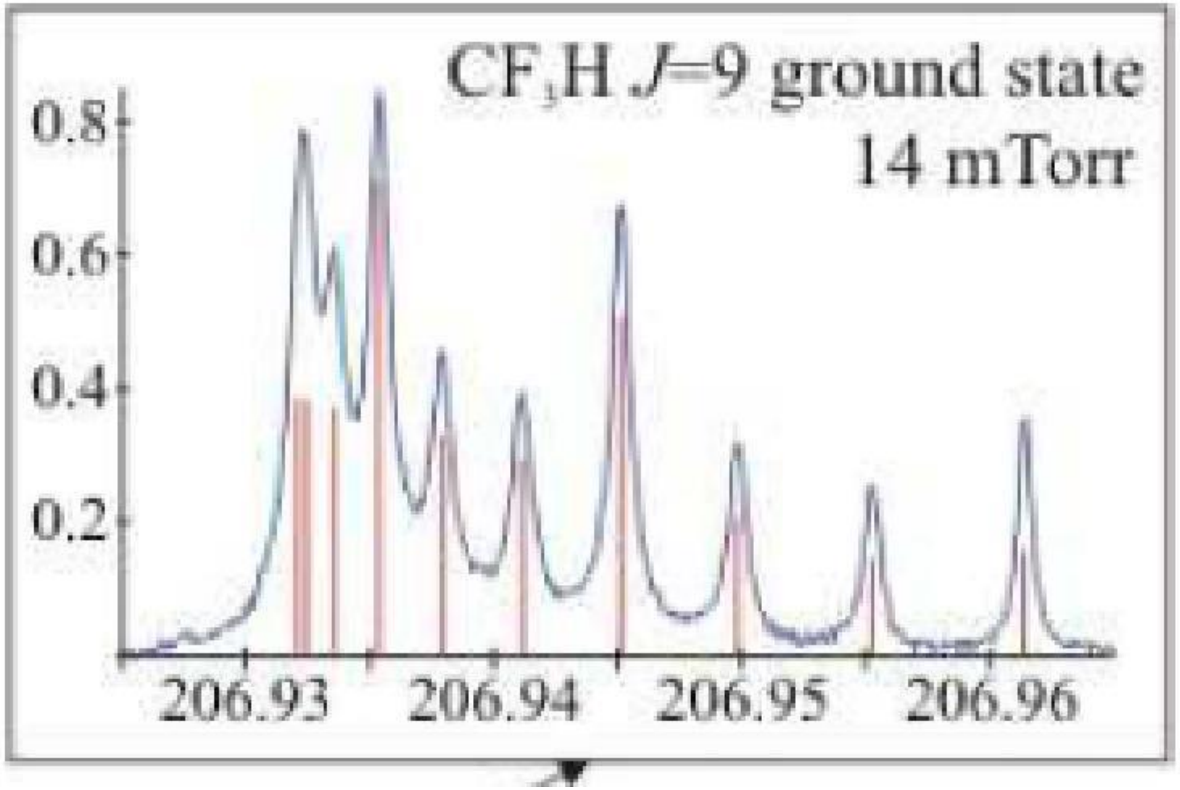
Ядерные спиновые изомеры молекул

П. Л. Чаповский

ИАиЭ СО РАН; НГУ

Вращательный спектр поглощения CF3H

(ИПФ РАН, Нижний Новгород)



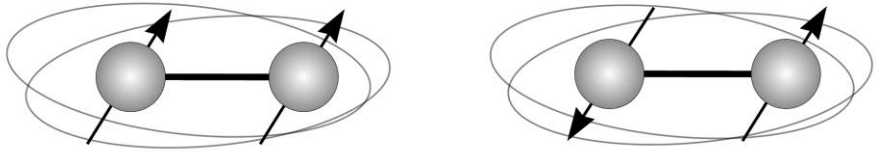
The hydrogen isomers

Discovery: **Eucken, 1912; Mecke, 1924; Bonhoeffer and Harteck, 1929.**

Contest for explanation: **Einstein and Stern, 1913.**

Heisenberg Nobel prize in physics, 1932:
"for the creation of quantum mechanics, the application of which has, inter alia, led to the discovery of the allotropic forms of hydrogen"

Isomers of H_2



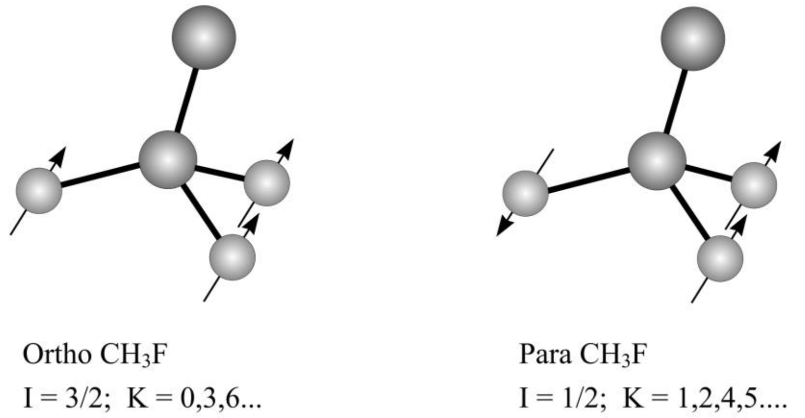
Ortho H_2
$I = 1; J = 1,3,5...$

Para H_2
$I = 0; J = 0,2,4...$

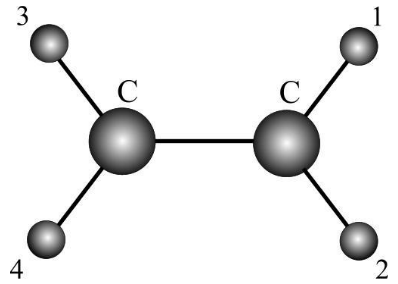
Physics: $\Psi = \varphi_{ns} \bullet \varphi_{rot} \bullet \varphi$

Spin isomers of polyatomic molecules

Isomers of CH_3F



Isomers of C_2H_4



4 isomers:

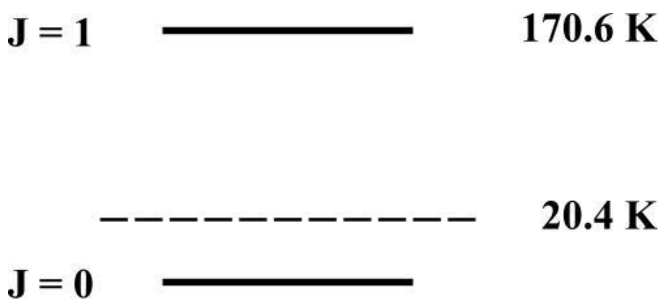
A_g, B_{3g}, B_{1u}, B_{2u}

Landau, Lifshitz,Quantum Mechanics

Enrichment

H_2 (by cooling,1929):

$$\Psi = \varphi_{ns} \bullet \varphi_{rot} \bullet \varphi$$



NMR enhancement

Liquid hydrogen storage

Enrichment of heavy isomers

Contest for enrichment

Deep cooling: Bonhoeffer and Harteck, 1929.

Fast evaporation: Curl, et al., 1966.

Light-Induced Drift: Chapovsky, et al., 1983.

Selective photodissociation: Schramm, et al., 1989.

Selective adsorption: Tikhonov and Volkov, 2002.

Separation in molecular beam by magnetic field: Alexandrowicz, et al., 2011.

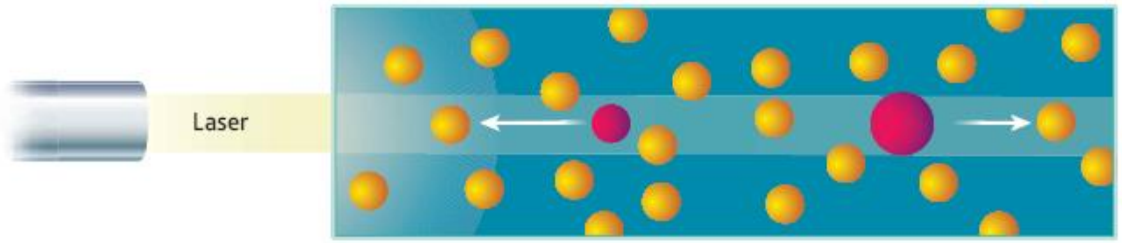
Separation in molecular beam by electric field: Küpper, et al., 2014.

Chemical synthesis: Zhivonitko, Kovtunov, Chapovsky, Koptyug, 2013.

Enrichment by Light-Induced Drift (LID)

Gel'mukhanov, Shalagin, 1979

CH_3F (by Light-Induced Drift):



