Phys. 42, 1055 (1974)

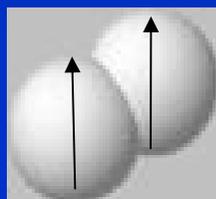
Nuclear spin isomers

Normal hydrogen H_2 is a mixture of two different types of molecules that have different thermal and optical properties



Para- H_2 , $I_{total} = 0$

$$\frac{1}{2} (|\alpha\beta\rangle - |\beta\alpha\rangle)$$

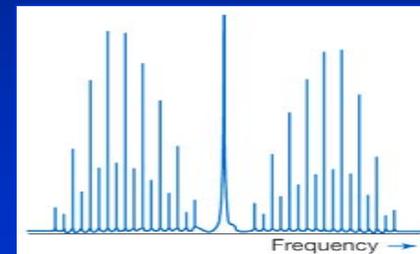


Ortho- H_2 , $I_{total} = 1$

$$|\alpha\alpha\rangle$$

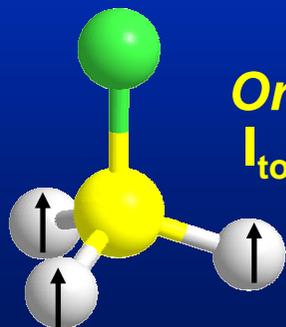
$$|\beta\beta\rangle$$

$$\frac{1}{2} (|\alpha\beta\rangle + |\beta\alpha\rangle)$$

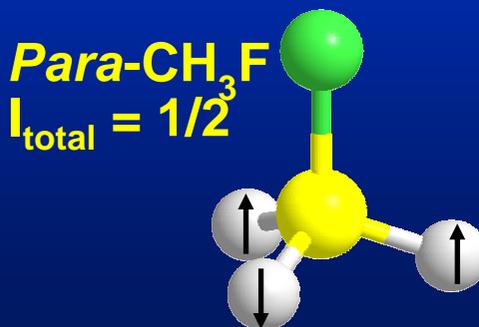


Statistical weight $g = (2I+1)$:
3 (ortho) to 1 (para) at room temperature

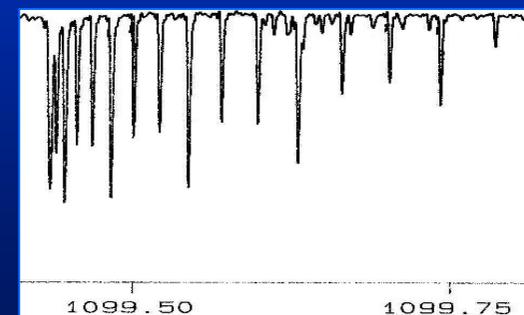
All molecules having identical non zero nuclear spin atoms (H, F ...) in symmetrical positions exist as nuclear spin isomers and are distinguished with the total nuclear spin of the equivalent atoms.



Ortho- CH_3F
 $I_{total} = 3/2$



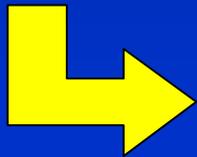
Para- CH_3F
 $I_{total} = 1/2$



Role of equivalent atoms

Pauli's Principle : the total wavefunction has to be symmetric or antisymmetric with respect to permutation of identical atoms

The particle type determines the properties of the total wavefunction



Fermi-Dirac

$$(12)\psi = -\psi$$

Bose-Einstein

$$(12)\psi = \psi$$

fermions (*I* half-integer)

$\frac{1}{2}$: H, ^{13}C , ^{15}N , F

$\frac{3}{2}$: Cl, Br, Na

$\frac{5}{2}$: I, ^{17}O , Al

$\frac{7}{2}$: ^{73}Ge , ^{83}Kr

bosons (*I* integer)

0 : ^{12}C , $^{16/18}\text{O}$

1 : D, ^{14}N

2 : n/a

6 : V

Molecular symmetry group

$$(12) \Psi^{\text{tot}} = \pm \Psi^{\text{tot}}$$

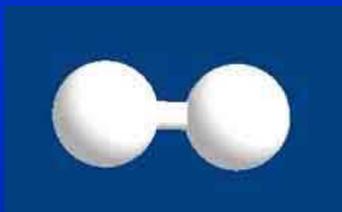
$$\Psi^{\text{tot}} = \Psi^e \Psi^{\text{vib}} \Psi^{\text{rot}} \Psi^{\text{ns}} = \Psi^{\text{evr}} \Psi^{\text{ns}}$$



Molecular symmetry group is used to label the energy levels and Pauli's principle allows only certain combinations.

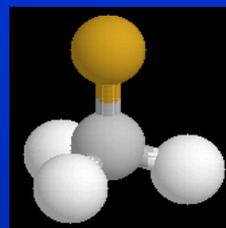
The total nuclear spin I is connected to the rotational quantum numbers

H_2



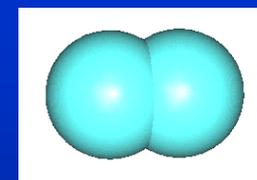
Ortho states $I=1$ \longrightarrow J odd
Para states $I=0$ \longrightarrow J even

CH_3F



Ortho states $I=3/2$ \longrightarrow J, K=3n
Para states $I=1/2$ \longrightarrow J, K=3n±1

O_2



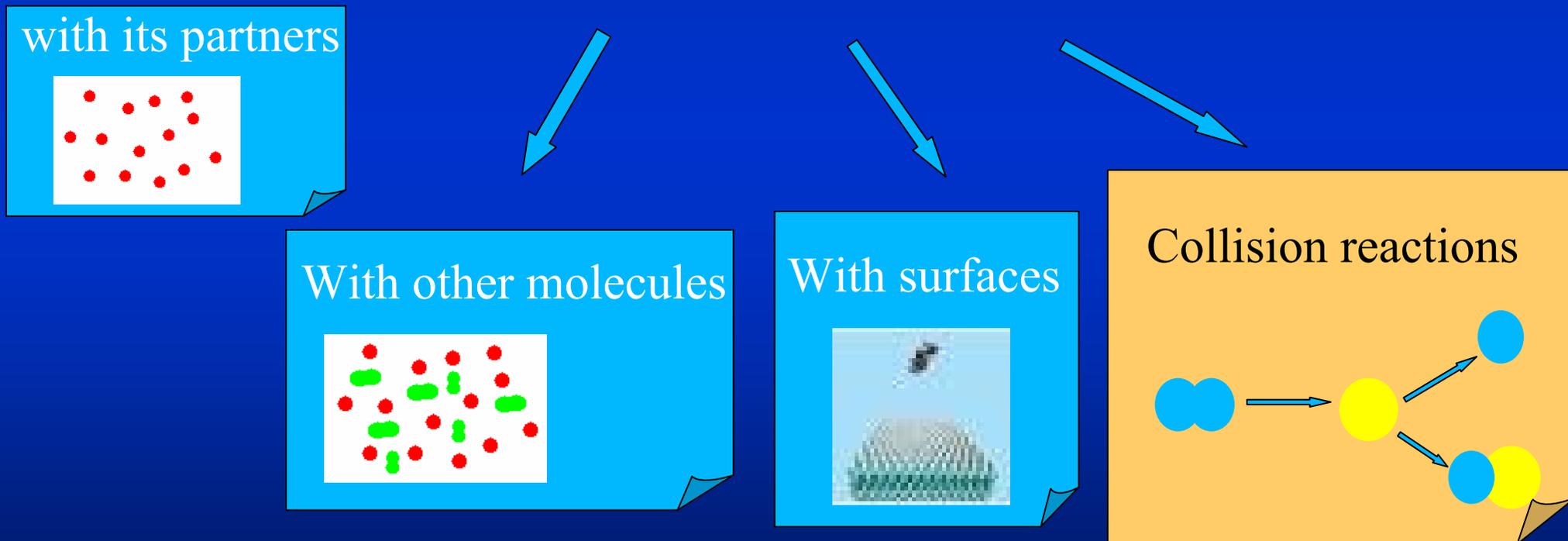
Only J even
 $I=0$

Each spin isomer can be identified by its own rotation-vibration spectrum

Spin conversion definition

Spin conversion is a dynamical property of molecules embedded in an environment and results in the possible change of the total nuclear spin of the molecule (ortho \leftrightarrow para).

The simplest situation is a gas sample where a molecule undergoes collisions



Such a hidden characteristic is quite robust versus collisions and fields : isomers can be regarded as different species.

Physical Origin of Conversion

Flipping the spin requires a gradient of magnetic field strong enough at the molecular scale

External magnetic field

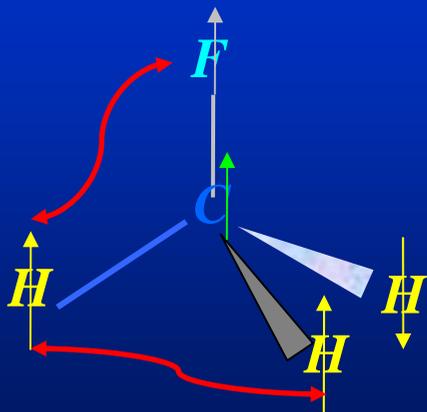
Collisions with paramagnetic molecules (O_2)

H_2 , H_2O in rare gas matrices, CH_3F

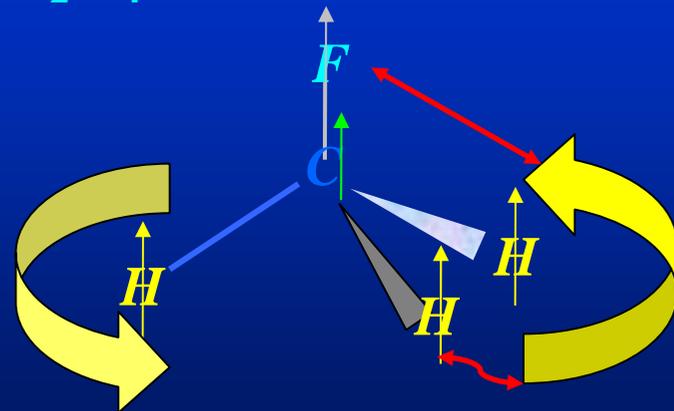
Magnetic field inside the molecule

Interaction between spins (spin-spin) - Rotation of charges (spin-rotation)

CH_3F , H_2CO , C_2H_4



Spin-spin



Spin-rotation

If the existence of spin isomers is accepted,
the dynamics of conversion of one isomer to the other is
not well understood.

Our PROJECT

**Provide experimental observations leading to a quantitative explanation of the
mechanism of nuclear spin conversion.**

(validation and universality of the Quantum Relaxation Model)

**Extract informations about physical properties of molecules and their behavior
in their environment.**

(collisional efficiency ; surface effect)

**Make some predictions through theoretical model and spectroscopic data to
evaluate spin conversion rates**

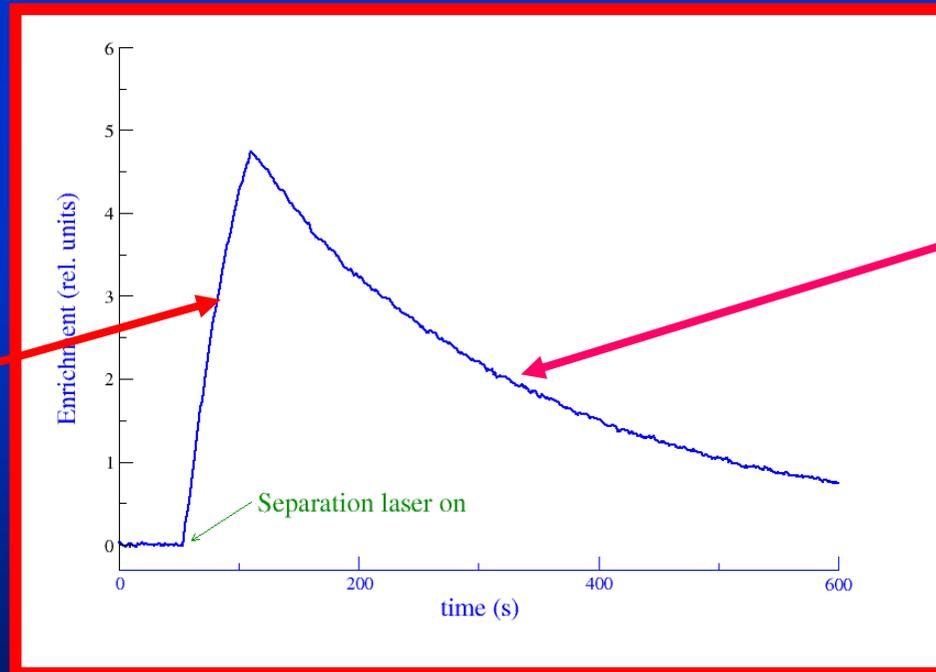
(ISM)

Experiment

« Observation of isomerization rates would require the preparation of a non equilibrium isomeric mixture »

Curl *et al* J. Chem. Phys. 46(8), 3220 (1967)

One must be able to create a disequilibrium between the populations of the different spin configurations to measure the kinetics of the recovering of the Boltzmann distribution.



