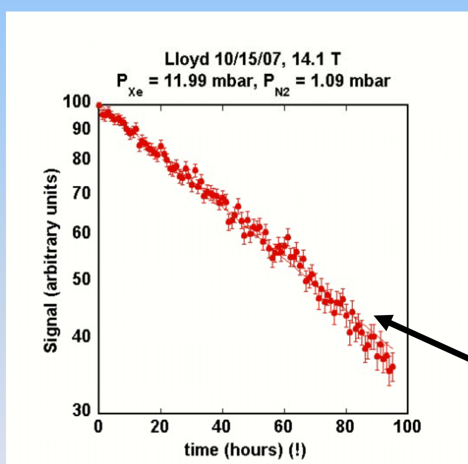
Gas-phase spin relaxation of ^{129}Xe

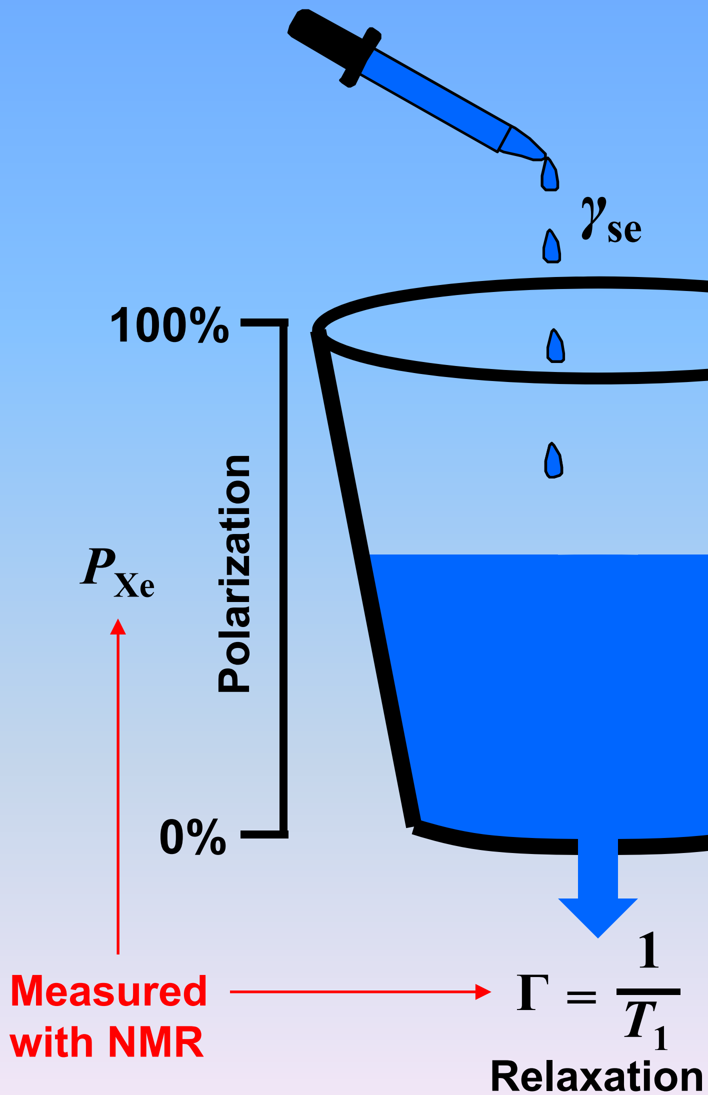


T_1 = 100 hours!

Brian Saam
Department of Physics

Workshop on Physics & Applications of Polarized Noble Gases
University of Virginia, 19 May 2009

Filling the Polarization Bucket



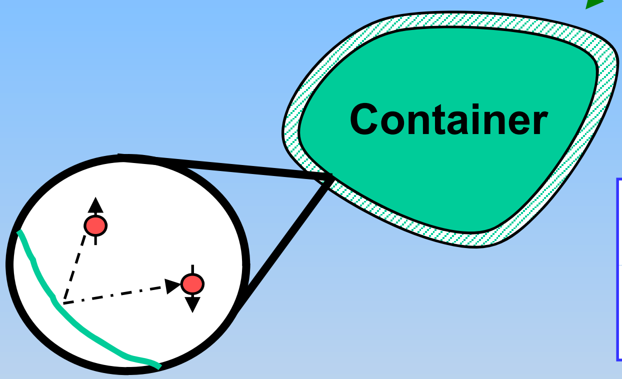
$$\lim_{t\to\infty} P_{\mathrm{Xe}}(t) = \langle P_{\mathrm{Rb}} \rangle \left(\frac{\gamma_{\mathrm{se}}}{\gamma_{\mathrm{se}} + \Gamma} \right)$$

$$\gamma_{\mathrm{se}} = [\mathrm{Rb}] \langle \sigma_{\mathrm{se}} v \rangle$$

- To maximize P_{Xe} , want γ_{se} >> Γ AND $\langle P_{Rb} \rangle \approx 1$.
- γ_{se} limited by available laser light.
- Goal: understand and minimize Γ.