Chapovsky, et al., 1983

Chapovsky, Hermans,
Ann. Rev. Phys. Chem. 1999

Hougen, Oka,
Science, 2005

Enrichment by LID

Inst. of Automation and
Electrometry, RAS

Inst. of Chemical Kinetics
and Combustion, RAS

Leiden University,
The Netherlands

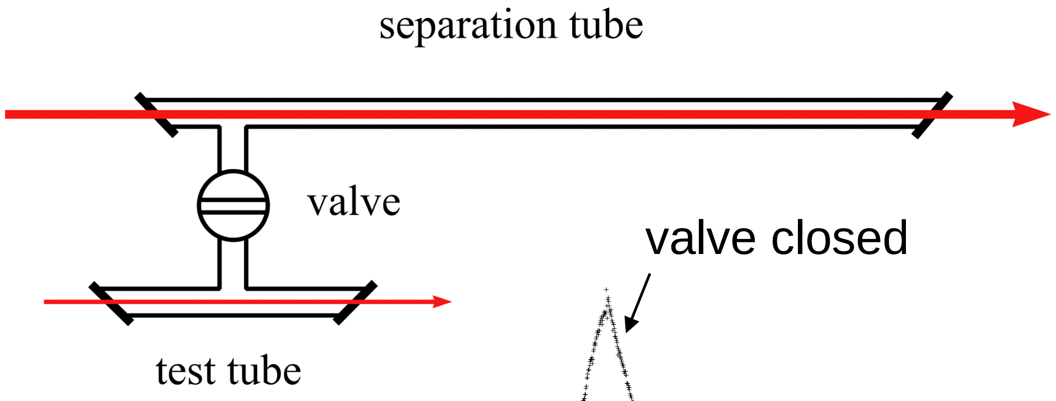
Lille University, France

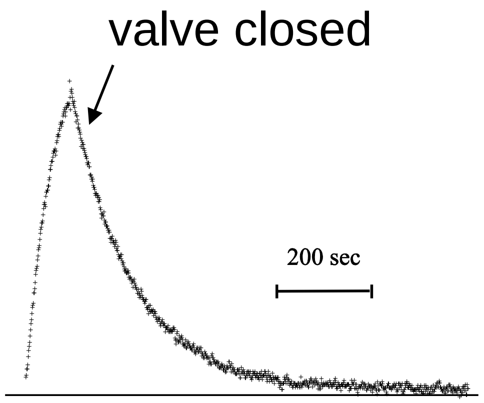
Toyama University, Japan

Shandong University, China

Enrichment and relaxation of $^{13}CH_3F$ isomers

Principle of the setup





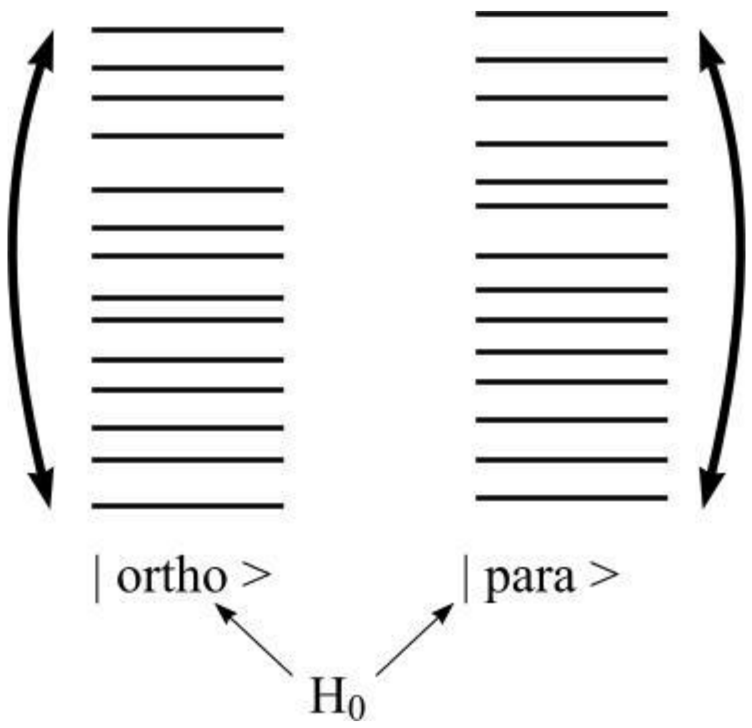
τ = 100 sec.

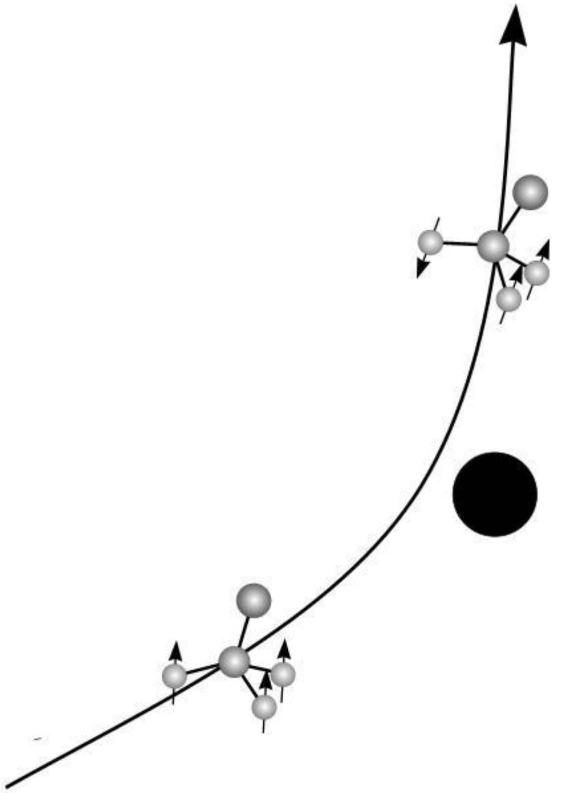
10^{10} gas collisions

Isomer relaxation on the wall ? No pressure dependence.

Standard relaxation model

H_2 (1 month), **CH_3F** (100 sec)





Anomalous isotope effect and pressure dependence

$^{13}CH_3F$: $\gamma_{13} = (0.85 \pm 0.06)$ min^{-1}/Torr

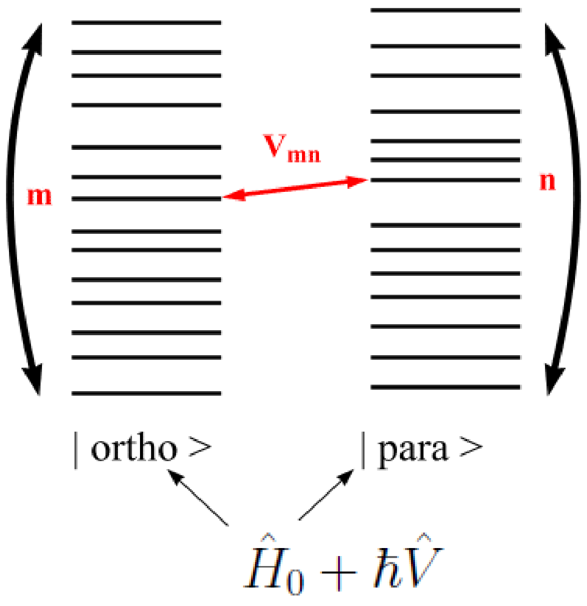
$^{12}CH_3F$: $\gamma_{12} = (1.1 \pm 0.1)$ hour^{-1}/Torr

$$\gamma_{13} / \gamma_{12} = 46 \pm 5$$

Chapovsky, Sov. Phys. JETP, **70**, 895 (1990)

Quantum relaxation

Wigner, 1933. Curl, et al., 1967



* Counterintuitive process

* Unusual pressure dependence

* Similar processes in physics

* Analogy with spectroscopy

* No such process in H_2

Chapovsky, PRA, 1991

$$(\hat{H}_0 + \hbar\hat{V})\Psi = E\Psi \qquad P = Sp(\hat{\rho}\hat{P})$$

$$\frac{\partial\hat{\rho}}{\partial t} = -i[\hat{V},\hat{\rho}] + \hat{S}$$

Special representation:

$$\Sigma S_{\alpha\alpha} = \Sigma S_{\alpha'\alpha'} = 0; \quad \alpha \in ortho$$

$$S_{\alpha\alpha'} = -\Gamma\,\rho_{\alpha\alpha'}; \quad \alpha' \in para$$

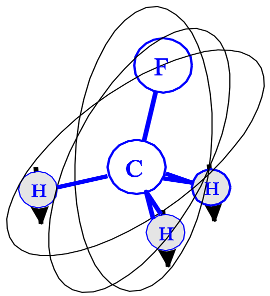
$$\frac{\partial}{\partial t}\sum_{\alpha\in o}\rho_{\alpha\alpha} = 2Re\sum_{\alpha\in o,\alpha'\in p} i\rho_{\alpha\alpha'}V_{\alpha'\alpha}$$

$$\frac{\partial n_{ortho}}{\partial t} = -\gamma\, n_{ortho}$$

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

HYPERFINE INTERACTIONS

$$\hat{H} = \hat{H}_0 + \hat{H}_{St} + \hat{H}_{SR} + \hat{H}_{SS}$$



$$\hat{H}_{HR} + \hat{H}_{FR} + \hat{H}_{CR}$$

$$\hat{H}_{HH} + \hat{H}_{HF} + \hat{H}_{HC} + \hat{H}_{CF}$$

$$\hat{\mathbf{I}}^{H} \cdot \mathbf{C}^{H} \cdot \hat{\mathbf{J}}$$

$$\sum_m \hat{H}^{(m)}_{HF}$$

$$V^{H}_{SR}$$

$$\hat{\mathbf{I}}^{F}\, \hat{\mathbf{I}}^{H^{(1)}} : \hat{\mathbf{T}}^{FH^{(1)}}$$

$$V^{FH}_{SS}$$

H_{HH} does not conserve the total spin of 3 protons

Selection rules

$^{13}CH_3F$

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

Close level pairs in $^{13}CH_3F$:

9,3 – 11, 1 (131 MHz)

20,3 – 21,1 (351 MHz)