Enrichment

Nuclear spin conversion

Difficulty : identical physical and chemical properties

Experiment

No general process for enrichment

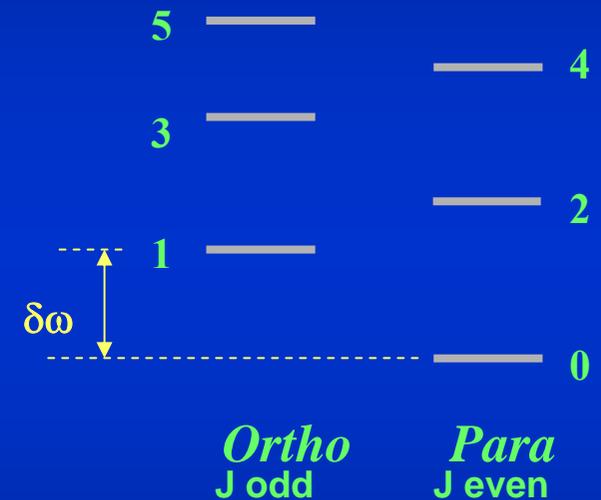
H_2 ($\delta\omega$ # 170.6 K) : cooling below 20.4 K (boiling temperature)

Selective adsorption : H_2O

Reaction from enriched reactants : H_3^+

Selective UV laser photodissociation : H_2CO

Rapid cooling (in matrices) : CH_4 (para - H_2) ; H_2O (Ar)

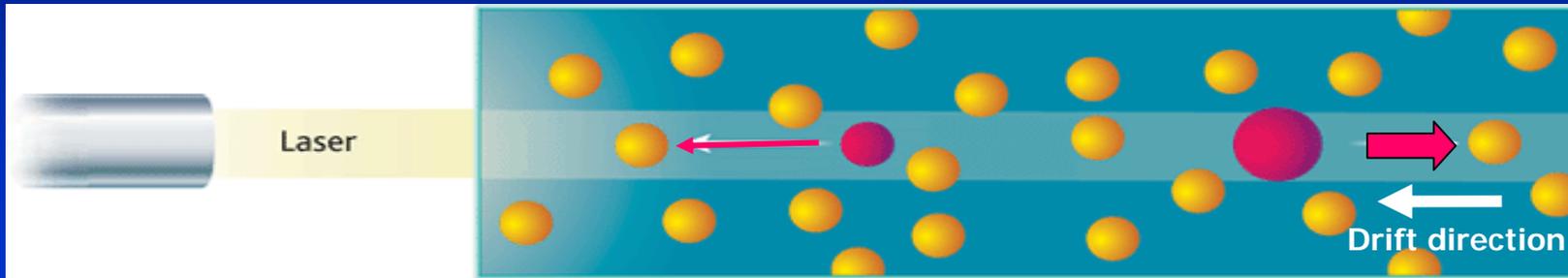


Light-induced drift

Clean environment – gas phase

Light-Induced Drift

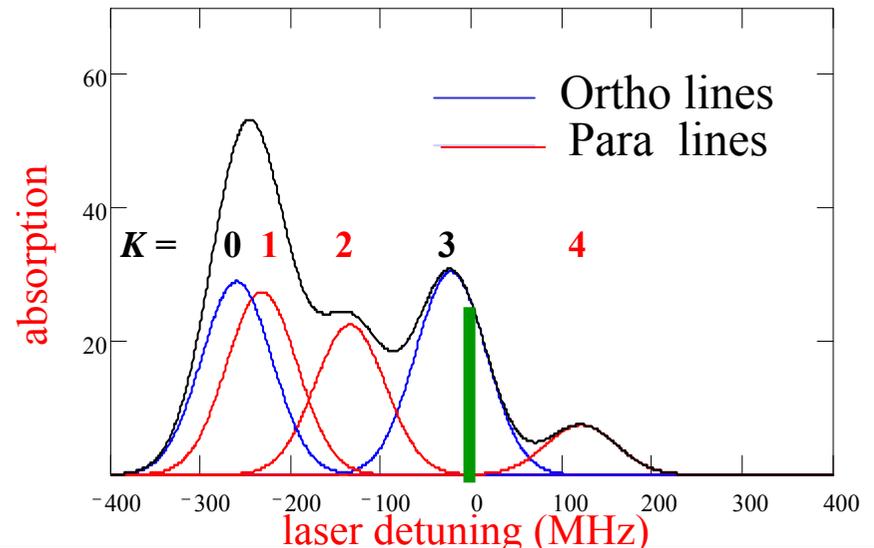
Vibrational and velocity-selective excitation ...



... produces a change of collisional cross section of one isomer species

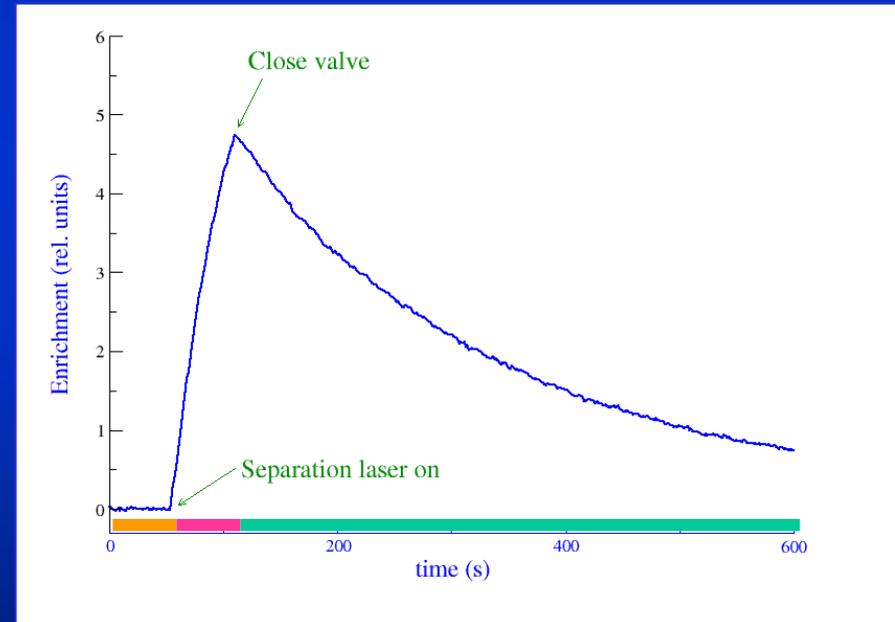
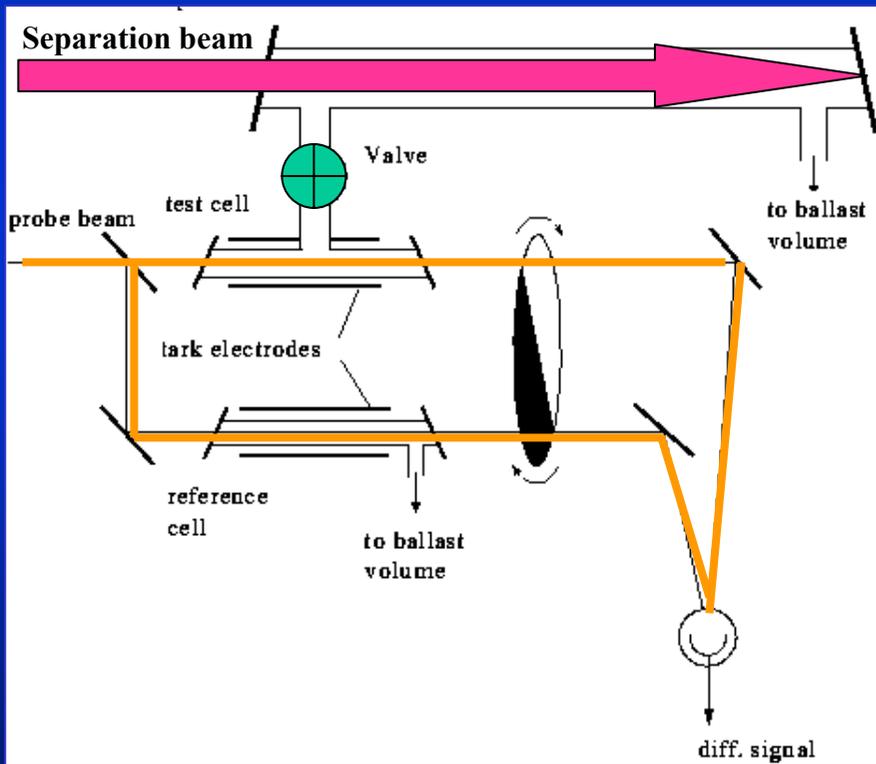
R(4, K) absorption lines of of
the ν_3 band of $^{13}\text{CH}_3\text{F}$

P(32) line of CO_2 laser
(9.6 μm band)

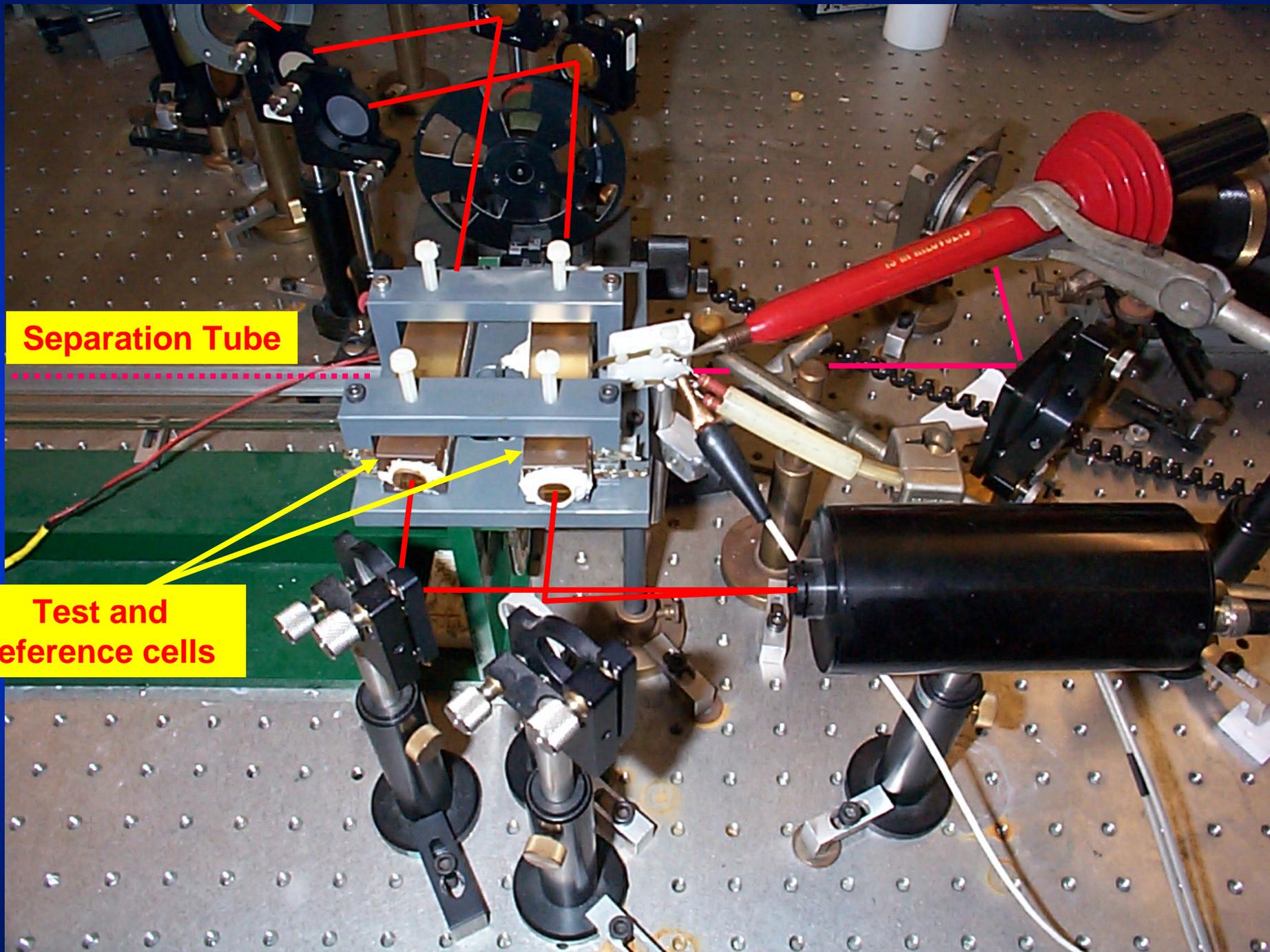


Experiment

Record of the enrichment phase followed by the conversion phase in $^{13}\text{CH}_3\text{F}$