Longitudinal Spin Relaxation in Noble Gases

$$\Gamma = \Gamma_{\text{wall}} + \Gamma_{\text{gradient}} + \Gamma_{\text{intrinsic}} = \frac{1}{T_1}$$

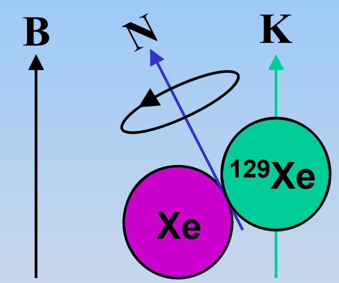


$1/\Gamma_{\text{wall}}$ = 0.1 – 1 h typically @ 30 G.

Density *independent*!

$$\Gamma_{\text{gradient}} = D\frac{|\nabla_\perp B|^2}{B_0^2}$$

Negligible in our experiments.



spin-rotation interaction:

$C_K(R)\ \mathbf{N}\cdot\mathbf{K}$

Occurs during binary collision AND during the lifetime of a molecule.

- Prior to work on dimers: Gas phase T_1 typically a few tens of minutes for ^{129}Xe; assumed dominated by wall interactions!

Early Studies of Intrinsic ^{129}Xe Relaxation

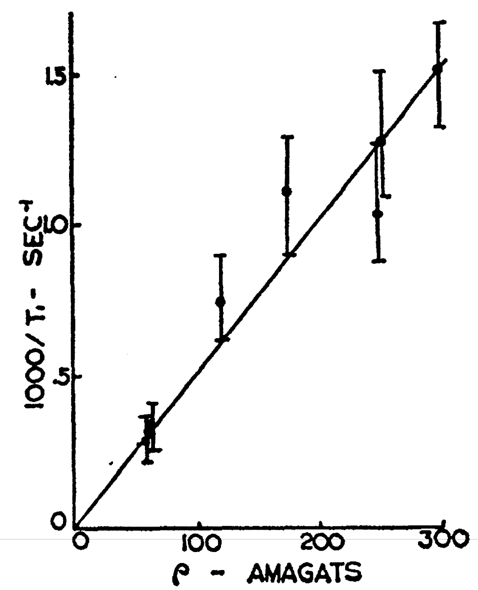


FIG. 3. The Xe^{129} relaxation rate $1/T_1$ in the gas at 25°C as a function of density ρ.

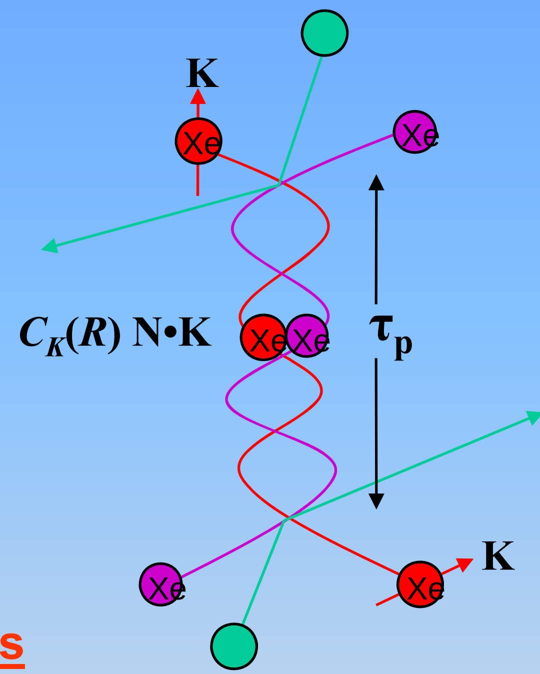
$\Gamma \propto [Xe]$

E.R. Hunt and H.Y. Carr, *Phys. Rev.* **130**, 2302 (1963).