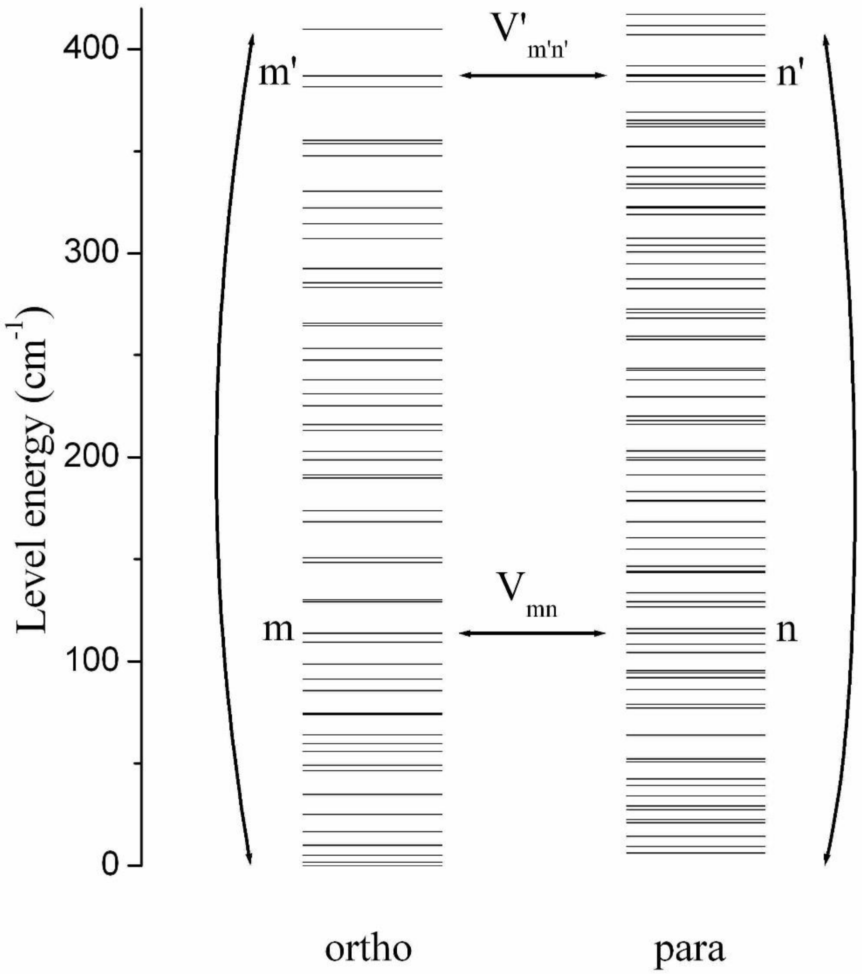
Experiment:

$$\gamma_{13}/P = (12.2 \pm 0.6) \cdot 10^{-3}\, s^{-1}/Torr$$

Theory:

$$\gamma_{13}/P = 15.5 \cdot 10^{-3}\, s^{-1}/Torr$$

Anomalous isotope effect



C_2H_4

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

Close level pair in **C_2H_4 :**

1,23,10 – 1,21,11 (46 MHz)

Experiment: Sun, et al. Science, 2005

$$\gamma = (5.5 \pm 0.8) \times 10^{-4} s^{-1}/Torr$$

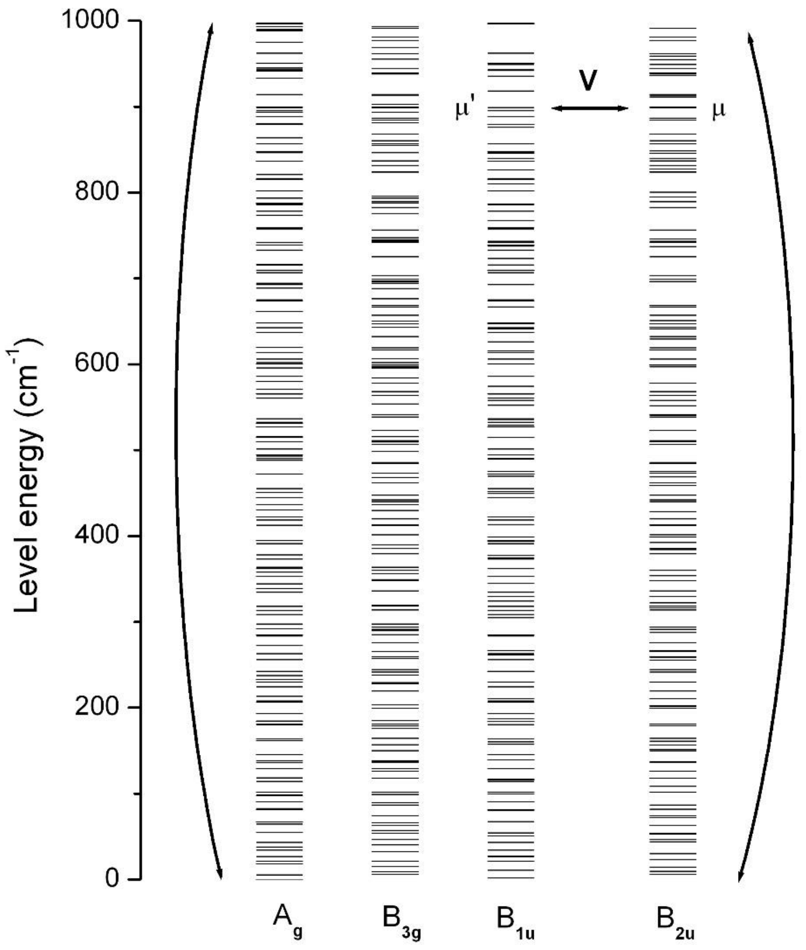
Theory: Chapovsky, et al., JPCA, 2013

$$\gamma = 5.2 \times 10^{-4} s^{-1}/Torr$$

Spin-spin interaction ~60 kHz

$$\hat{V}_{SS}^{(1,4)} = P_{14} \sum_{i,j} \hat{I}_i^{(1)} \hat{I}_j^{(4)} T_{ij}^{(1,4)}; \quad T_{ij}^{(1,4)} = \delta_{ij} - 3n_i^{(1,4)} n_j^{(1,4)}.$$

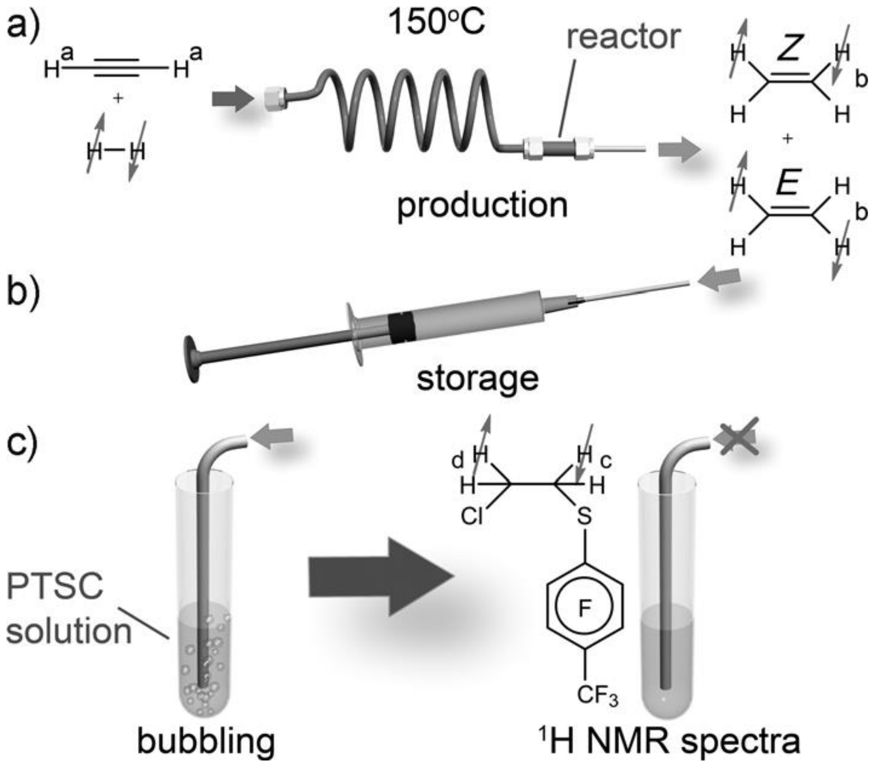
Spin-rotation contribution ?

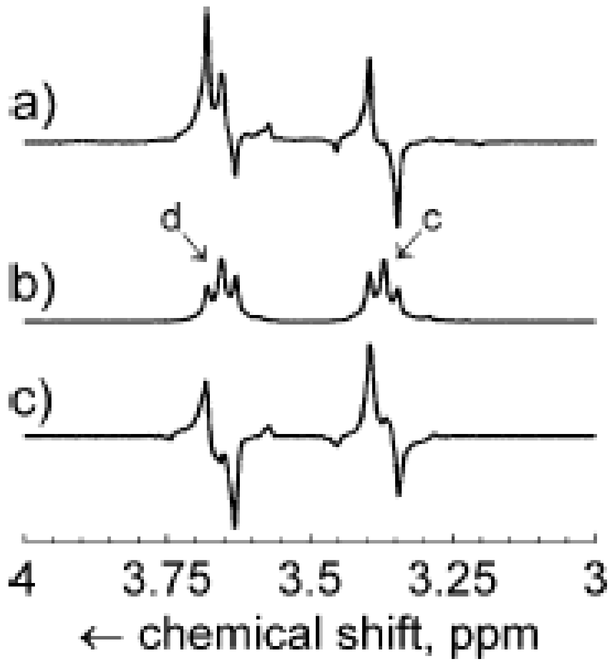


Enrichment by chemical synthesis

Zhivonitko, Kovtunov, Chapovsky, Koptyug, 2013

para-H_2 + C_2H_2 -> C_2H_4





Level-crossing resonances

$$\hat{H} = \hat{H}_0 + \hat{H}_{Stark} + \hbar\hat{V}$$

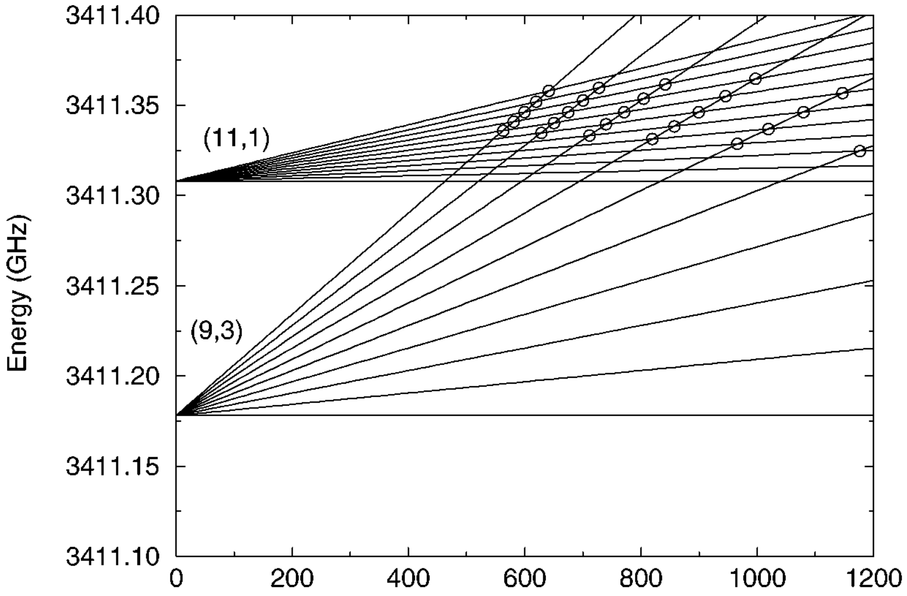
$$\gamma = \sum \frac{2\Gamma |V_{\alpha\alpha'}|^2}{\Gamma^2 + \omega^2_{\alpha\alpha'}} (W_\alpha + W_{\alpha'})$$