$$\delta\rho_o(t) = \delta\rho_o(0) \exp(-\gamma t)$$

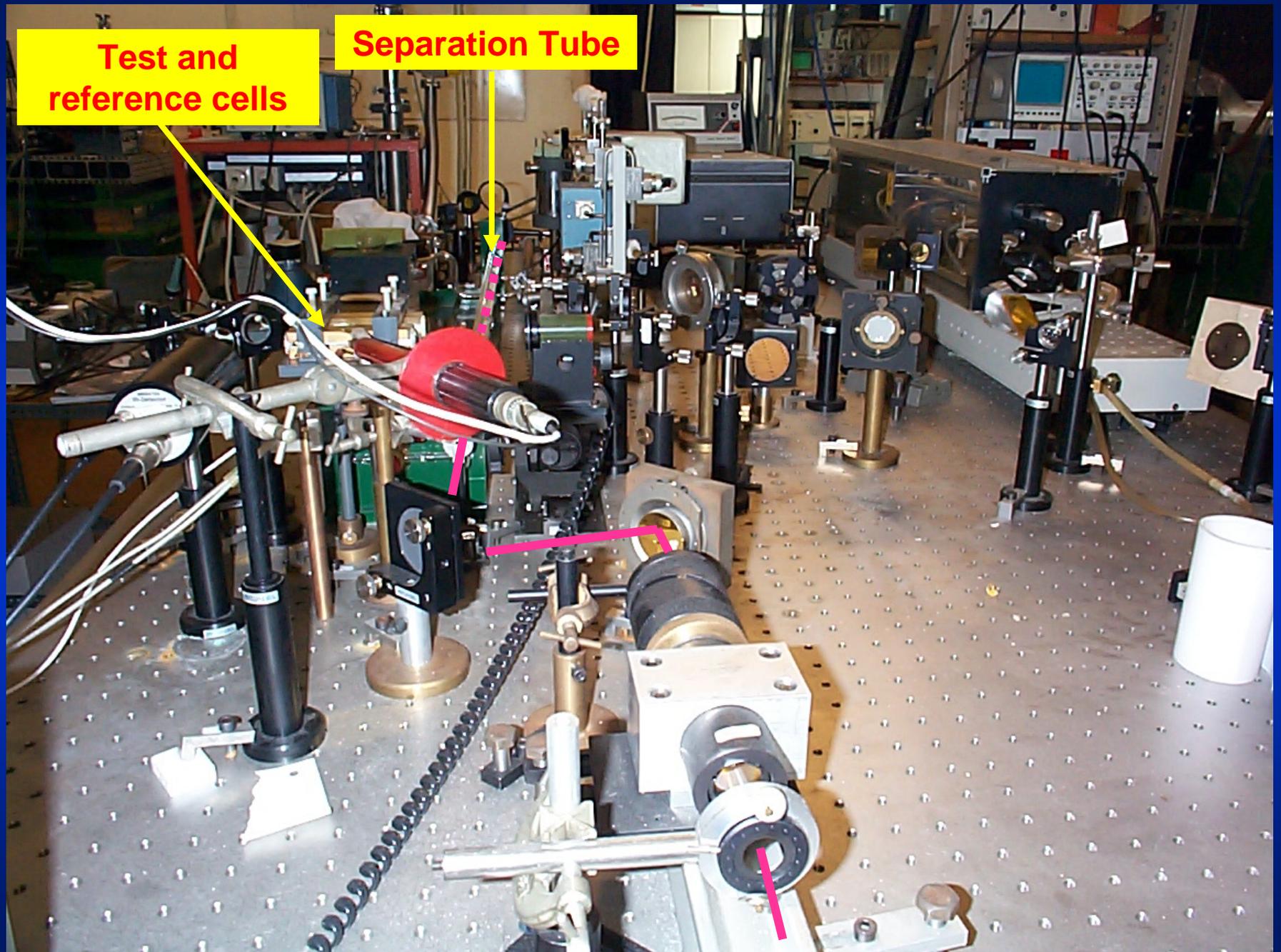


Separation Tube

Test and reference cells

**Test and
reference cells**

Separation Tube



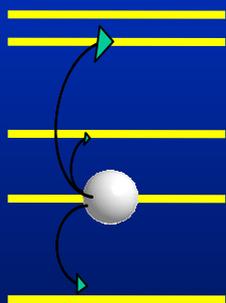
“Quantum Relaxation” model

For nonlinear molecules with identical nuclei an important pathway leading to equilibration of nuclear spin statistics isomers is provided by **wavefunction mixing** induced by the spin-rotation interaction and in some cases the spin-spin interaction.

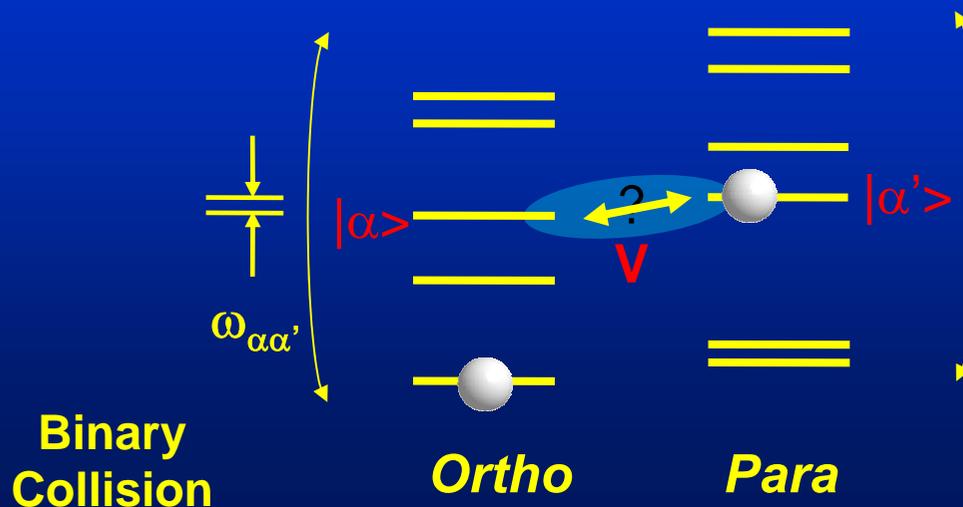
[...] The spin-rotation mixing may be very important if there is an accidental **near degeneracy** of the right sort. Then most of the isomerization « **funnels** » through the near – degenerate levels.

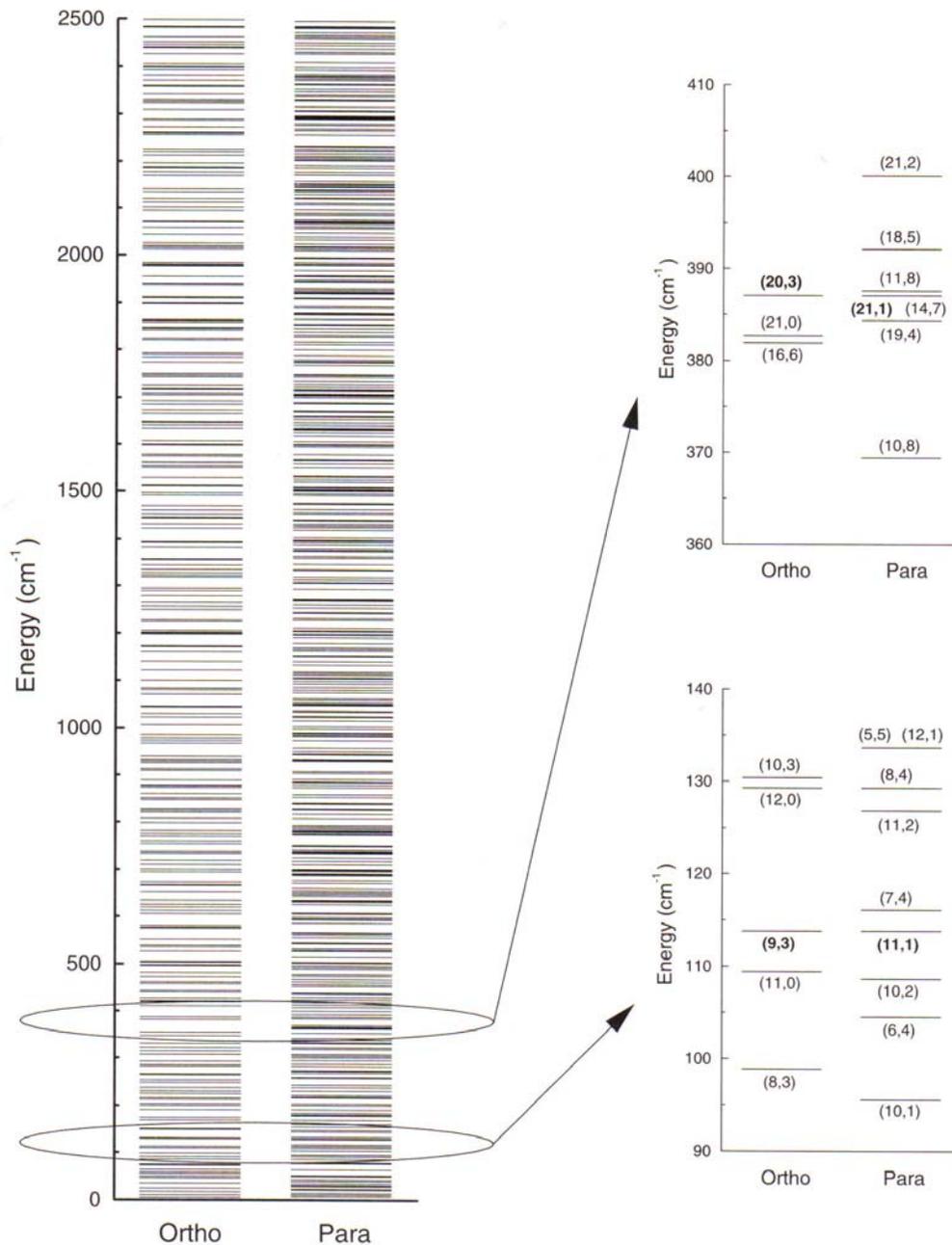
R. F Curl *et al* J. Chem. Phys. 46(8), 3220 (1967)

Energy levels and transitions for a molecule having no equivalent atoms



Energy levels and transitions for a molecule existing as two isomers





Spin-spin interaction

$$\Delta J \leq 2, \Delta K \leq 2$$

Spin-rotation interaction

$$\Delta J \leq 1, \Delta K \leq 2$$

H₂CO

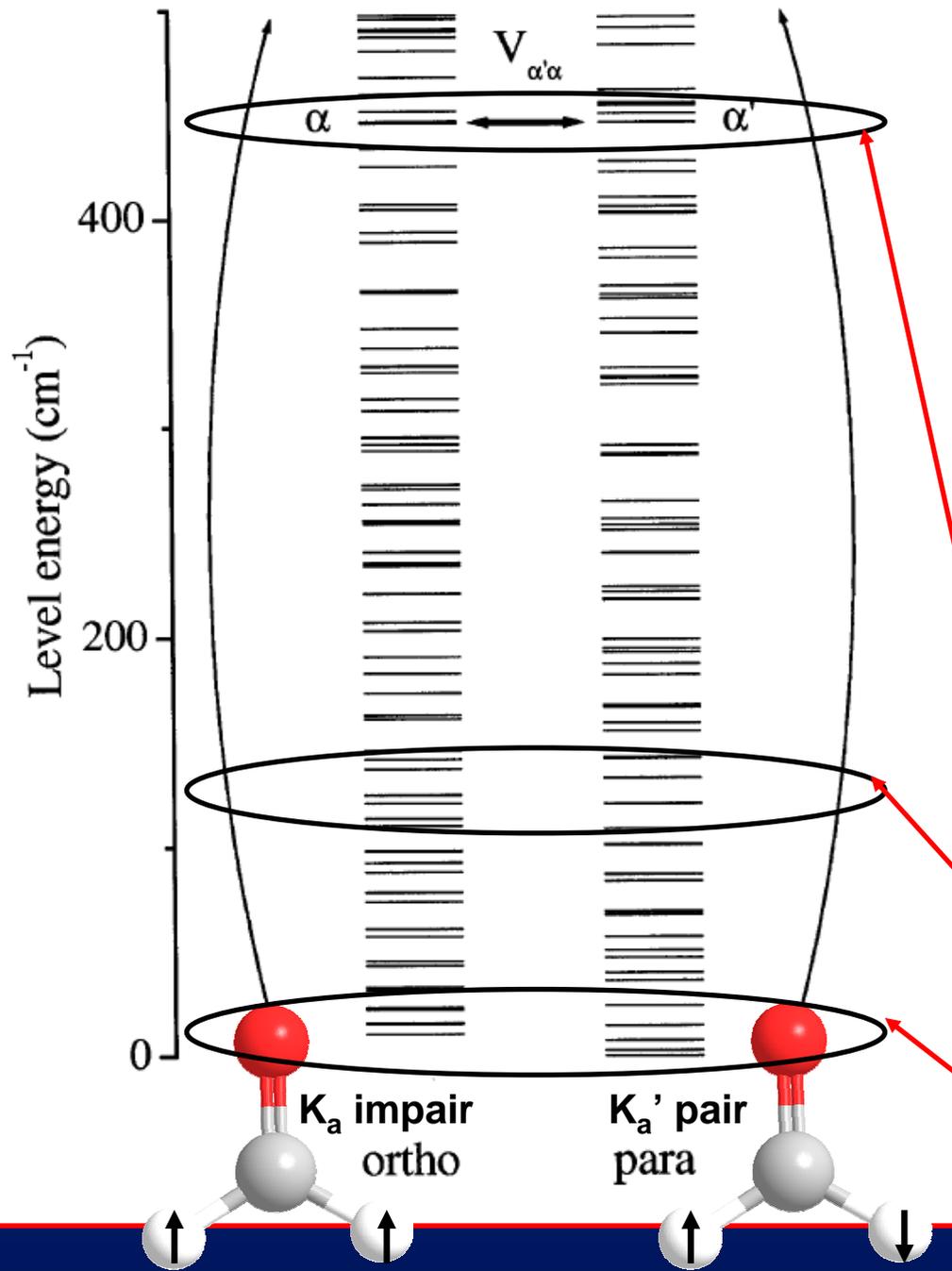
Interaction spin-rotation

Selection rules :

$$\Delta J \leq 1$$

K_a et K_a' of different parity

K_c et K_c' of same parity



$$(J_o, K_a, K_c) - (J_p, K_a', K_c') :$$
$$(17, 3, 15) - (18, 2, 17)$$
$$\hbar\omega = -6.162 \text{ GHz}$$