- **Assumes binary collisions only (transient dimers).**
- ***Lowest* density studied is [Xe] = 50 amagats.**
- **$\Gamma_{bulk} \approx$ 0.019 h/amagat ($T_1 \approx$ 52 h for 1 atm Xe)**

Transient vs. Persistent Dimers

$$\Gamma_{intrinsic} = \Gamma_t + \Gamma_p$$



Transient Dimers

- binary collisions of duration $\tau_t \approx 1$ ps.
- $\Gamma_t \propto$ [Xe].
- $\Gamma_t^{-1} \approx$ 52 h•amagat: Hunt and Carr (1963); Moudrakovski, et al. (2001).

Persistent Dimers

- Form/break up in 3-body collisions.
- Last for lifetime $\tau_p \approx 1$ ns (until next collision).
- Γ_t is independent of [Xe] (for fixed gas composition).

Theory of Persistent-Dimer Relaxation*

$$\Gamma_\mathrm{p} = \left(\frac{2}{3} \frac{\langle c_K^2 N^2 \rangle}{\hbar^2} \right) \left(\frac{\tau_\mathrm{p}}{1+\Omega^2 \tau_\mathrm{p}^2} \right) \left(2\mathcal{K}[\mathrm{Xe}] \right)$$

Chemical Equilibrium Coefficient

$$\mathcal{K} \equiv \frac{[\mathrm{Xe}_2]}{[\mathrm{Xe}][\mathrm{Xe}]}$$

- **Mean-squared spin-rotation interaction energy.**
- **Power spectrum $J(\omega)$ for field fluctuations**
  - $\tau_\mathrm{p} \sim 10^{-9}$ **seconds for [Xe] = 1 amagat.**
  - **$\omega/2\pi$ = 11.8 MHz for B_0 = 1 T.**
  - **Can often assume** $\Omega^2\tau_\mathrm{p}^2 << 1$ (fast-fluctuation limit).
- **Fraction of atoms bound in molecules, assumes $[\mathrm{Xe}_2] << [\mathrm{Xe}]$.**

➢ **Key point for SEOP regime, where $\Omega^2\tau_\mathrm{p}^2 << 1$:**

$[\mathrm{Xe}] \propto \frac{1}{\tau_\mathrm{p}} \implies \Gamma_\mathrm{p}$ ***is independent of*** [Xe]; **looks like wall relaxation!**

*See: B. Chann, et al., *Phys. Rev. Lett.* **88**, 113201 (2002).

Low-field (2 mT) Results*

$$\Gamma_{\rm p} = \left(\frac{4\mathcal{K}\langle c_K^2 N^2\rangle}{3\hbar^2}\right)[\mathrm{Xe}]\tau_{\rm p} = \left(\frac{4\mathcal{K}\langle c_K^2 N^2\rangle}{3\hbar^2}\right)\left(\frac{1}{k_{\rm Xe}}\right)\left(\frac{1}{1+r_B([\mathrm{B}]/[\mathrm{Xe}])}\right)$$

$\Gamma_{\rm vdW}^{\rm Xe}$ = pure-Xe rate   Correction for 2nd gas

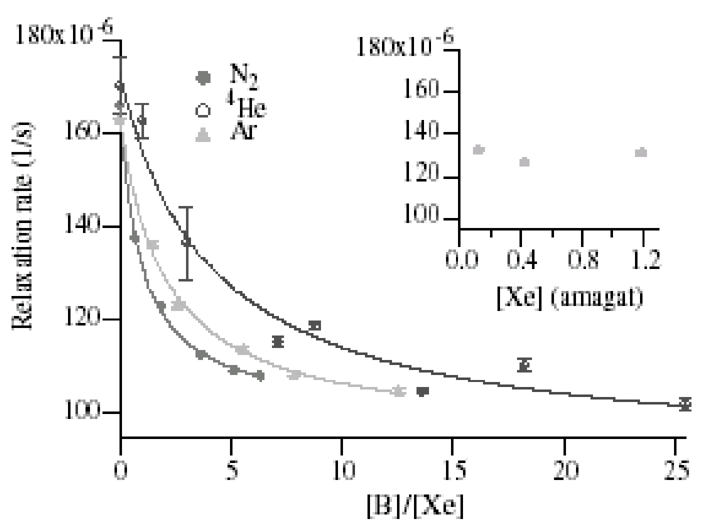


FIG. 1. Xe spin-relaxation rate as a function of composition, for various buffer gases, at a fixed Xe density of 0.15 amagat. Inset: Relaxation rate for [Ar]/[Xe] = 1.75 as a function of Xe density.

*B. Chann, *et al.*, *Phys. Rev. Lett.* **88**, 113201 (2002).