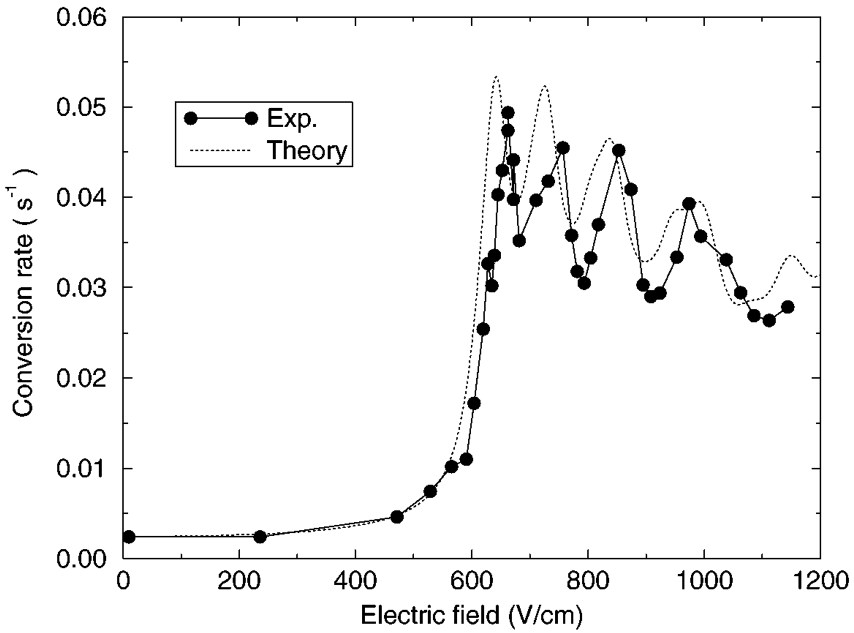
$^{13}CH_3F$ (level crossings)

Chapovsky et al.,
Phys.Rev.Lett.1996
Phys.Rev.Lett.1997

Spin-spin interaction: 69 kHz

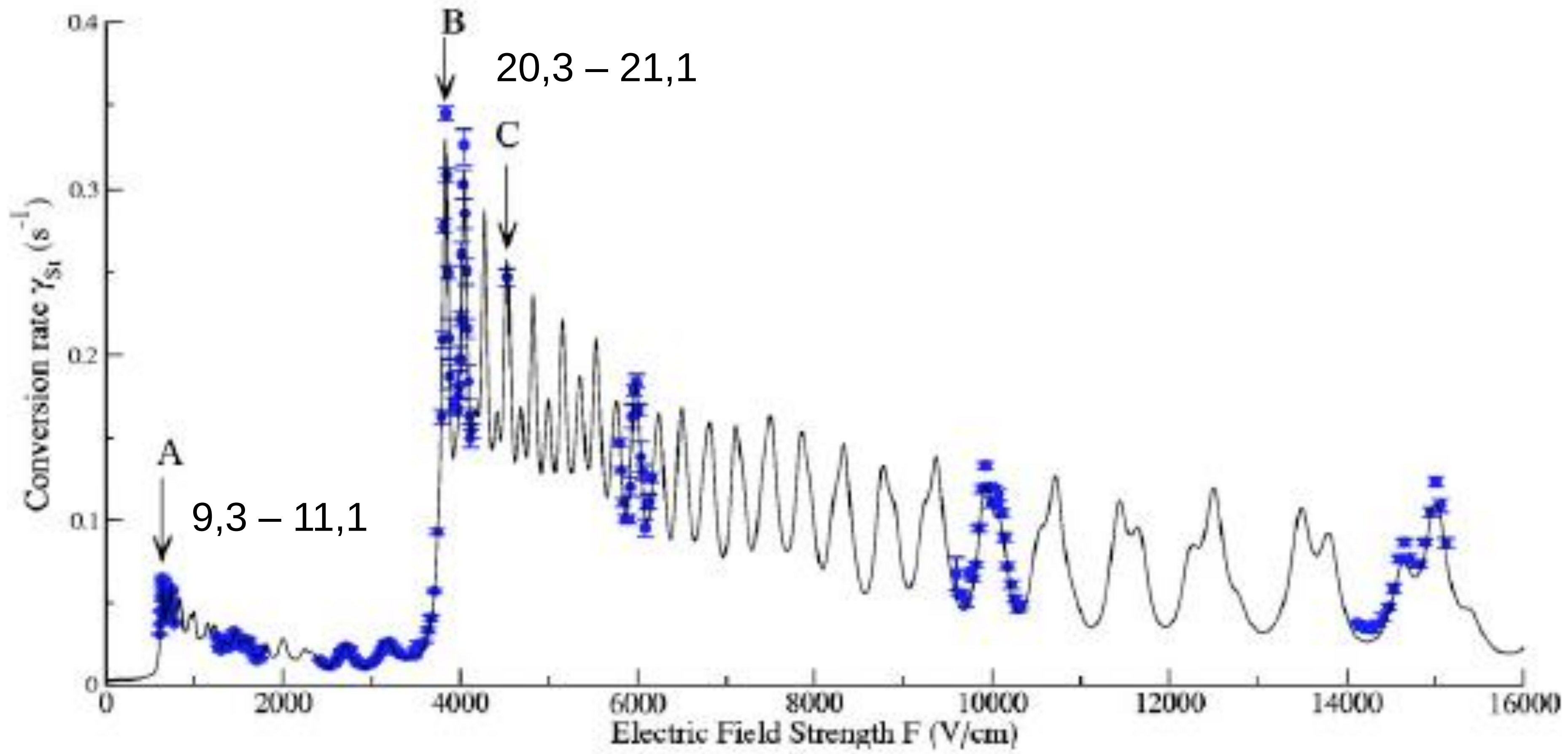
One adjustable parameter: Γ





Level-crossing resonances

$^{13}CH_3F$: Cacciani et al., Phys.Rev.A, 2004



Measurements of the hyperfine interactions in **$^{13}CH_3F$.** Off-diagonal terms.

Future experiments

Optical enrichment of spin isomers

Applications:

New access to weak interactions in molecules

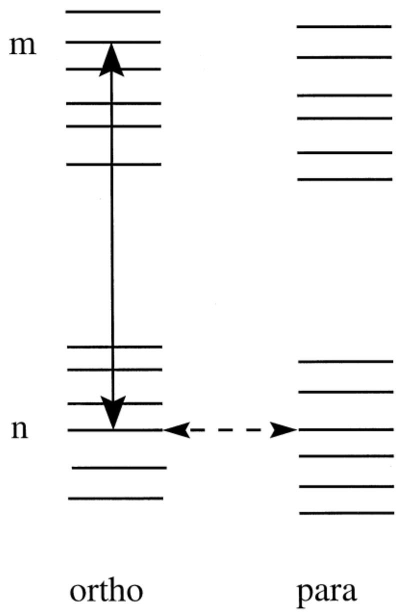
NMR signal enhancement by nuclear spin isomers

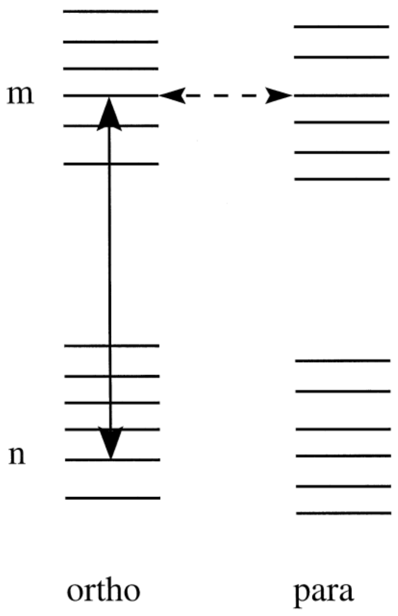
Optical enrichment

Il’ichov, Hermans, Shalagin, Chapovsky, 1998

$$\partial\hat{\rho}/\partial t = -i[\hat{G} + \hat{V}, \hat{\rho}] + \hat{S}$$

$$\frac{\partial}{\partial t}\sum_{\alpha\in o}\rho_{\alpha\alpha} = 2Re\sum_{\alpha\in o,\alpha'\in p} i\rho_{\alpha\alpha'}V_{\alpha'\alpha}$$