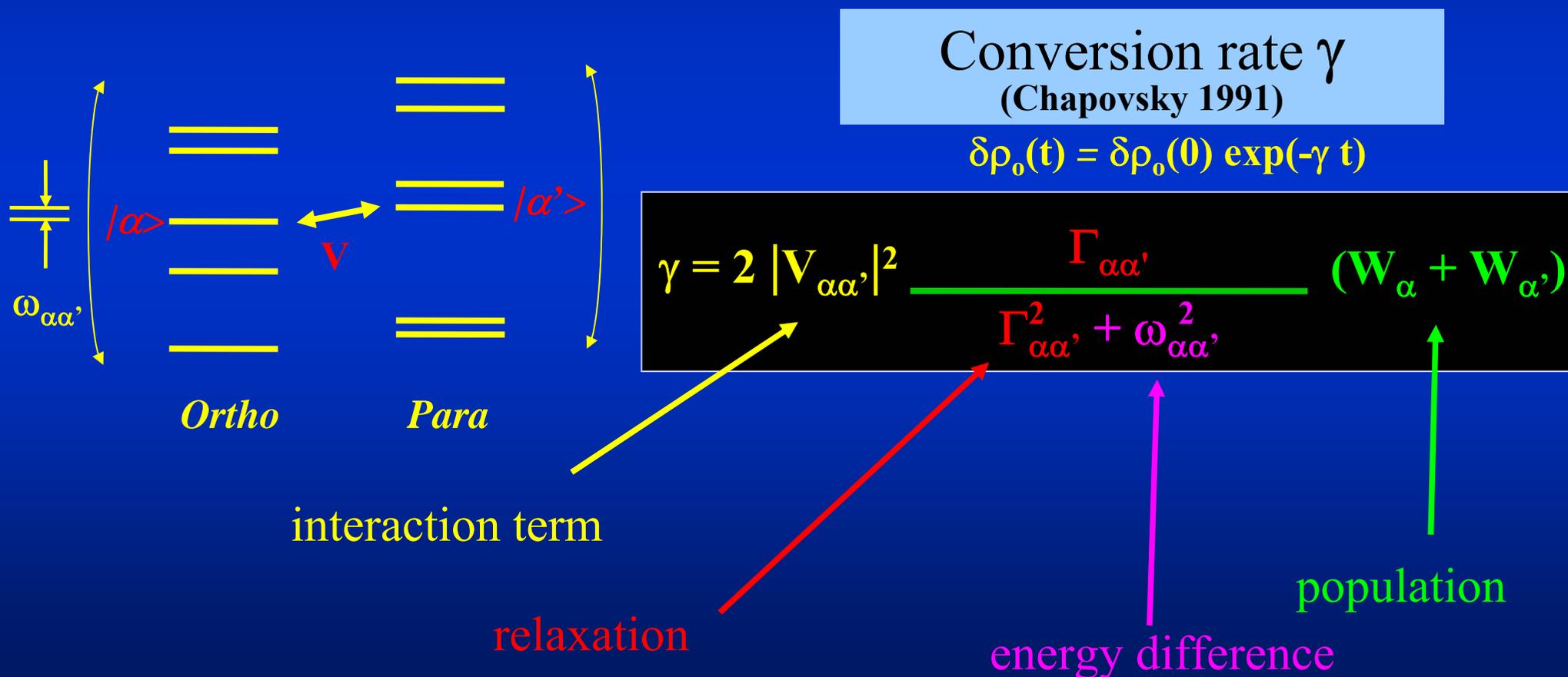
$$(J_o, K_a, K_c) - (J_p, K_a', K_c') :$$
$$(9, 1, 8) - (8, 2, 6)$$
$$\hbar\omega = 9.252 \text{ GHz}$$

$$(J_o, K_a, K_c) - (J_p, K_a', K_c') :$$
$$(3, 1, 2) - (4, 0, 4)$$
$$\hbar\omega = -30.31 \text{ GHz}$$

“Quantum Relaxation” model

Ingredients:

- Energetically close ortho and para levels
- Intramolecular interaction coupling these levels
- Collisional relaxation (Maxwell Boltzmann distribution)



Verification of the model

Pressure dependence of the conversion rate

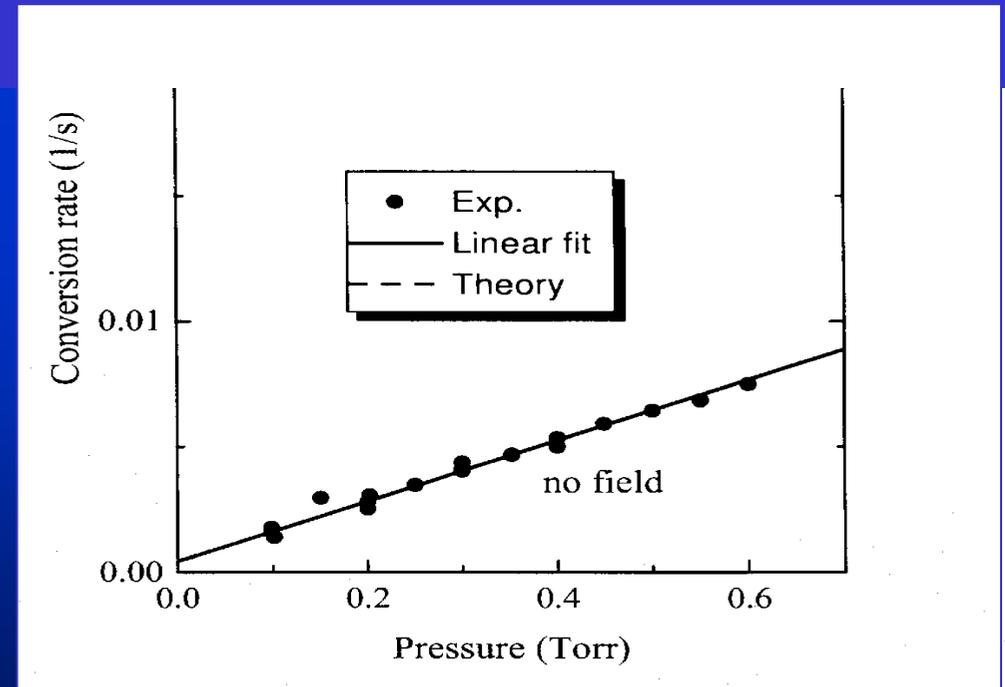
$$\gamma = 2 |\mathbf{V}_{\alpha\alpha'}|^2 \frac{\Gamma_{\alpha\alpha'}}{\Gamma_{\alpha\alpha'}^2 + \omega_{\alpha\alpha'}^2} (W_{\alpha} + W_{\alpha'})$$

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

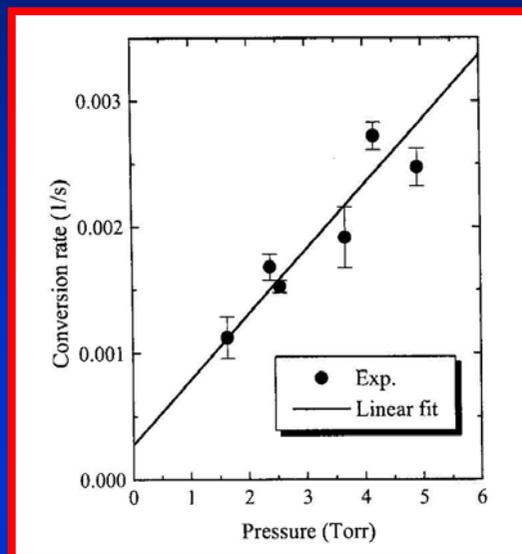
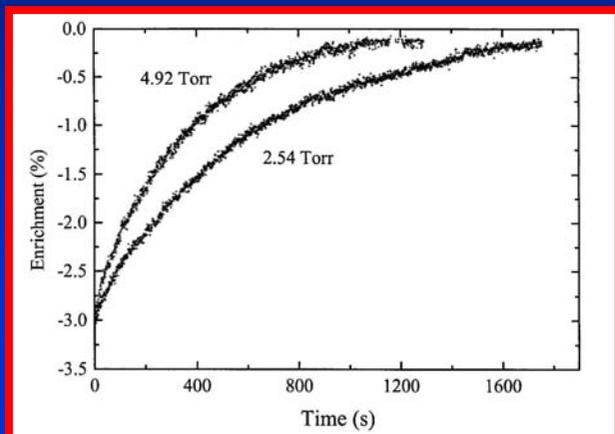
γ proportional to Γ and to pressure



$$\gamma/P = 14 \cdot 10^{-3} \text{ s}^{-1}/\text{torr}$$

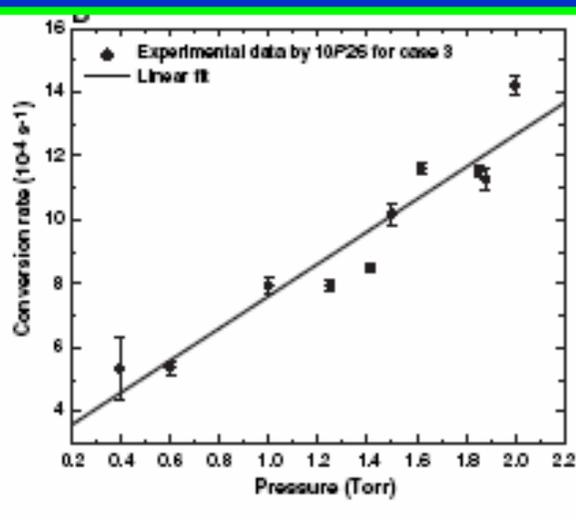
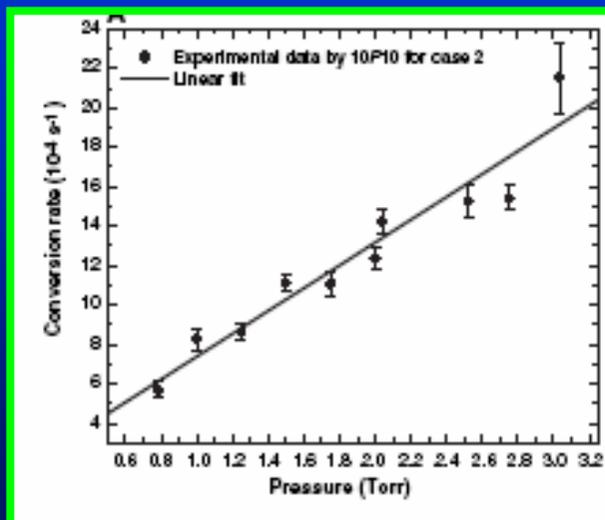


Nuclear spin conversion in ethylene $\text{H}_2\text{C}=\text{CH}_2$



$$\text{H}_2^{13}\text{C}=\text{CH}_2$$
$$\gamma/P = 5 \cdot 10^{-4} \text{ s}^{-1}/\text{torr}$$

Chem. Phys. Lett. 322, 424 (2000)