With:

$$\frac{1}{\tau_{\rm p}} = k_{\rm Xe}[\mathrm{Xe}] + k_{\rm B}[\mathrm{B}] + \cdots$$

$$r_{\rm B} \equiv k_{\rm B} / k_{\rm Xe}$$

- **Need constant $\Gamma_{\rm wall}$ (asymptote).**
- **No observed [Xe] dependence for fixed gas composition (inset).**
- **$\Gamma_{\rm vdW}^{\rm Xe}$, $\Gamma_{\rm wall}$, $r_{\rm B}$ extracted from fits.**
- **$\Gamma_{\rm vdW}^{\rm Xe} \approx 0.25\ \mathrm{h}^{-1}$, ten times faster than binary collisions at 1 atm!**

High-field Experiments: Theory

$$\Gamma_{\mathrm{p}} = \left(\frac{2}{3} \frac{\langle c_K^2 N^2 \rangle}{\hbar^2} \right) \left(\frac{\tau_{\mathrm{p}}}{1+\Omega^2 \tau_{\mathrm{p}}^2} \right) \left(2\kappa [\mathrm{Xe}] \right)$$

Magnetic-field decoupling term important for large Ω, small τ_{p}.

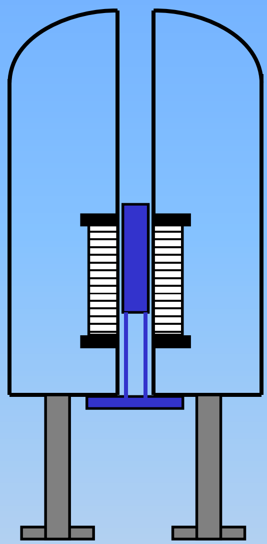
$$\left(\frac{2}{3} \frac{\langle c_K^2 N^2 \rangle}{\hbar^2} \right) + \left(\frac{2}{15} \frac{\mu_{\mathrm{B}}^2 B_0^2}{\hbar^6} \langle c_K^2 \Theta_\perp^2 \rangle \right)$$

$$M^{\mathrm{sr}} \quad + \quad M^{\mathrm{csa}}$$

Additional term due to chemical-shift anisotropy (CSA) interaction has dependence on B_0^2.

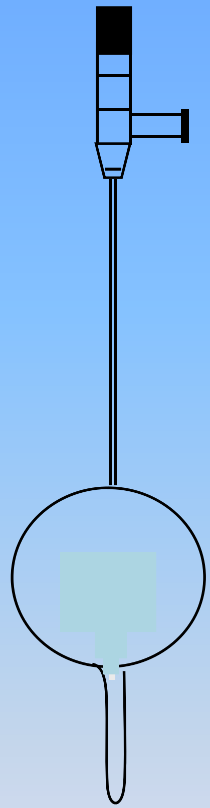
$$\Rightarrow \quad \Gamma_{\mathrm{p}} = \left(M^{\mathrm{sr}} + M^{\mathrm{csa}} \right) \left(\frac{\tau_{\mathrm{p}}}{1+\Omega^2 \tau_{\mathrm{p}}^2} \right) \left(2\kappa [\mathrm{Xe}] \right)$$

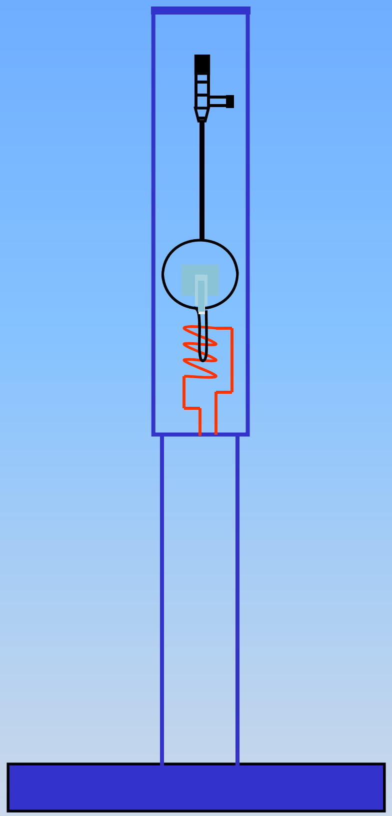
High-Field Experiment: NMR Probe & Cell



Field strengths B_0:

- 1.5 T (17.7 MHz)
- 4.7 T (55.3 MHz)
- 8.0 T (94.2 MHz)
- 14.1 T (166 MHz)





- 6.7 cm diam spherical “measurement” cell.
- Silicone-coated.
- Contains no Rb (HP gas transferred in).
- Long and robust wall relaxation times.