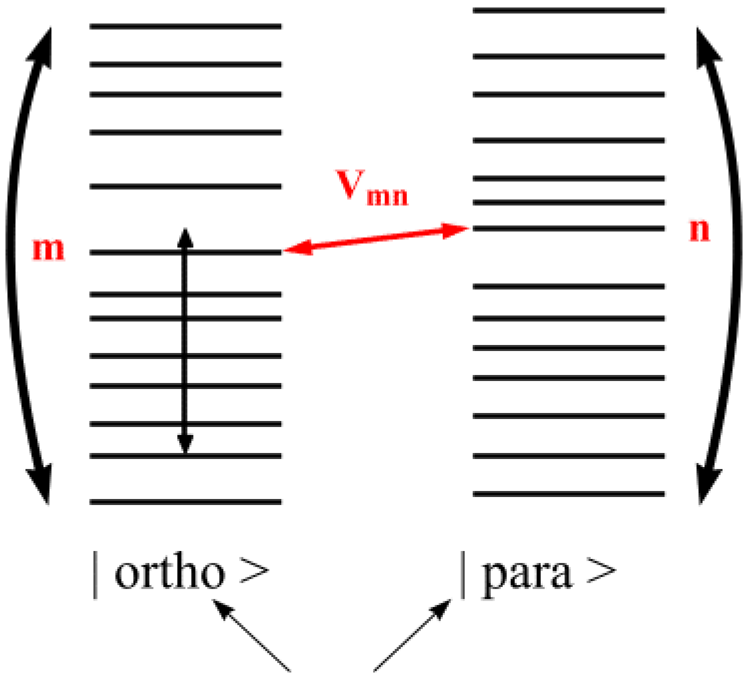


Coherent optical control

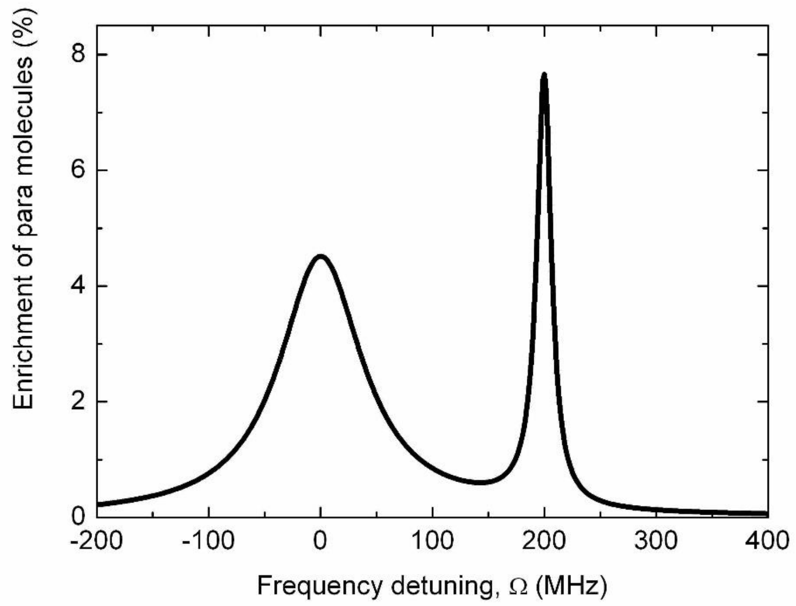
Chapovsky, PRA, 2001

$$\partial\hat{\rho}/\partial t = -i[\hat{G}+\hat{V},\hat{\rho}] + \hat{S}$$

$$\frac{\partial}{\partial t}\sum_{\alpha\in o}\rho_{\alpha\alpha} = 2Re\sum_{\alpha\in o,\alpha'\in p} i\rho_{\alpha\alpha'}V_{\alpha'\alpha}$$



$$\hat{H} = \hat{H}_0 + \hbar\hat{G} + \hbar\hat{V}$$

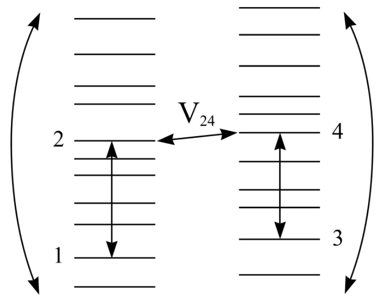


Coherent control by bichromatic field

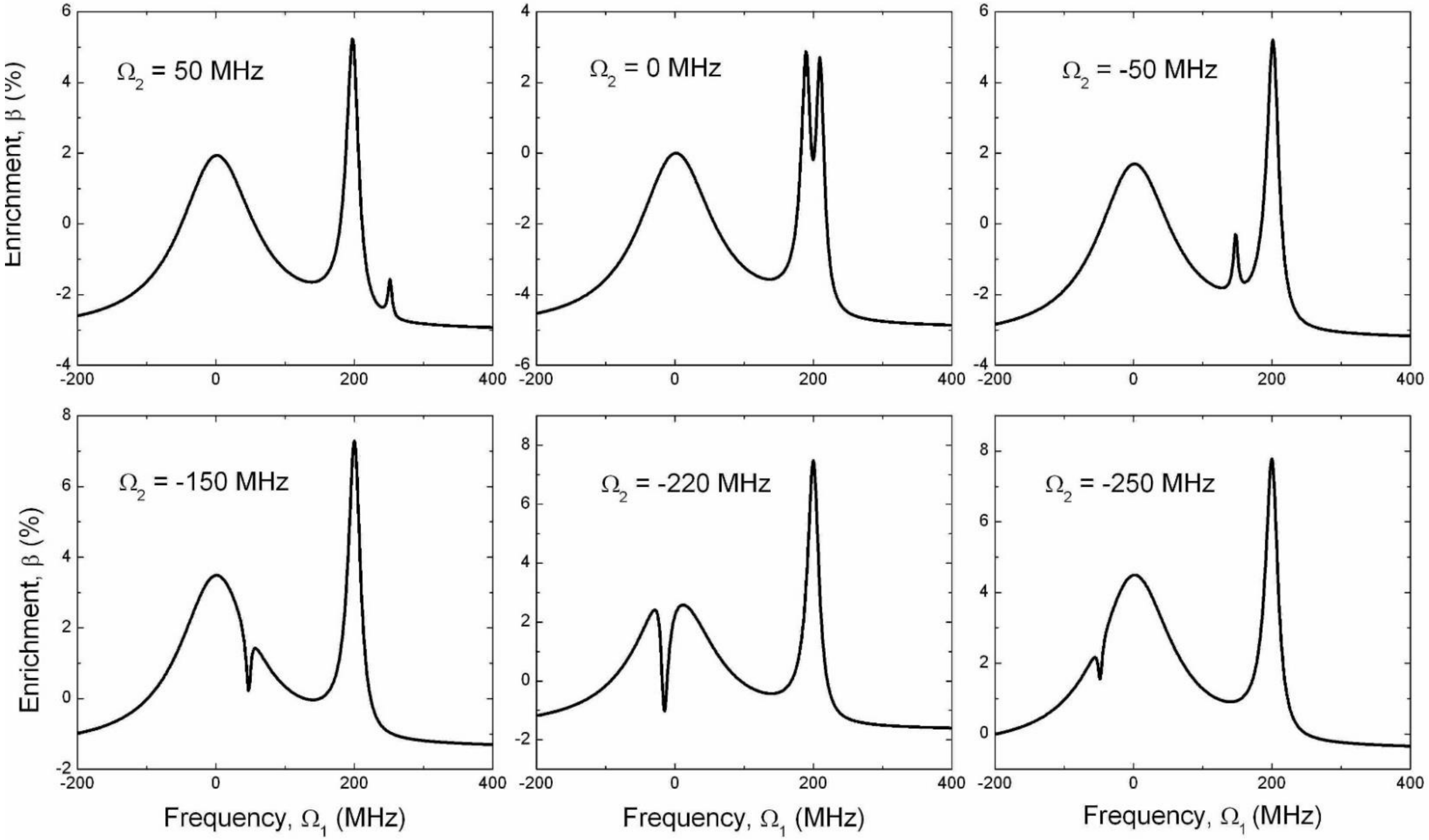
Chapovsky, Wilson-Gordon, 2015

$$\partial\hat{\rho}/\partial t = -i[\hat{G} + \hat{V}, \hat{\rho}] + \hat{S}$$

$$\frac{\partial}{\partial t}\sum_{\alpha\in o}\rho_{\alpha\alpha} = 2Re\sum_{\alpha\in o,\alpha'\in p} i\rho_{\alpha\alpha'}V_{\alpha'\alpha}$$