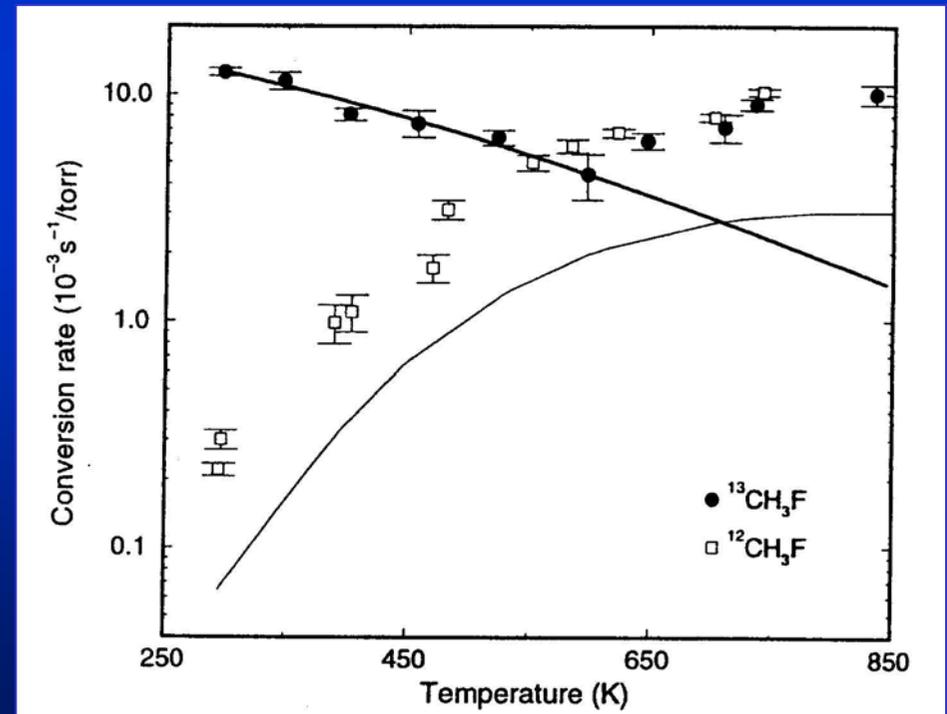
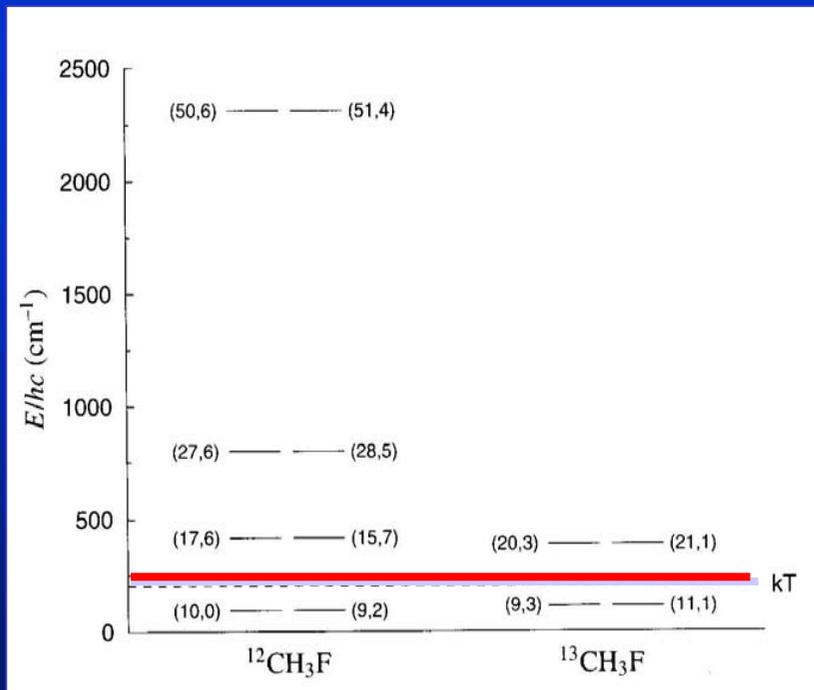
$$\text{H}_2\text{C}=\text{CH}_2$$
$$\gamma/P = 5.5 \cdot 10^{-4} \text{ s}^{-1}/\text{torr}$$

Science. 310, 1938 (2005)

Verification of the model

Temperature dependence of the conversion rate

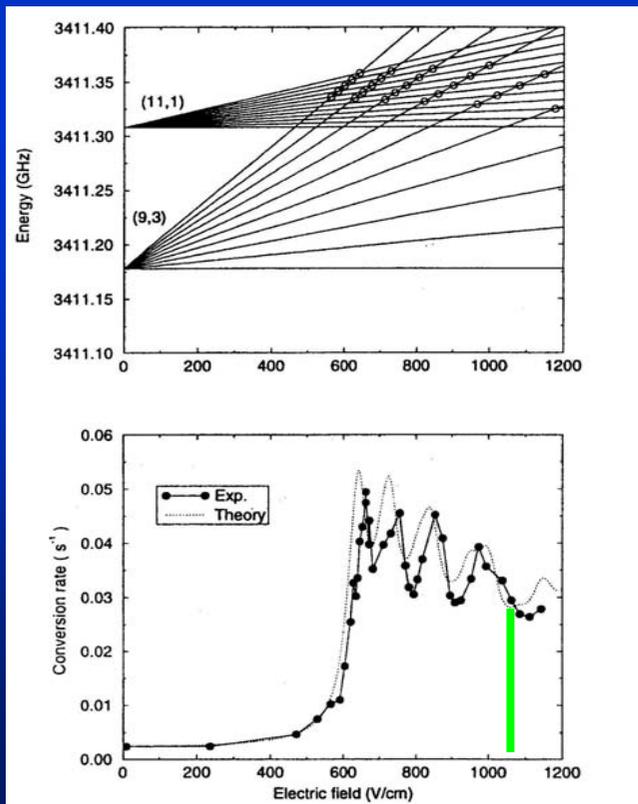
$$\gamma = 2 |\mathbf{V}_{\alpha\alpha'}|^2 \frac{\Gamma_{\alpha\alpha'}}{\Gamma_{\alpha\alpha'}^2 + \omega_{\alpha\alpha'}^2} (W_{\alpha} + W_{\alpha'})$$



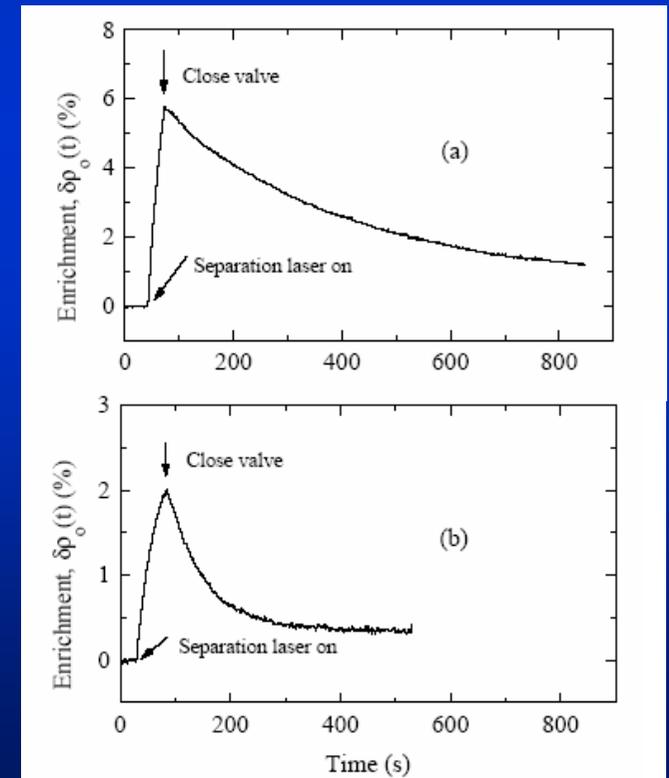
Verification of the model

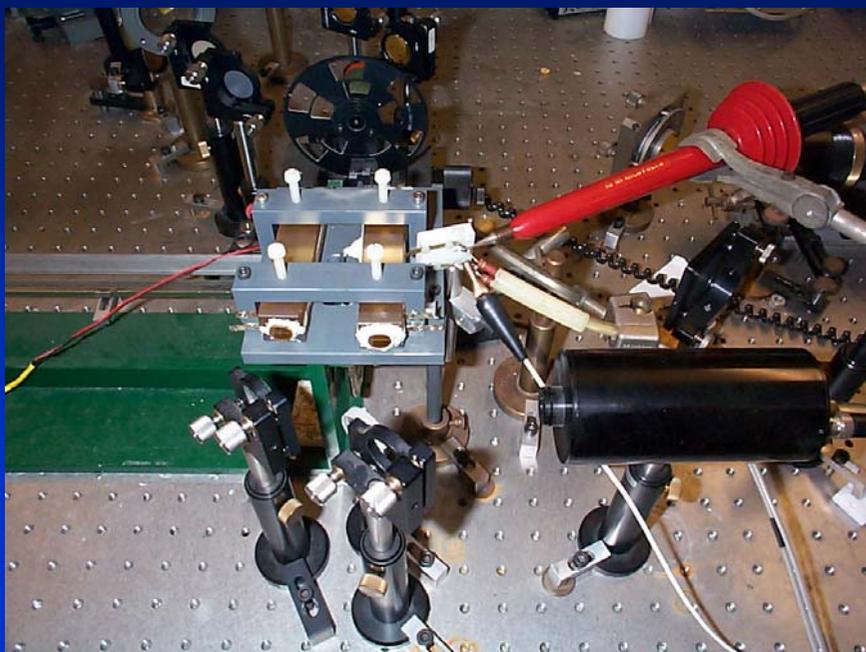
Level crossing resonance

$$\gamma = 2 |\mathbf{V}_{\alpha\alpha'}|^2 \frac{\Gamma_{\alpha\alpha'}}{\Gamma_{\alpha\alpha'}^2 + \omega_{\alpha\alpha'}^2} (\mathbf{W}_{\alpha} + \mathbf{W}_{\alpha'})$$



$$F = 1017 \text{ V.cm}^{-1}$$



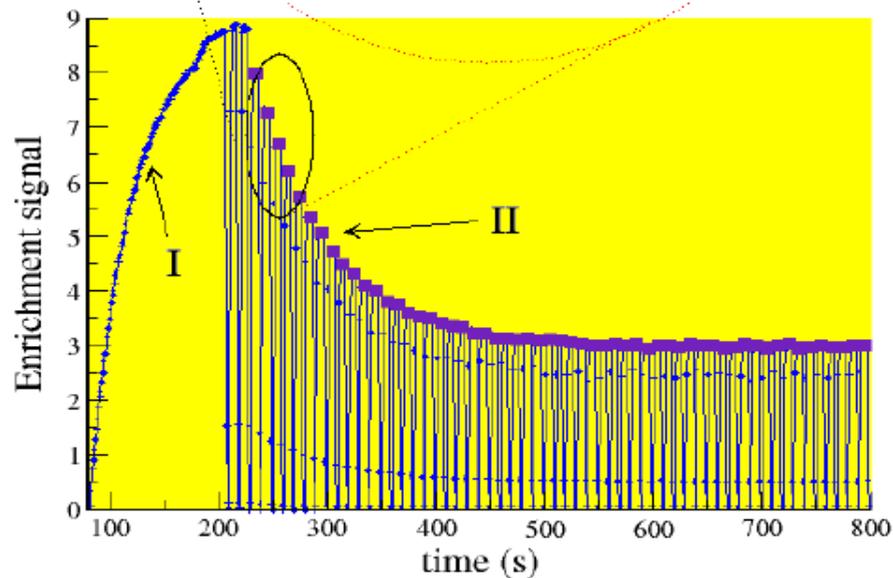
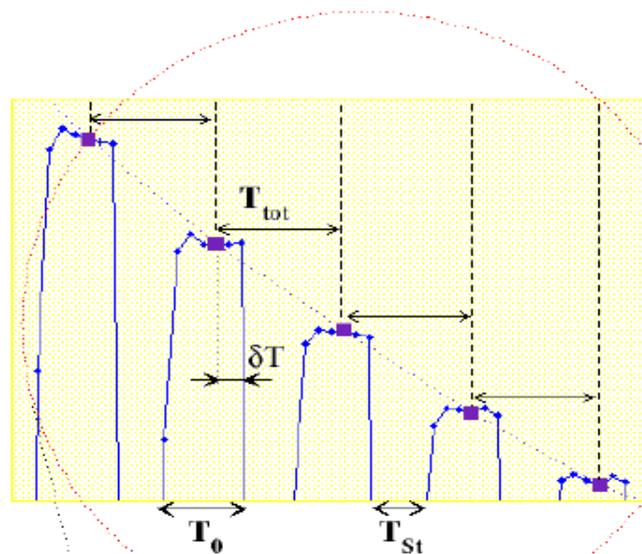