^{129}Xe Persistent-Dimer Relaxation: Results*

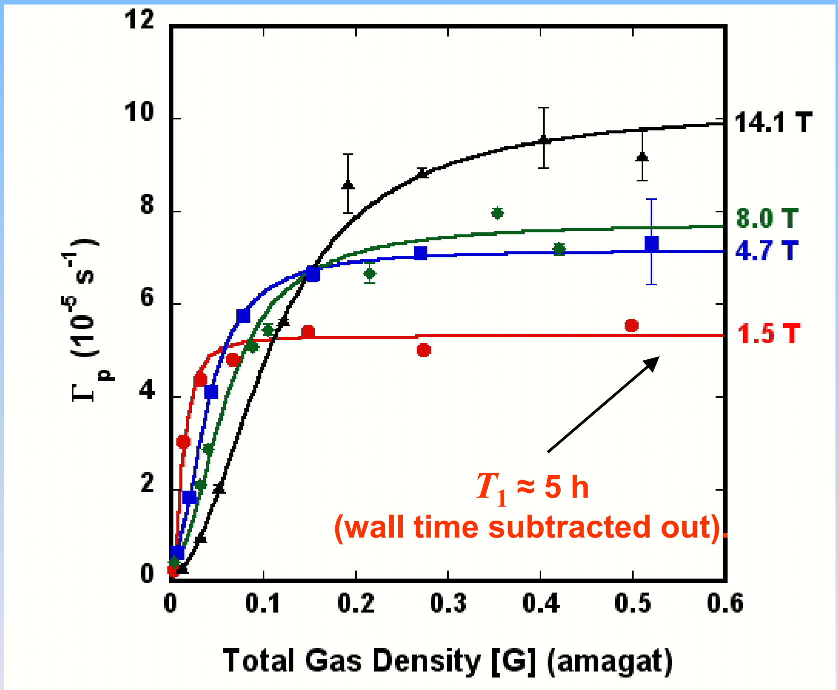
$$\Gamma_p = \left(M^{sr} + M^{csa}\right)\left(\frac{\tau_p}{1+\Omega^2\tau_p^2}\right)\left(2\kappa[\mathrm{Xe}]\right) \Longrightarrow \Gamma_p = 2\kappa\left(M^{sr} + M^{csa}\right)\left(\frac{\alpha k_\alpha [\mathrm{G}]^2}{k_\alpha^2[\mathrm{G}]^2+\Omega^2}\right)$$

reparam.