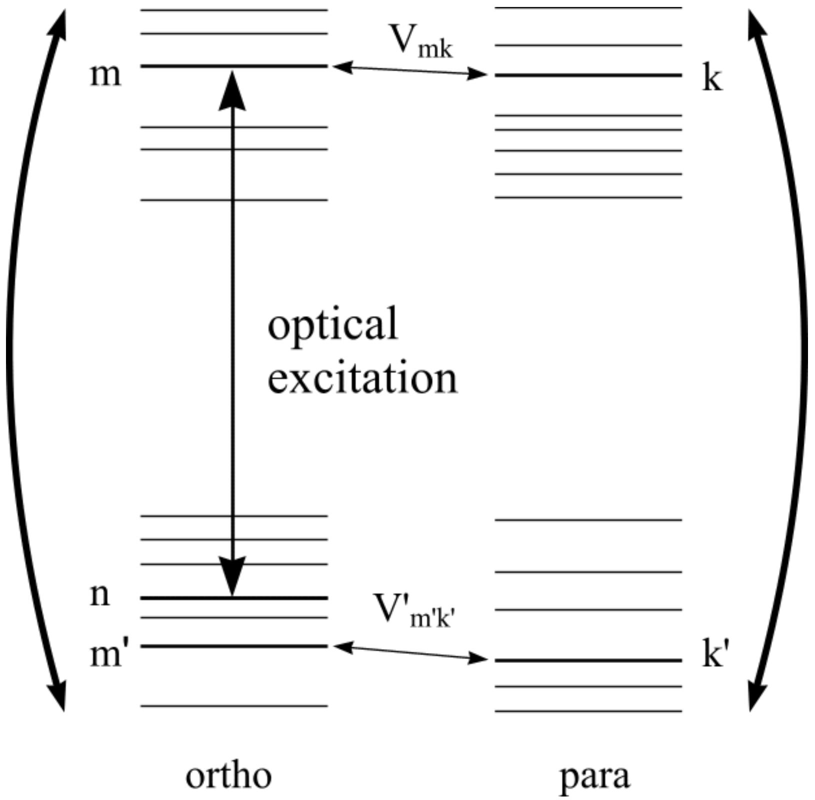


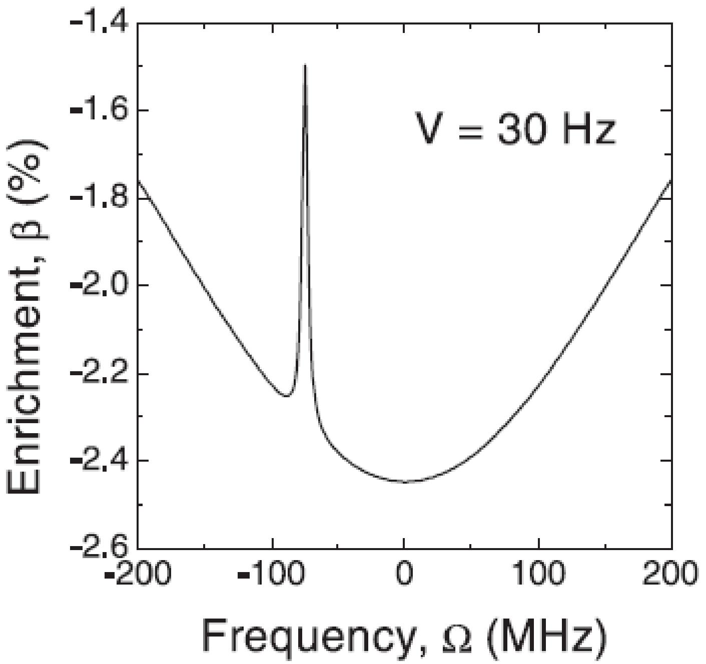
Enrichment of para molecules



New access to weak interactions in molecules

Chapovsky, J. Phys. B., 2001





Rabi frequency: 50 MHz

Ω_{mk} = 100 MHz

Γ = 2 MHz

Performed investigations

Enriched isomers: $^{13}CH_3F$, $^{12}CH_3F$, $^{13}CCH_4$, C_2H_4, CH_3OH

Relaxation in gaseous phase : $\gamma \sim P$; $\gamma \sim 1/P$

Level-crossing resonances

Relaxation by surfaces

Relaxation by oxygen

Relaxation under permanent electric field

Relaxation under alternating electric field

Temperature dependence

Theory for symmetric and asymmetric tops

Theory for the optical enrichment

Verification of the isomer quantum relaxation

IAE SB RAS, Novosibirsk, Russia

Leiden University, The Netherlands

University Paris 7, France

Lille University, France

Toyama University, Japan

Shandong University, China

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J. Legrand
D. Papousek

Israel

A.D. Wilson-Gordon

Спасибо за внимание!

C_2H_4

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

Close level pair in **C_2H_4 :**

1,23,10 – 1,21,11   (46 MHz)

Experiment: Sun, et al. Science, 2005

$$\gamma = (5.5 \pm 0.8) \times 10^{-4} s^{-1}/Torr$$

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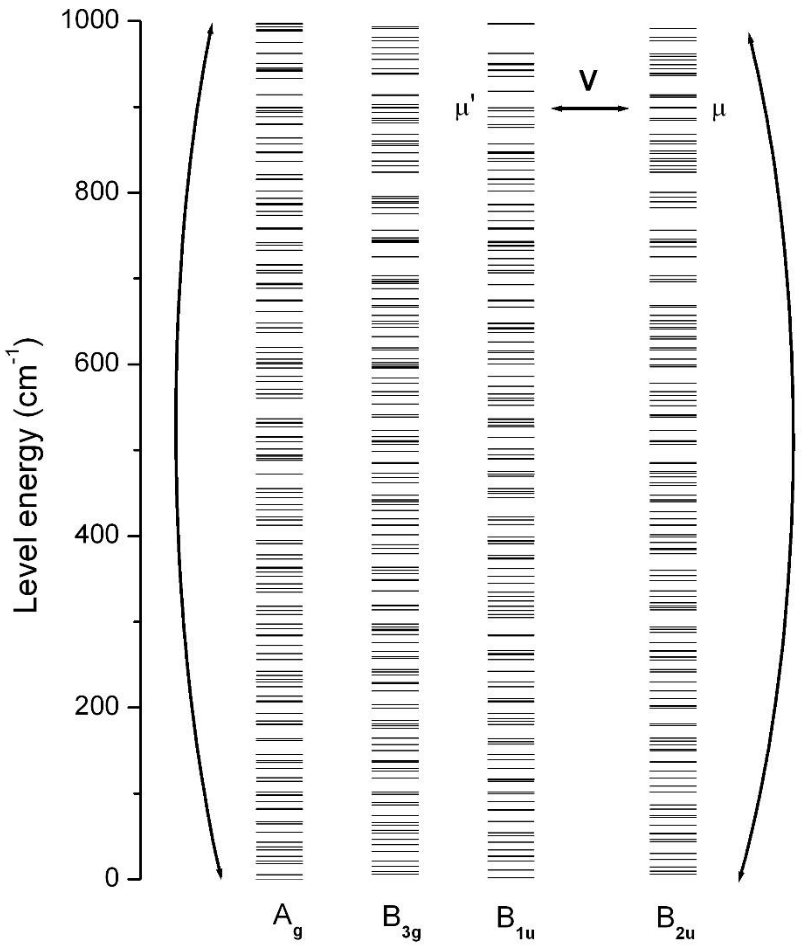

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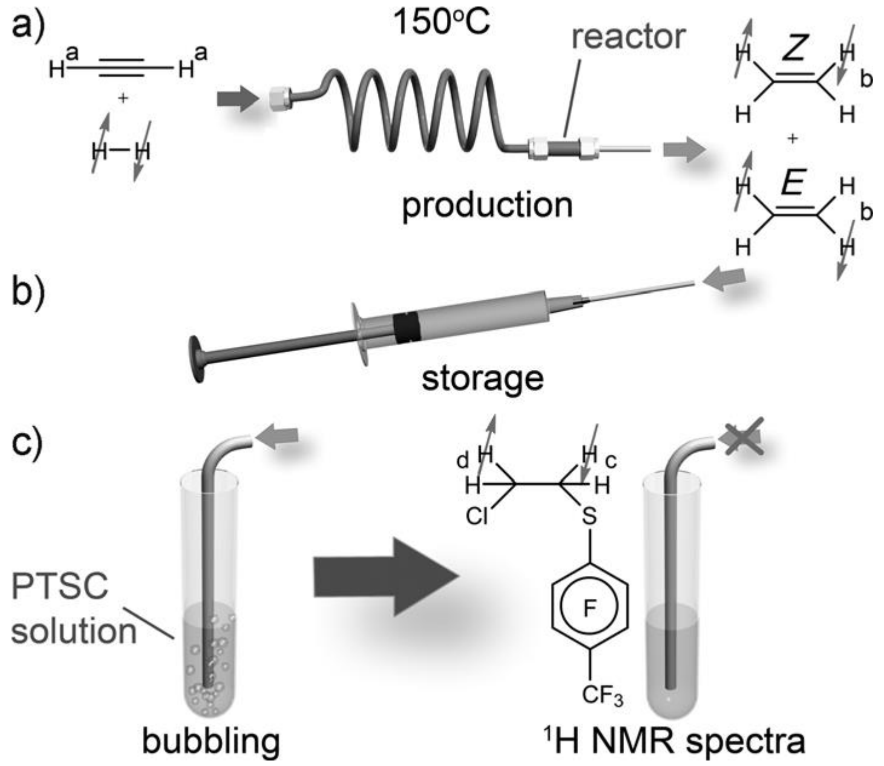

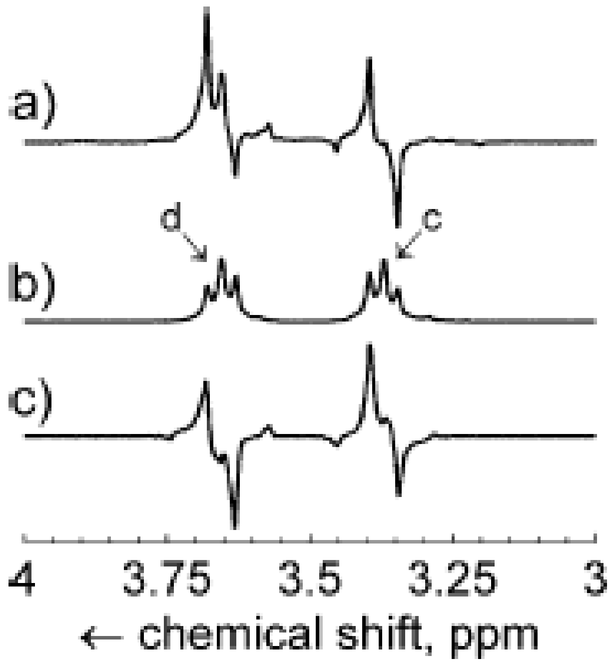

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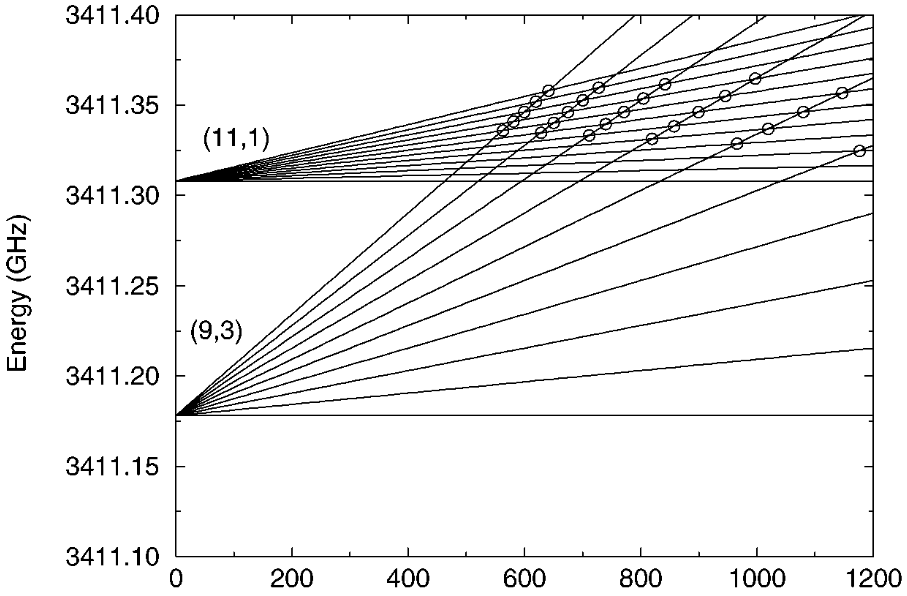