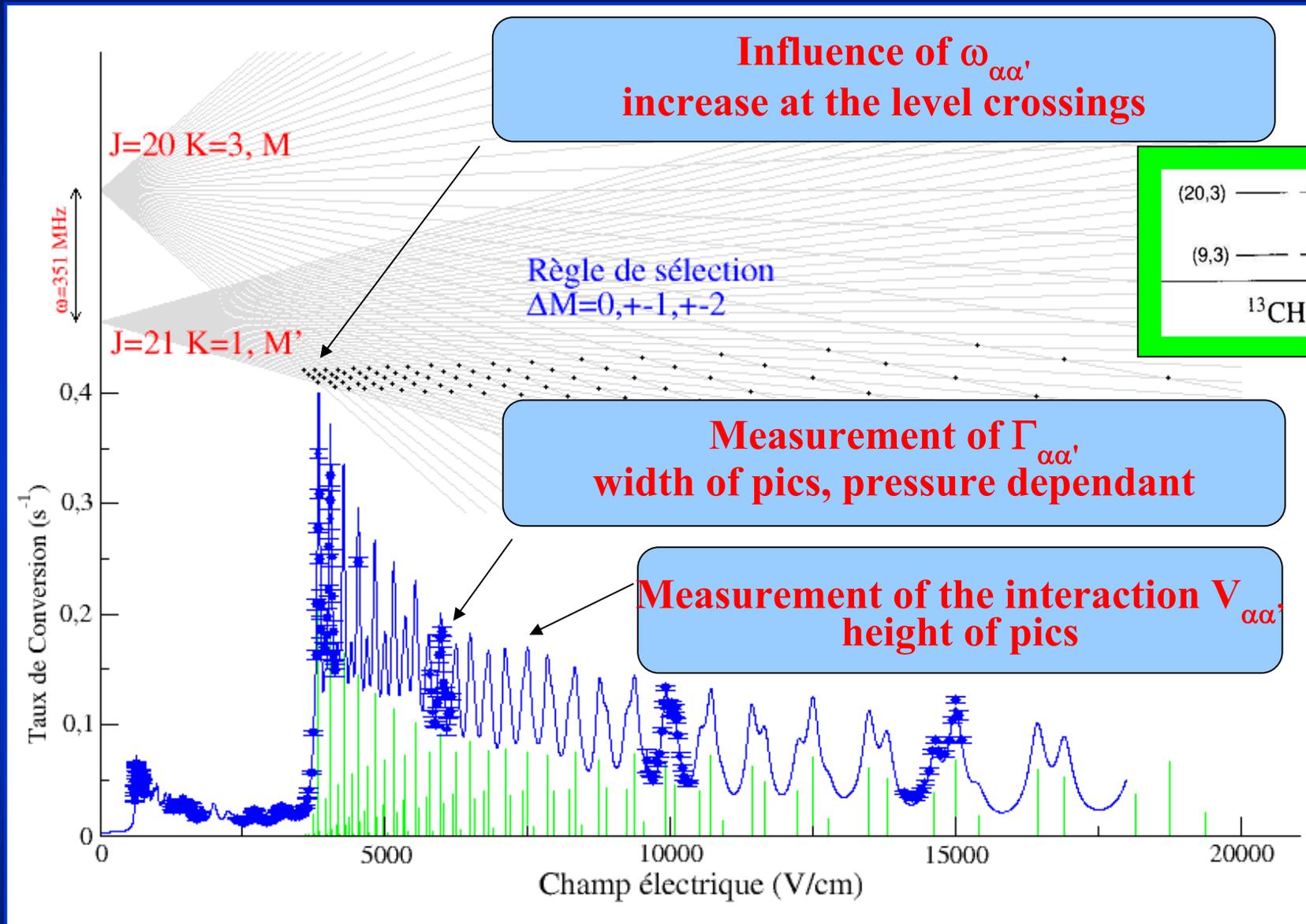
Time sequence with and without Stark field

$$T_{\text{tot}} = T_0 + T_{\text{St}}$$

$$\gamma_{\text{exp}} T_{\text{tot}} = \gamma_0 T_0 + \gamma_{\text{St}} T_{\text{St}}$$

Enrichment probe during T_0 (field off)





All the parameters derived from our experiments within the quantum relaxation model have a physical meaning.

Magnetic interactions

Interaction spin – spin

		<i>Ab initio</i>	experimental
$^{13}\text{CH}_3\text{F}$	T_{22}	69.2	67.93 (25)

C. Puzzarini J. Cosléou, P. Cacciani,
F. Herlemont & M. Khelkhal,
Chem. Phys. Lett. 401 357-362 (2005)

CASSCF, ACES2

$$C_{\perp} = (C_{xx} + C_{yy})/2$$

$$\Delta C_{\perp} = (C_{xx} - C_{yy})/2$$

Interaction spin – rotation

		<i>Ab initio</i>	experimental
$^{12}\text{CH}_3\text{F}$			Klemperer (1971)
$\text{C}(^{19}\text{F})$	$C_{xx} = C_{yy}$	2.07	4.0 (19)
	C_{zz}	- 52.85	-51.1 (13)
$\text{C}(\text{H}_1)$	C_{\perp}	15.92	14.66 (70)
	C_{zz}	0.67	0.8 (15)
$^{13}\text{CH}_3\text{F}$			This work
$\text{C}(\text{H}_1)$	ΔC_{\perp}	- 1.88	1.995 (10)

All the parameters derived from our experiments within the quantum relaxation model have a physical meaning.

Consequences for a molecule of C_{3v} symmetry

- N being isotrope in the perpendicular plane ($N_{xx} = N_{yy}$), the transverse anisotropy is entirely of electronic origin : $\Delta C_{\perp} = \Delta E_{\perp}$.
- Non-diagonal components of the spin-rotation tensor are entirely of nuclear origin et appear unscreened by electrons : $C_{\alpha z} = N_{\alpha z} (E_{\alpha z} = 0)$ $\alpha = x, y$

Specific selection rules for spin-rotation interaction

- $\Delta J \leq 1, \Delta k = 2$: coupling term proportional to $|\Delta C_{\perp}|^2$
Exemple : $^{13}\text{CH}_3\text{F}$: $(J, k) = (21, 1) - (20, 3)$
- $\Delta J \leq 1, \Delta k = 1$: coupling term proportional to $|C_{\alpha z}|^2$
Exemple : $^{12}\text{CH}_3\text{F}$: $(J, k) = (28, 5) - (27, 6)$

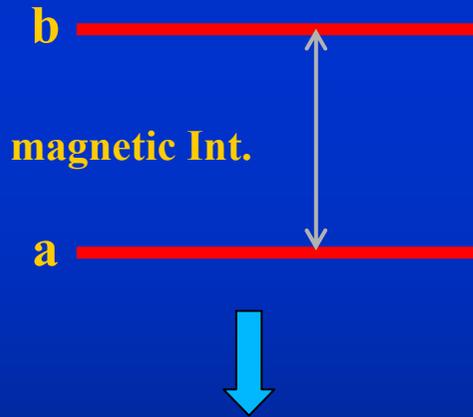


CH_3F is a molecule for which it is possible to derive the complete spin-rotation tensor

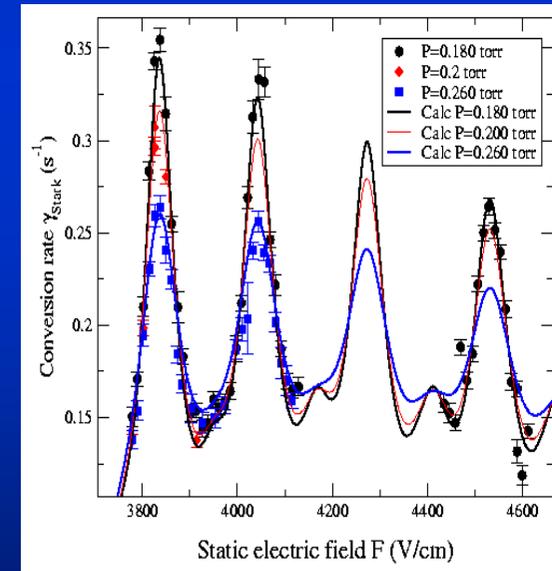
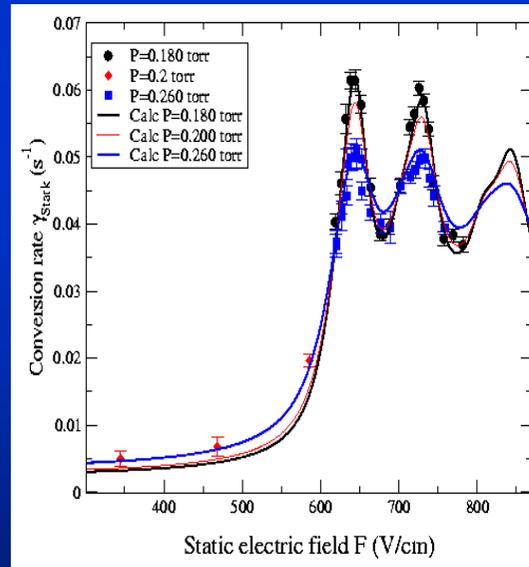
All the parameters derived from our experiments within the quantum relaxation model have a physical meaning.

Relaxation rates of coherence Γ

Coherence : created by an *interaction* and broken by *collisions*



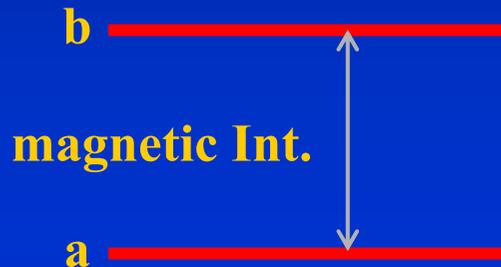
Pressure dependence of the nuclear spin conversion rate



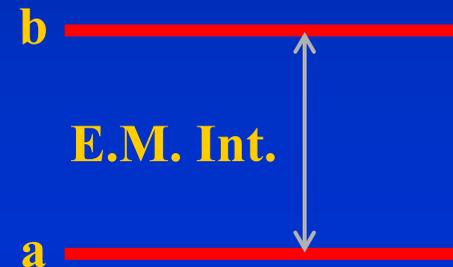
All the parameters derived from our experiments within the quantum relaxation model have a physical meaning.

Relaxation rates of coherence Γ

Analogy with collisional broadening of molecular transitions



Pressure dependence of the nuclear spin conversion rate



Pressure broadening

Despite the final measurements are very different, the treatment of the relaxation developed for the line shape can be transferred to the nuclear spin conversion rate.

All the parameters derived from our experiments within the quantum relaxation model have a physical meaning.

Relaxation rates of coherence Γ

The relaxation parameter Γ , presented as a phenomenological parameter by Chapovsky, can be efficiently calculated with the help of models developed for collisional broadening of molecular transitions.

Parameter	Fitted Value	Calculated value
$\Gamma_{9,3/11,1}$	$1.55 \cdot 10^8 \text{ s}^{-1} \cdot \text{Torr}^{-1}$	$1.59 \cdot 10^8 \text{ s}^{-1} \cdot \text{Torr}^{-1}$
$\Gamma_{20,3/21,1}$	$1.34 \cdot 10^8 \text{ s}^{-1} \cdot \text{Torr}^{-1}$	$1.21 \cdot 10^8 \text{ s}^{-1} \cdot \text{Torr}^{-1}$



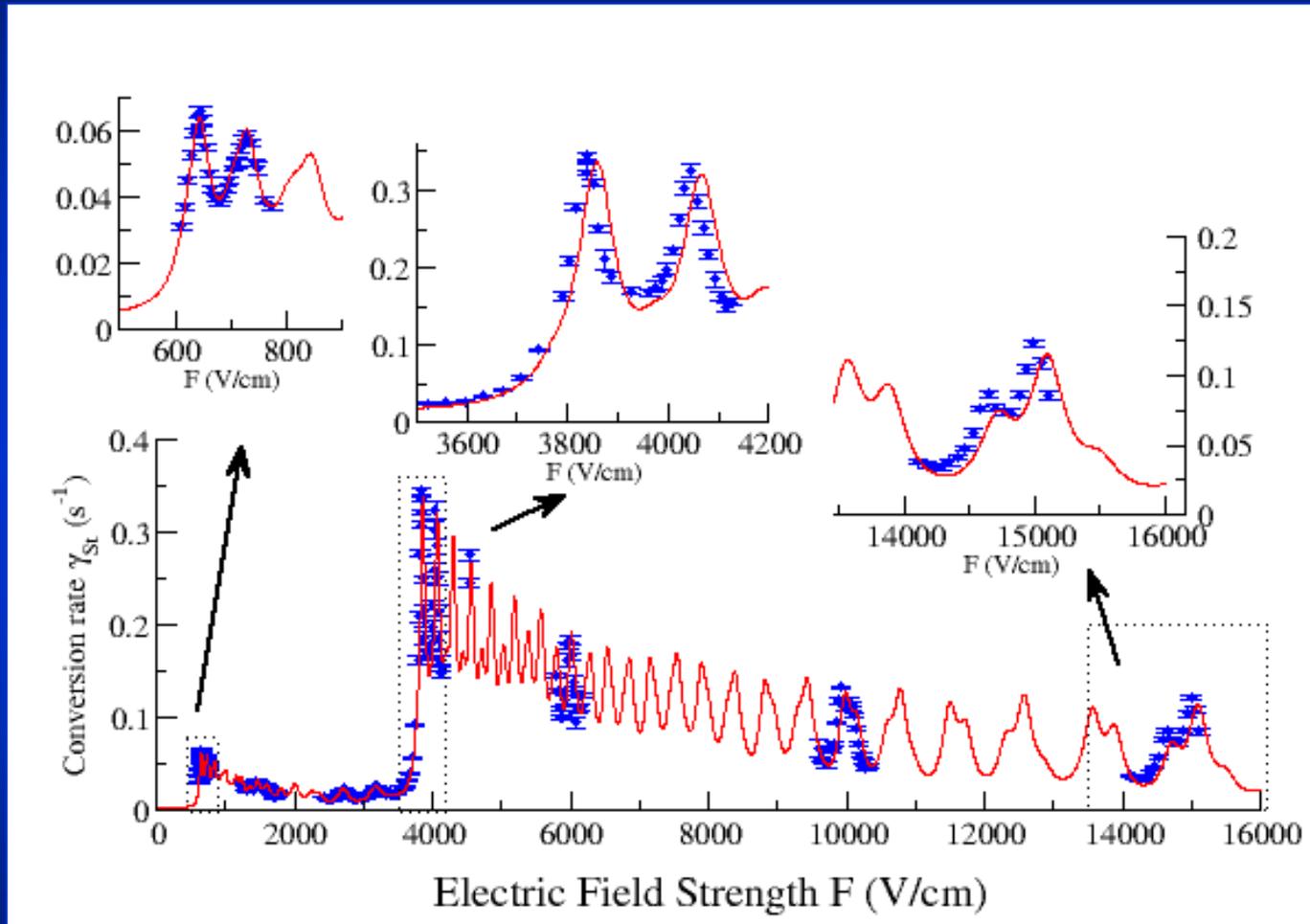
*Within the quantum
relaxation model*

*Collisional inelastic
cross-sections*

P. Cacciani, J. Cosléou, F. Herlemont, M. Khelkhal, C. Boulet & J.-M. Hartmann

J. Mol. Struct., 780-781, 277 (2006)

All the parameters derived from our experiments within the quantum relaxation model have a physical meaning.