Total gas density: $[\mathrm{G}] = [\mathrm{Xe}] + [\mathrm{N}_2]$

Xe concentration (FIXED): $\alpha \equiv [\mathrm{Xe}]/[\mathrm{G}]$

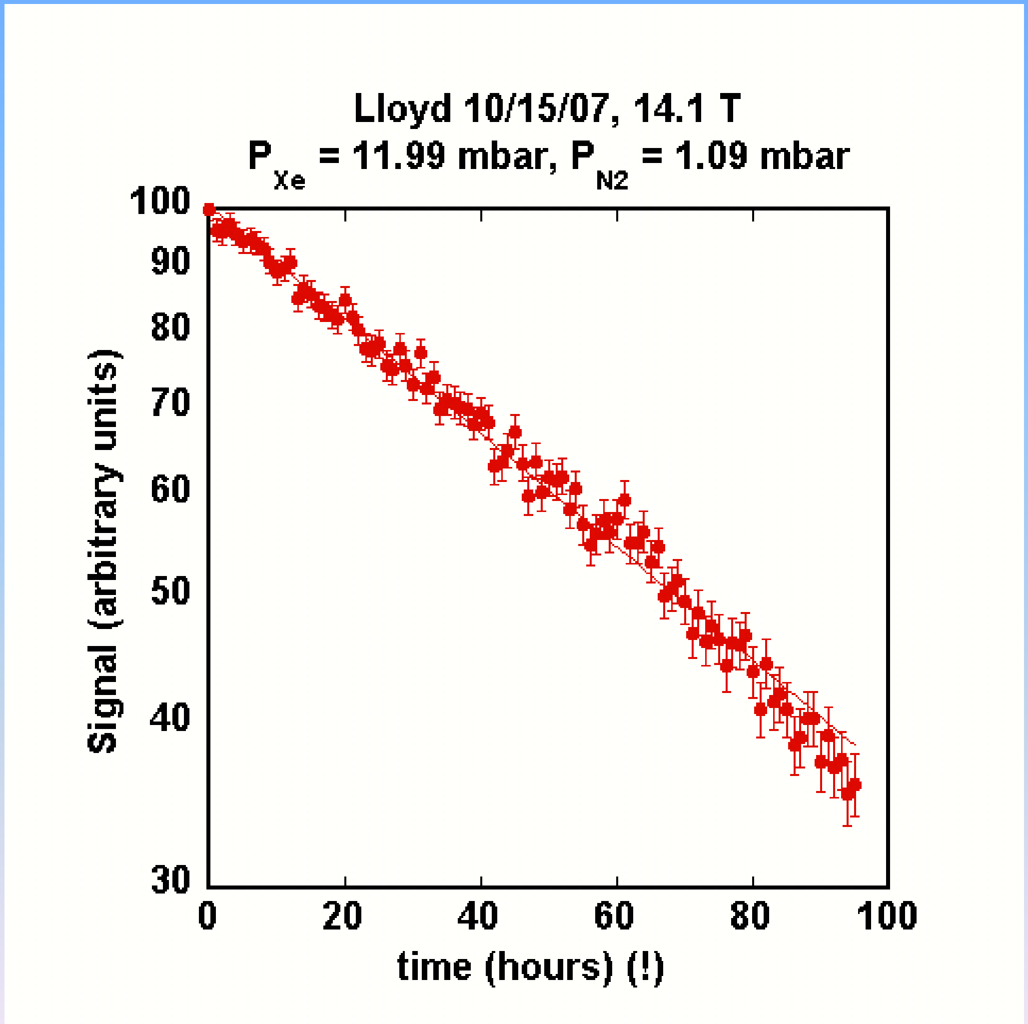
Breakup coefficient: $\tau_p^{-1} = k_\alpha [\mathrm{G}]$



- **High density: Γ_p independent of density.**
- **Low density: magnetic-field supression of Γ_p.**
- **Γ_p decreases for decreasing [Xe] at fixed total gas density [G].**

*B.N. Berry-Pusey, *et al.*, Phys. Rev. A **74**, 063408 (2006); B.C. Anger, *et al.*, Phys. Rev. A **78**, 043406 (2008).

100-Hour Gas-Phase T_1 for ^{129}Xe

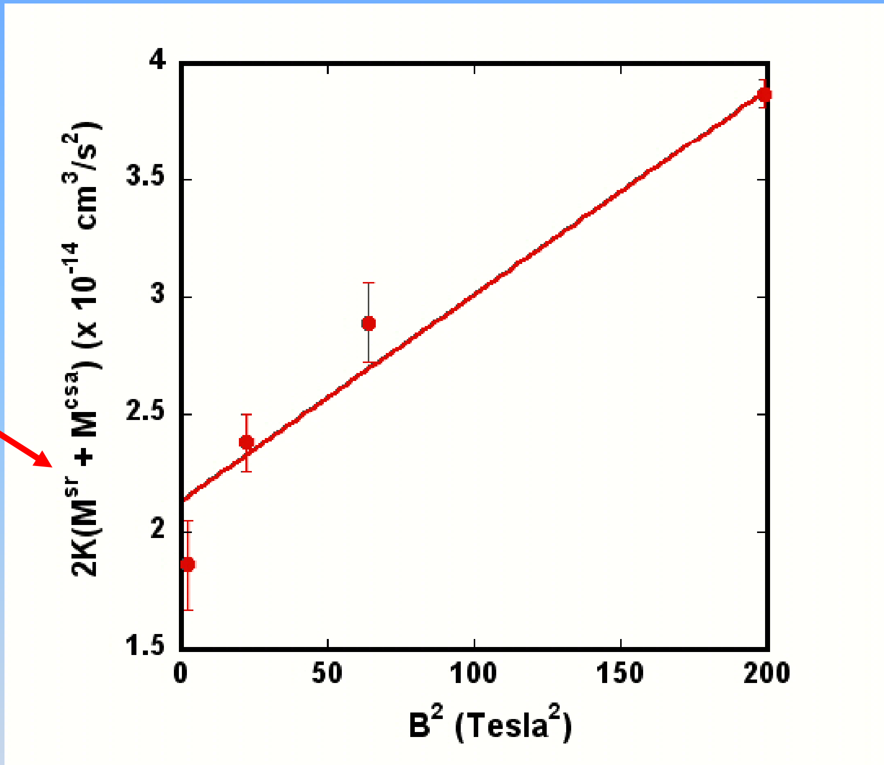


- Inferred wall relaxation time: T_1 (wall) = 175 h!!
- Obeys the Driehuys Axiom concerning HP xenon.