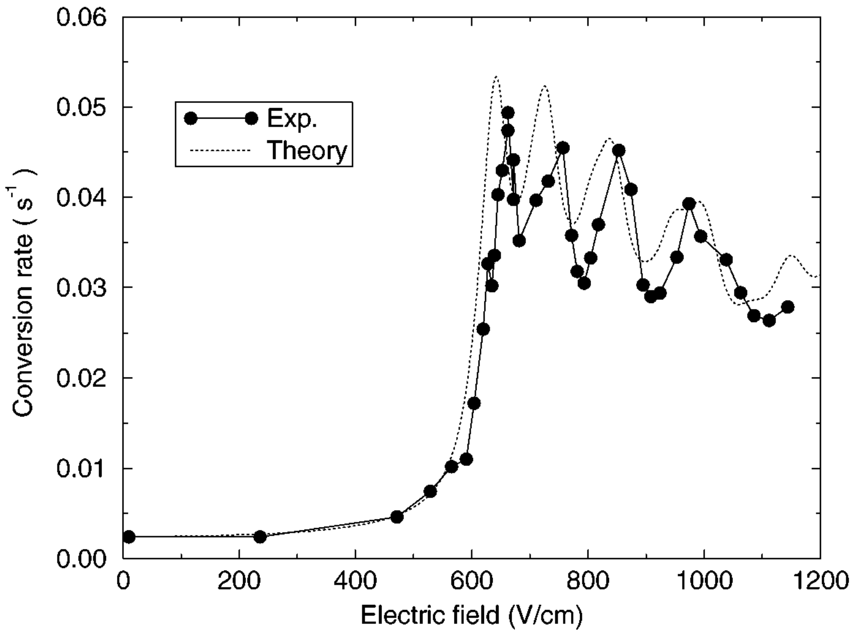

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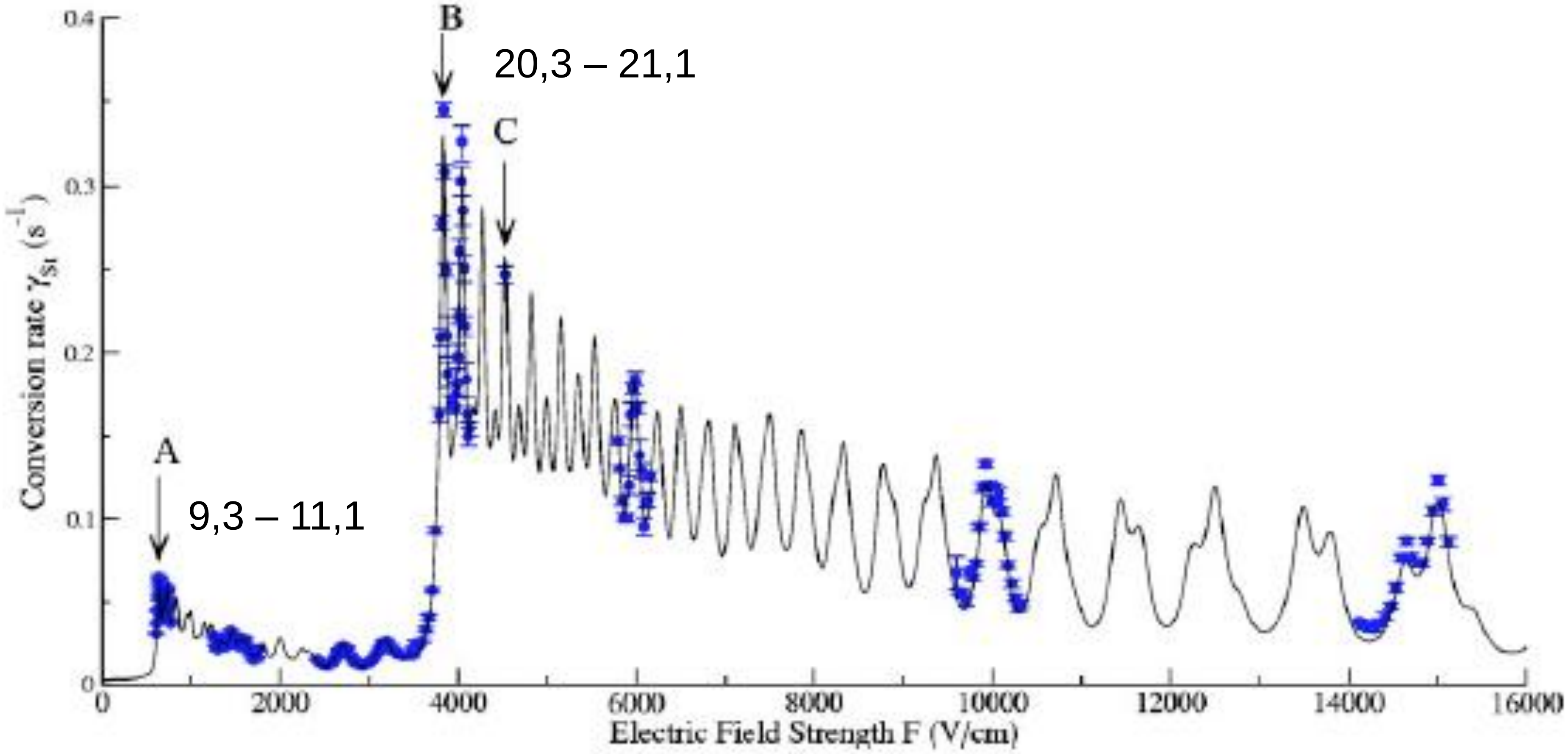

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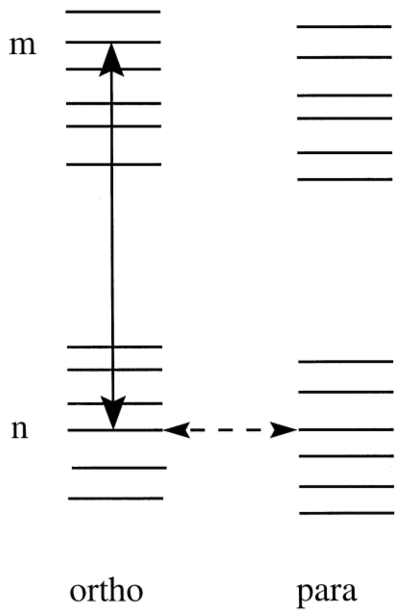

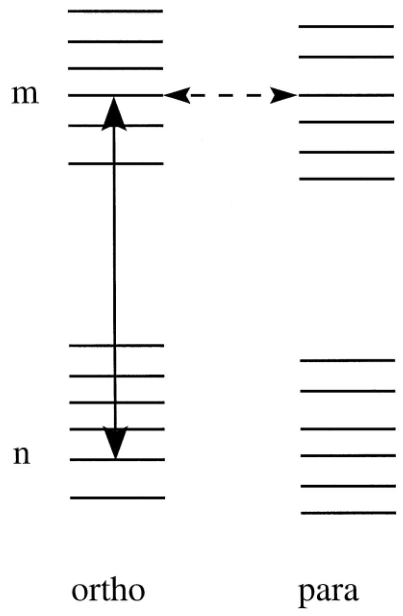

Coherent optical control

Chapovsky, PRA, 2001

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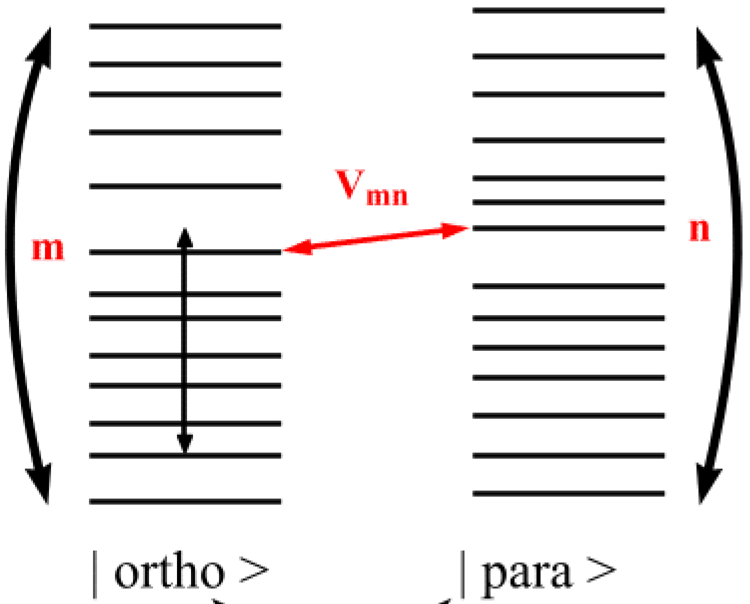
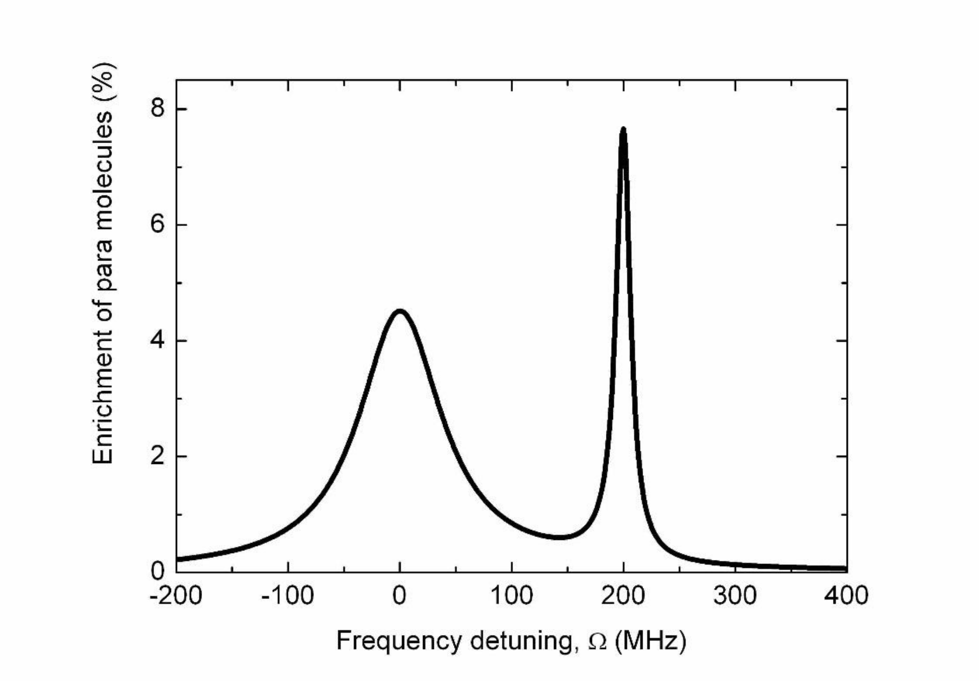