1st pair: matching of experimental and calculated positions of maxima

2nd pair : disagreement !

All the parameters derived from our experiments within the quantum relaxation model have a physical meaning.

Rotational dependence of the dipole moment

$$\mu = \mu_0 + \mu_J J(J+1) + \mu_K K^2$$

$$\mu_J (\text{exp}) = 2.72 (1.71) 10^{-5} \text{ D}$$

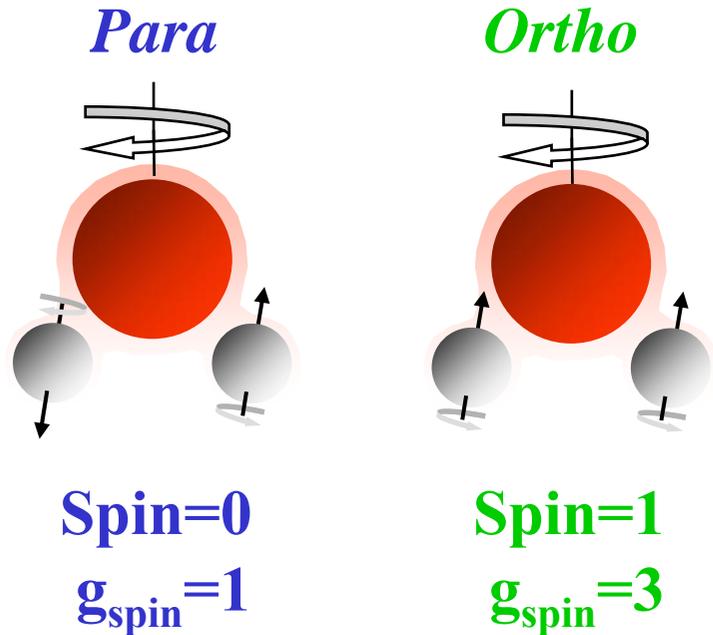
(figures in parentheses = 3 times the s.d.)

$$\mu_J (\text{th}) = 1.492 10^{-5} \text{ D}$$

$$\mu_K (\text{th}) = - 3.695 10^{-5} \text{ D}$$

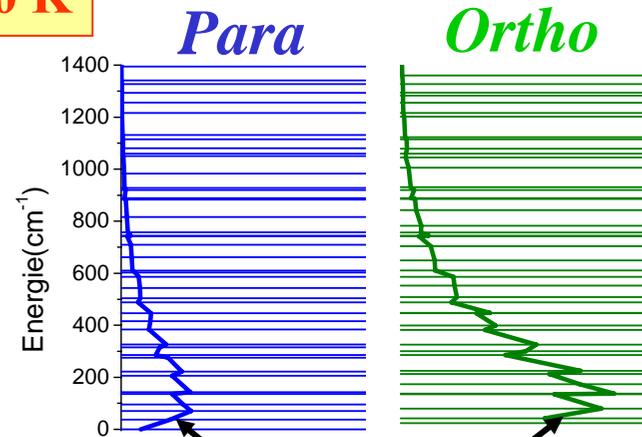
Application to astrophysics

Water molecule

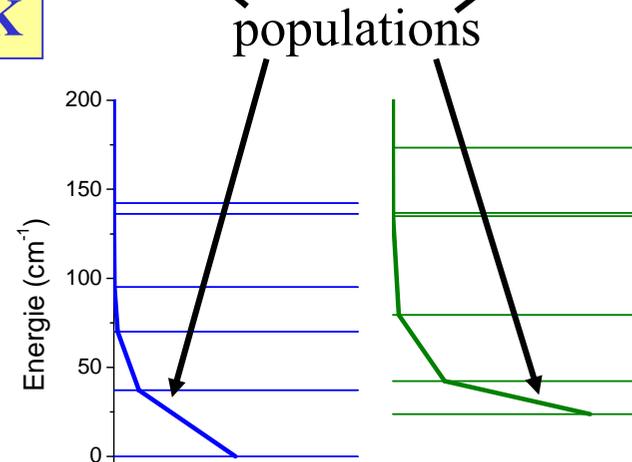


300 K

Rotational levels



20 K

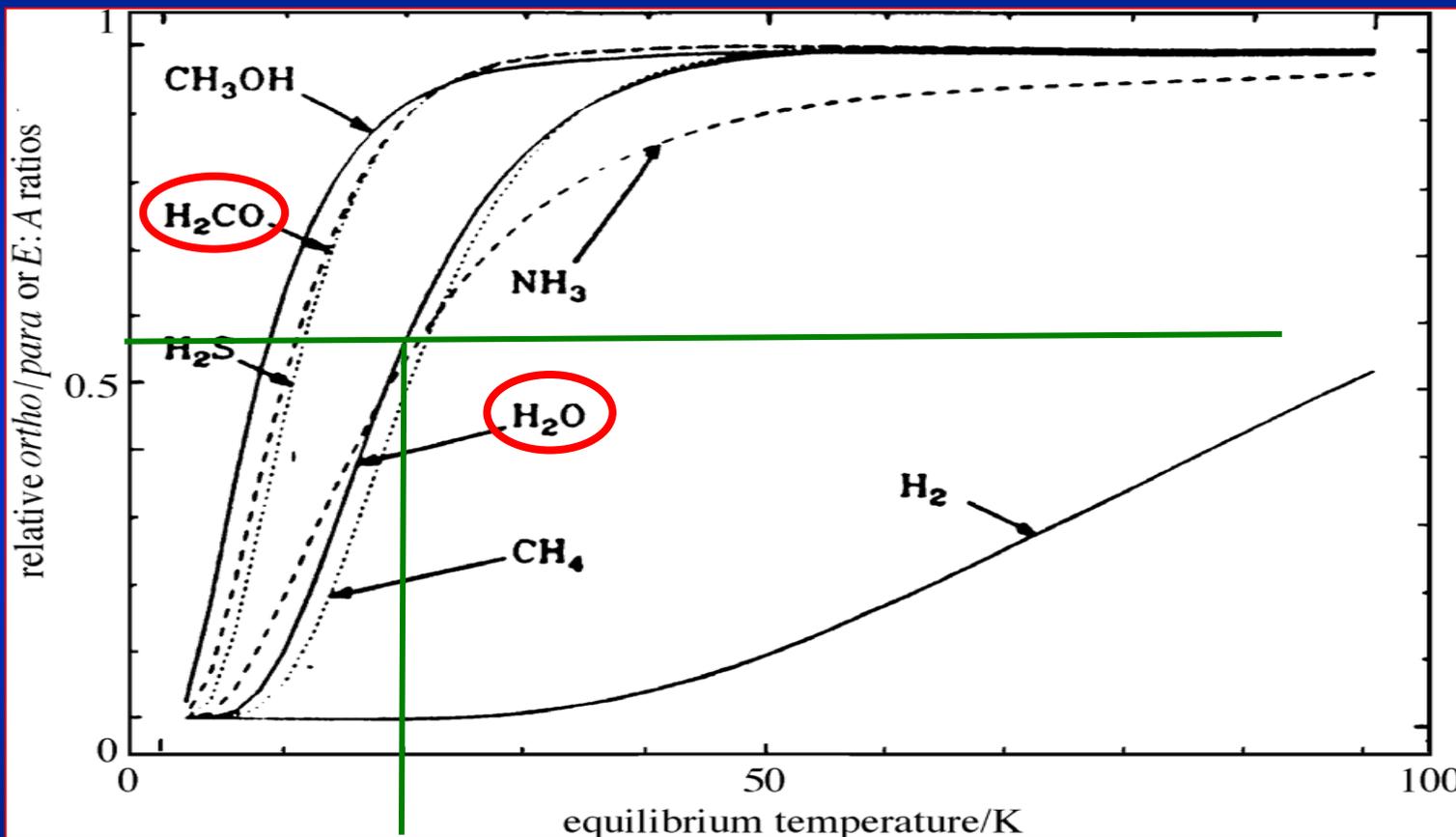


OPR

($T > 60$ K)
 ~ 3

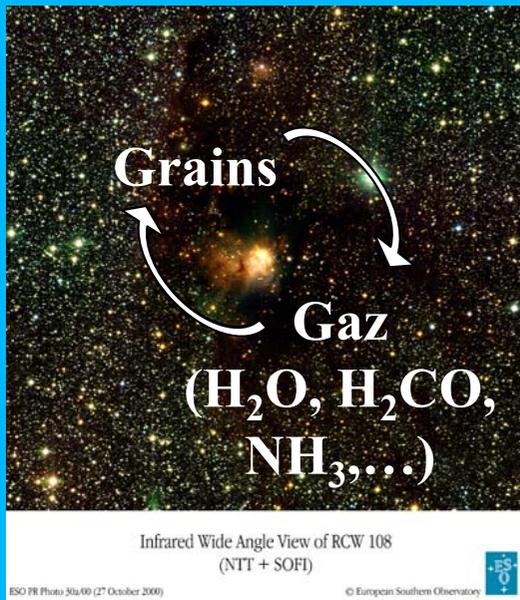
1.7

Ortho/para ratio (OPR) can be measured from observation of interstellar medium or comets. It allows to derive a spin temperature T_{spin}



T_{spin}

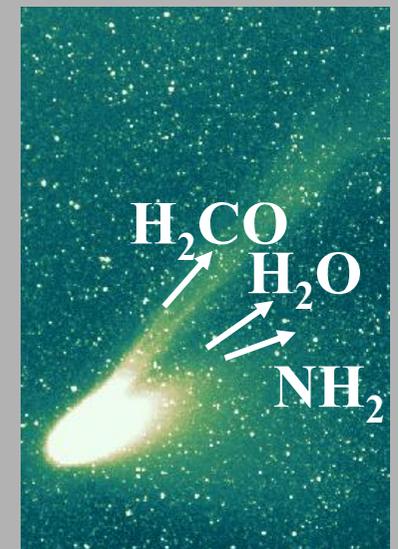
Molecular formation deduced from T_{spin}



- Prestellar clouds (L723,...) : $T_{spin} \sim 10$ K of H_2CO close to $T_{kinetic}$ indicates the formation of molecules or the thermal equilibration on cold grains
- Others cases (L1498, ...) : an $OPR = 3:1$ whereas $T_{kinetic} \sim 10$ K indicates a formation at high temperature before it cooled down

(Dickens, Astrophys. J. 1999)

- For most comets (various distances from the Sun, different origins), the measured *OPR* for NH_3 , H_2O et CH_4 correspond always to a spin temperature of about 30 K : no re-equilibration
- In the ice, these molecules could have maintained a memory of their formation temperature in the protosolar nebulae
- « ..., we conclude that the Sun was born in a warm molecular cloud near 30 K, not in a cold dark cloud near 10 K, as is usually assumed. » Kawakita et al, Astrophysical Journal 2005



Hale-Bopp Comet

A test of the hypothesis of forbidden conversion in gas phase

Nuclear spin conversion of formaldehyde
in star forming regions induced by non reactive collisions
using “quantum relaxation model”

In collaboration with C. PUZZARINI (Bologna), S. MARET and C. KAHANE (Grenoble)

Energy differences

Identification of the most important ortho-para pairs

Spin-rotation interaction V_{op}

non diagonal Terms of the tensor
never compared to experiment

Ab-initio Calculation of the spin-rotation tensor
(method CCSD(T), ACES2 program)