Quadratic Dependence on Applied Field

$$\Gamma_p = 2\kappa\left(M^{sr} + M^{csa}\right)\left(\frac{\alpha k_\alpha [G]^2}{k_\alpha^2 [G]^2 + \Omega^2}\right)$$

Combined interaction strength of SR and CSA



- **Data consistent with CSA interaction strength M^{csa} proportional to B_0^2.**
- **Intercept is proportional to SR interaction strength M^{sr}.**
- **Characteristic crossover field $B_0 \approx 16$ T.**

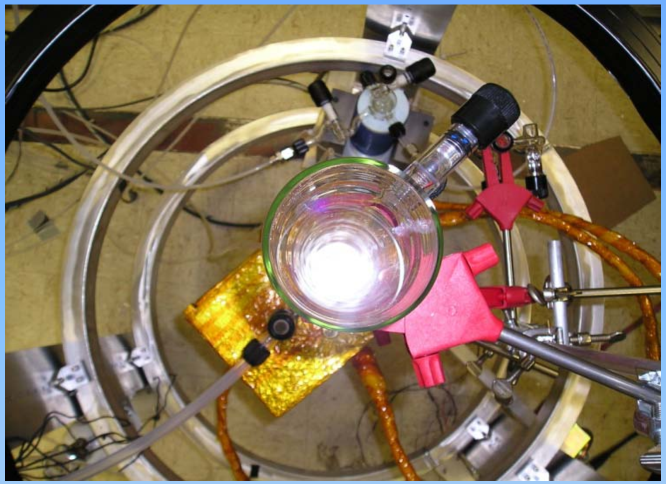
So what about [Xe] = 1 amagat; B_0 = 30 G?

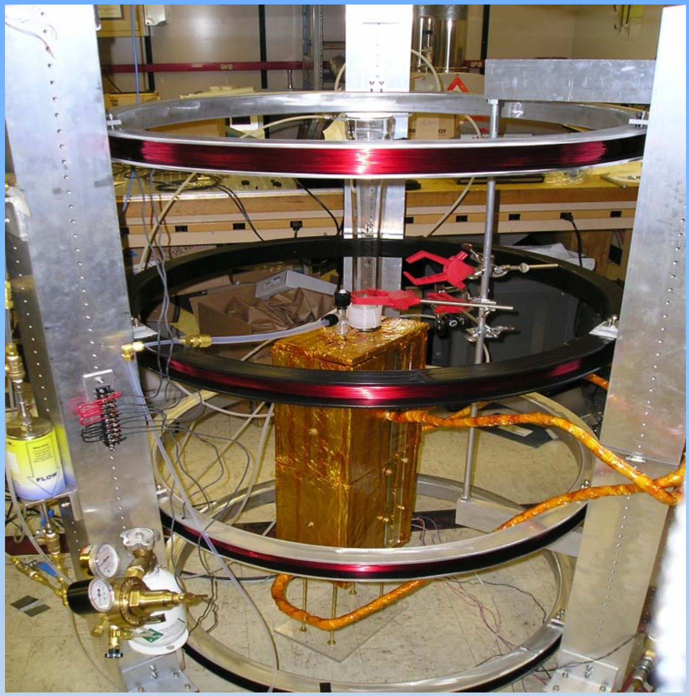
Cell	[Xe]	T_1 293 K	T_1 373 K	T_1 (wall) 293 K	T_1 (wall) 373 K
105B	1.5(1)	2.40(5)	3.66(11)	5.8(8)	8.7(1.1)
113A	≈1.5	1.30(4)	2.45(5)	1.9(1)	4.0(2)
113B	1.1(1)	2.57(15)	4.53(13)	6.6(1.3)	14.5(3.0)
139	0.7(1)	3.40(22)	5.75(23)	16(7)	35(18)

Table II taken from: B.C. Anger, et al., Phys. Rev. A **78**, 043406 (2008).

- **We've measured T_1 = 5.75 h in a large 12 cm diam spherical borosilicate-glass cell (DMDCS-coated) at 30 G, 100°C. (Still limited by wall relaxation!)**

Improvement to Flow-through ^{129}Xe Polarizer*?





- Long narrow cell (≈ 1 m long × 4 cm diam).
- [Xe] ≤ 1 amagat; use spectrally narrowed diode-laser array.
- Counterpropagation of gas and laser light.
- Cryogenic (LN_2) freeze out, separation, and storage of xenon (T_1 ≈ 2.5 h @ 77 K).