$$\hat{H} = \hat{H}_0 + \hbar\hat{G} + \hbar\hat{V}$$



Coherent control by bichromatic field

Chapovsky, Wilson-Gordon, 2015

$$\partial\hat{\rho}/\partial t = -i[\hat{G}+\hat{V},\hat{\rho}] + \hat{S}$$

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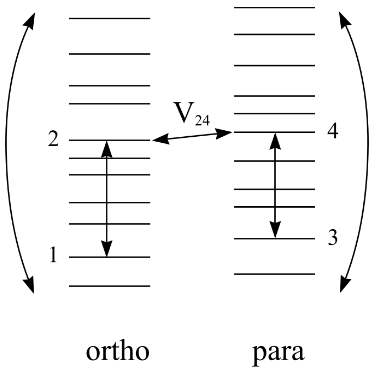

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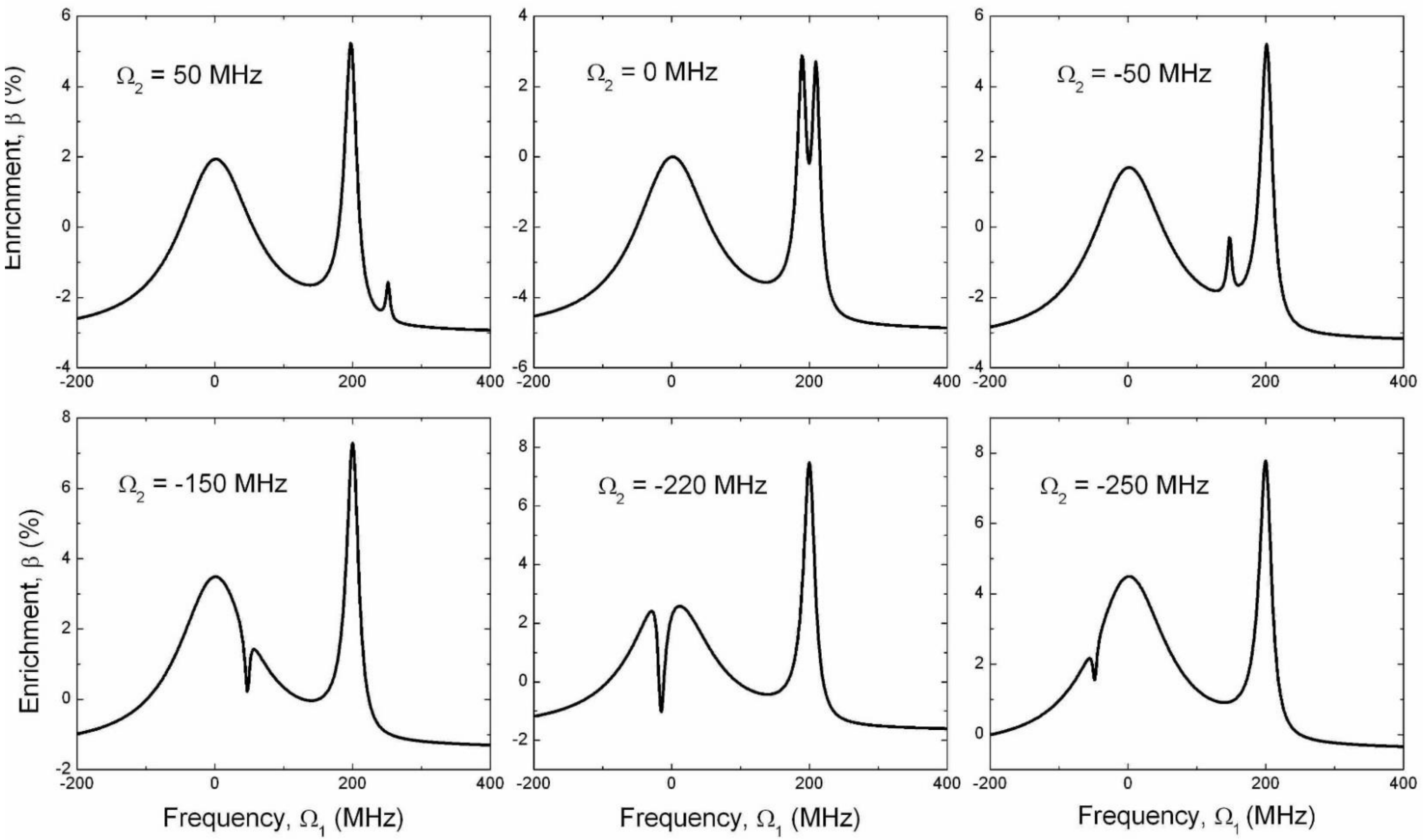

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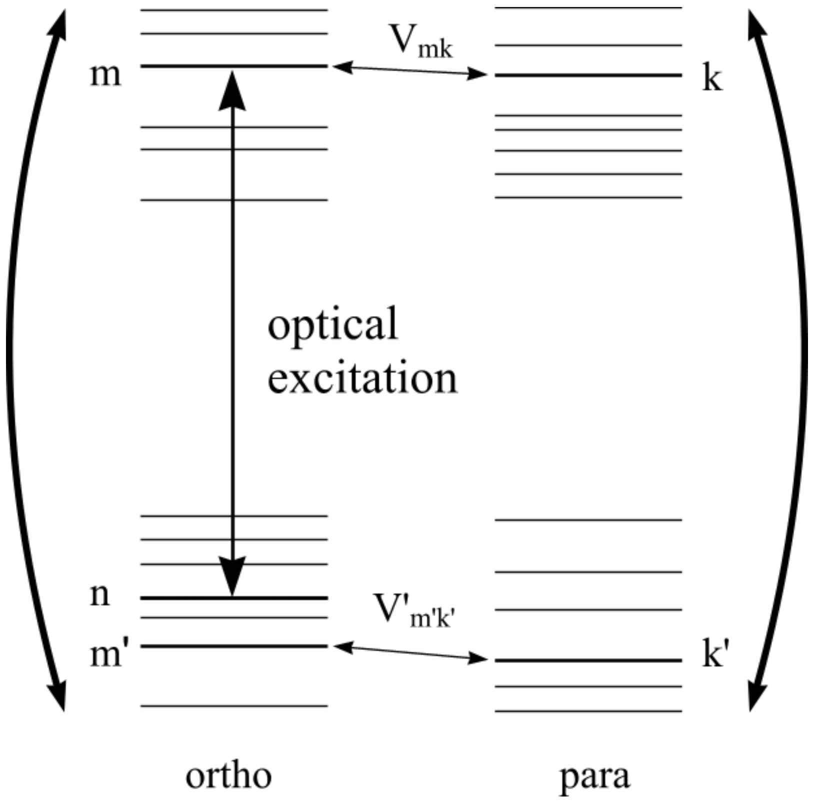
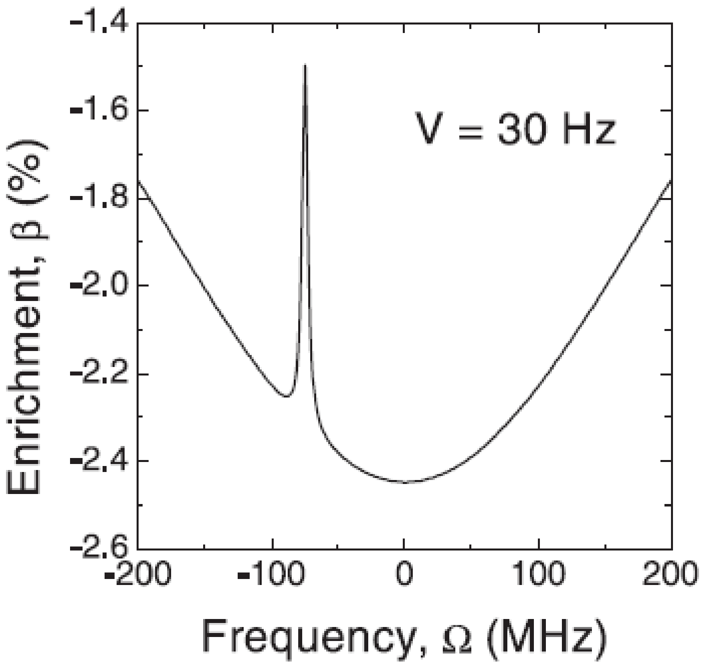
Chapovsky, J. Phys. B., 2001





Rabi frequency: 50 MHz

Ω_{mk} = 100 MHz

Γ = 2 MHz

Performed investigations

Enriched isomers: $^{13}CH_3F$, $^{12}CH_3F$, $^{13}CCH_4$, C_2H_4, CH_3OH

Relaxation in gaseous phase : $\gamma \sim P$; $\gamma \sim 1/P$

Level-crossing resonances

Relaxation by surfaces

Relaxation by oxygen

Relaxation under permanent electric field

Relaxation under alternating electric field

Temperature dependence

Theory for symmetric and asymmetric tops

Theory for the optical enrichment

Verification of the isomer quantum relaxation

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