Calculation of wavefunctions (asymmetric top)
and interaction terms

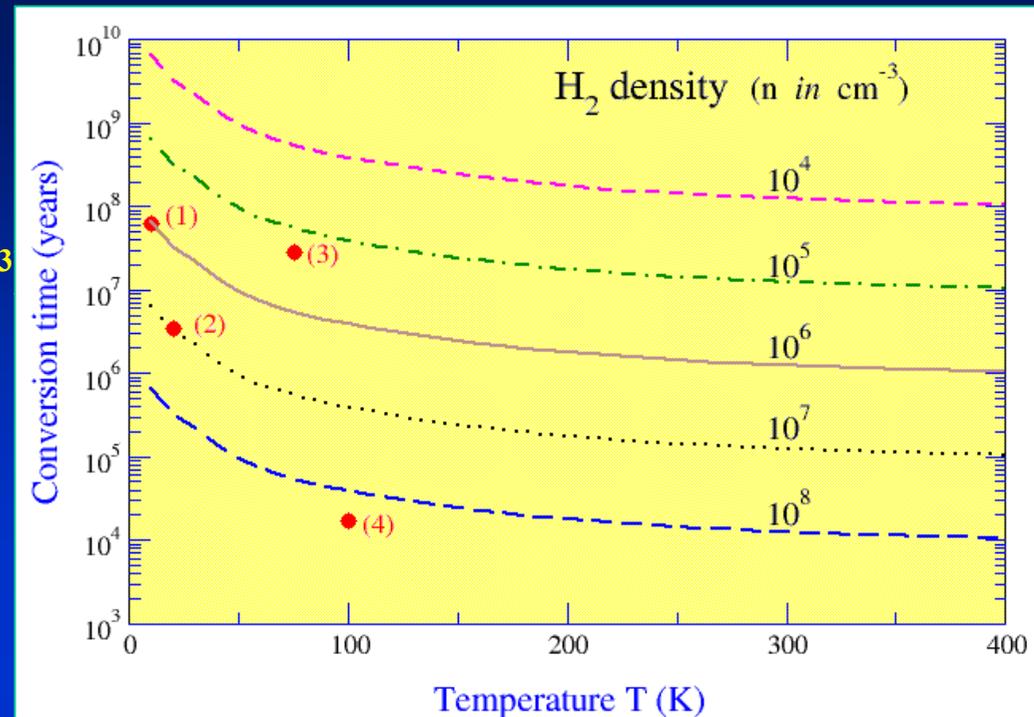
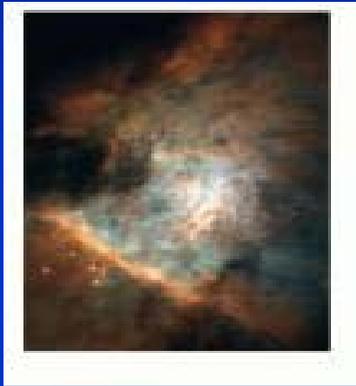
Decoherence induced by
collisions with H_2

Value estimated from the broadening of spectral lines
 $\Gamma = 5 \cdot 10^7 \text{ s}^{-1} \text{ Torr}^{-1}$

Dipole-quadrupole interaction between H_2CO and H_2
Temperature dependence

4 environments

- Prestellar core ($T = 5-10$ K, $n(\text{H}_2) = 10^6 \text{ cm}^{-3}$)
- Protoplanetary disk (30 K, 10^7 cm^{-3})
- Photodissociation region Orion (75 K, $2 \times 10^5 \text{ cm}^{-3}$)
- Protostar (100 K, $3 \times 10^8 \text{ cm}^{-3}$)



Spin conversion characteristic times are much longer than H_2CO lifetime (~ 10000 years).

Potential sources of nuclear spin conversion :

- proton exchange with interstellar H^+
- exchange of protons attached to C and O atoms within H_2COH^+ (protonation of H_2CO by H_3^+)
- adsorption-desorption on grains.

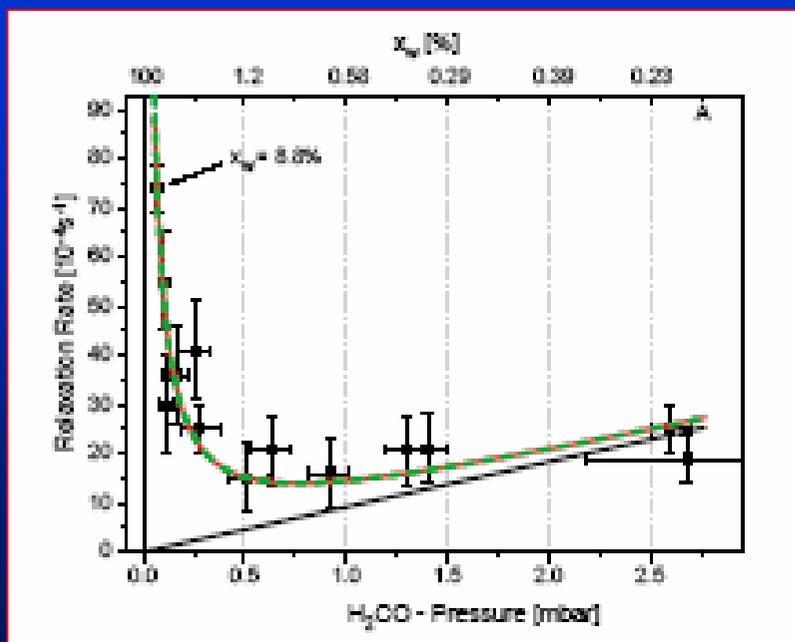
ISM \rightarrow low pressure range

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

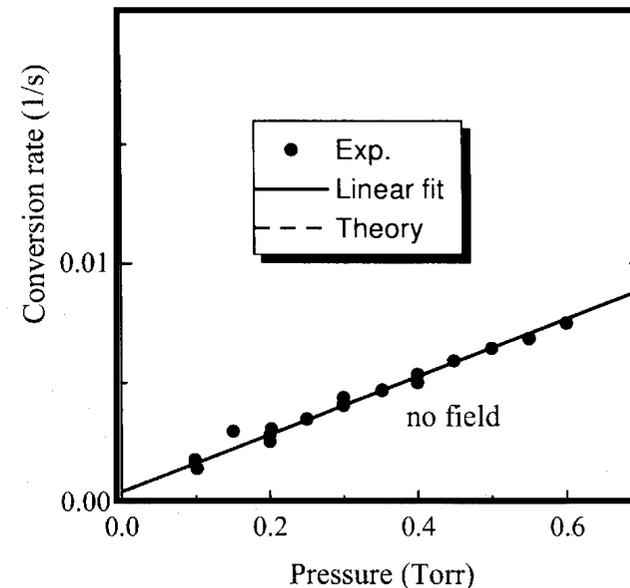
Low pressure range ($\Gamma_{\alpha\alpha'} \ll \omega_{\alpha\alpha'}$)

γ proportional to Γ and to pressure

BUT ...



PRESSURE DEPENDENCE OF THE CONVERSION RATE



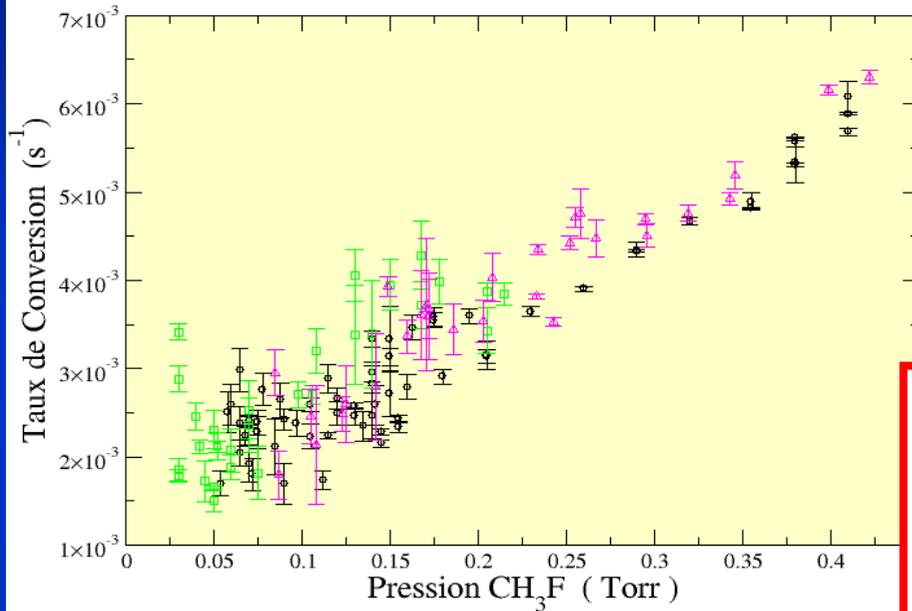
Eur. Phys. J. D 12, 297 (2000)

H_2CO : observation of an increase of γ at low pressure

(C. Bechtel, E. Elias, B.F. Schramm, J. Mol. Struct., 741, 97 (2005))

Pressure reduced to 30 mTorr ; 3 cells of different S/V ratio

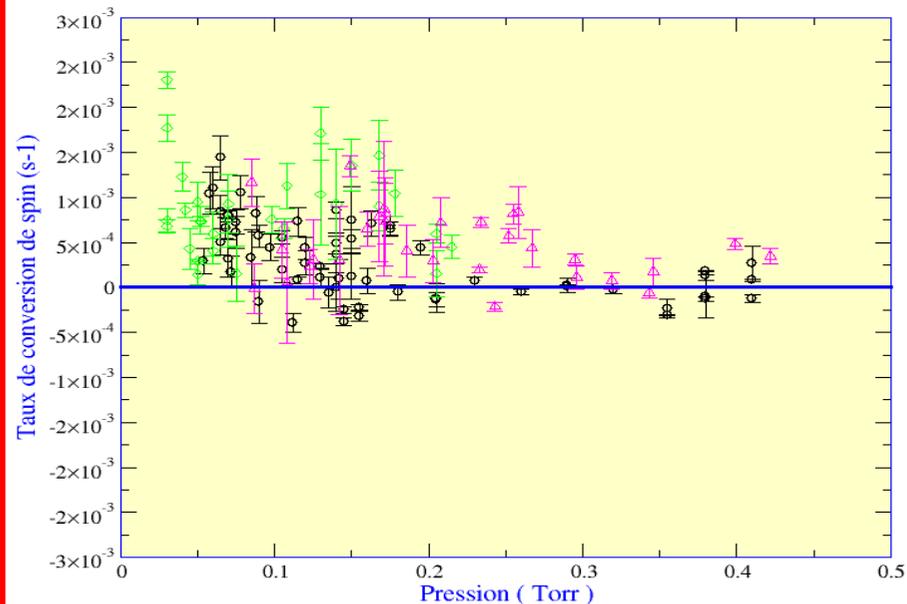
Conversion rate at lower pressure



$P > 200$ mTorr : aligned points

$P < 200$ mTorr : acceleration of the conversion

Surface effect



With linear dependence at high pressure subtracted.

Volume γ_g and non magnetic surface γ_s contributions

Number of collisions

Binary collisions

$$N_g = \frac{1}{2} n^2 \sigma \bar{v} V$$

$$x_s = \frac{N_s}{N_s + N_g}$$

Surface collisions

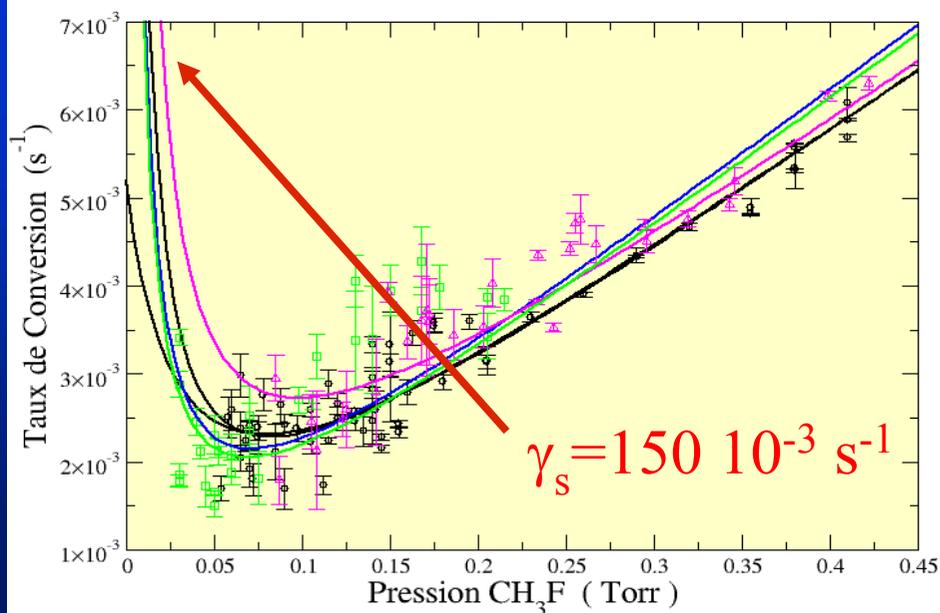
$$N_s = \frac{1}{4} n \bar{v} S$$

$$x_g = 1 - x_s$$



$$\gamma_{\text{total}} = x_s \gamma_s + x_g \gamma_g$$

Conversion rate at lower pressure



p_0 defined by $N_g = N_s$

$$p_0 = \frac{kT}{2\sqrt{2}\sigma} \times \frac{S}{V}$$

Cell type	Cross section (\AA^2)	p_0 (mTorr)	γ_g ($\text{s}^{-1}/\text{Torr}$)	γ_s (s^{-1})
Cylindrical cells 20 cm	4541,53 [3]	0,31	0,01384(11)	0,30(3)
Cylindrical cells 20 cm	44 [4]	31,98	0,01453(14)	0,0052(2)
Cylindrical cells 50 cm	4541,53 [3]	0,4	0,01469(13)	0,135(8)
Stark cells	4541,53 [3]	0,45	0,01481(22)	0,26(4)
All data	4541,53 [3]	0,4	0,01399(8)	0,151(8)