*See talk B4.00002, tomorrow 10:42 am.

- Goal: gas-phase storage cell (no cryogenics) with 3× storage time of frozen Xe having T_1 ≈ 10 h. (Preliminary patent application filed.)

Summary

We have thoroughly (exhaustively) characterized *intrinsic* gas-phase T_1-relaxation of ^{129}Xe due to persistent Xe_2 dimers—an important limit to production, accumulation, and storage of HP ^{129}Xe.

$$\Gamma_i = \frac{[\mathrm{Xe}]}{56.1\ \mathrm{h}} + \frac{1}{4.59\ \mathrm{h}}[1 + (3.65 \times 10^{-3})B_0^2]\left(1 + r\frac{[B]}{[\mathrm{Xe}]}\right)^{-1}$$

Transient-dimer contribution (binary collisions).

Persistent-dimer contribution (van der Waals molecules).

- **Competes (and gets confused) with wall relaxation in many cases, because of density-independence of Γ_p.**
- **Possibility of cryogen-free accumulation and storage with 2-3× longer storage times; significant improvement for state-of-the-art method in polarizing ^{129}Xe.**

Hyperpolarized Gas Research Group

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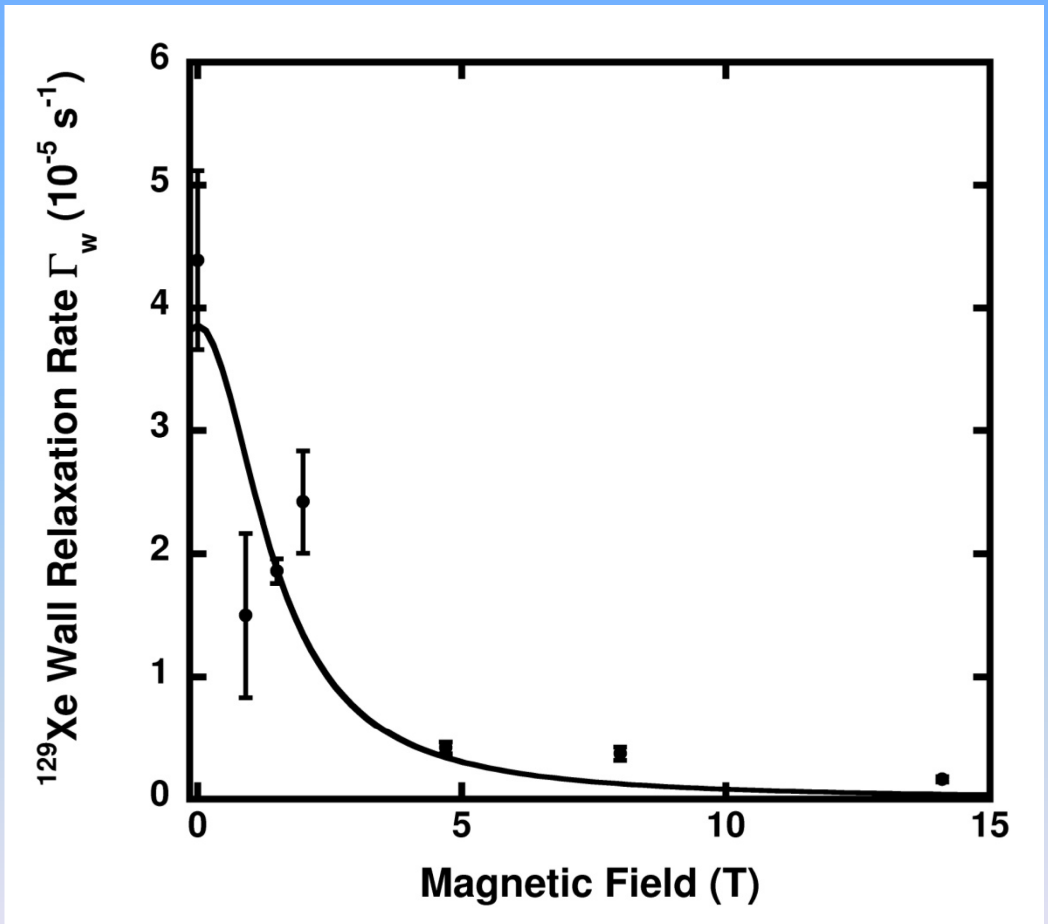
Thanks to M.S. Conradi for numerous helpful discussions.

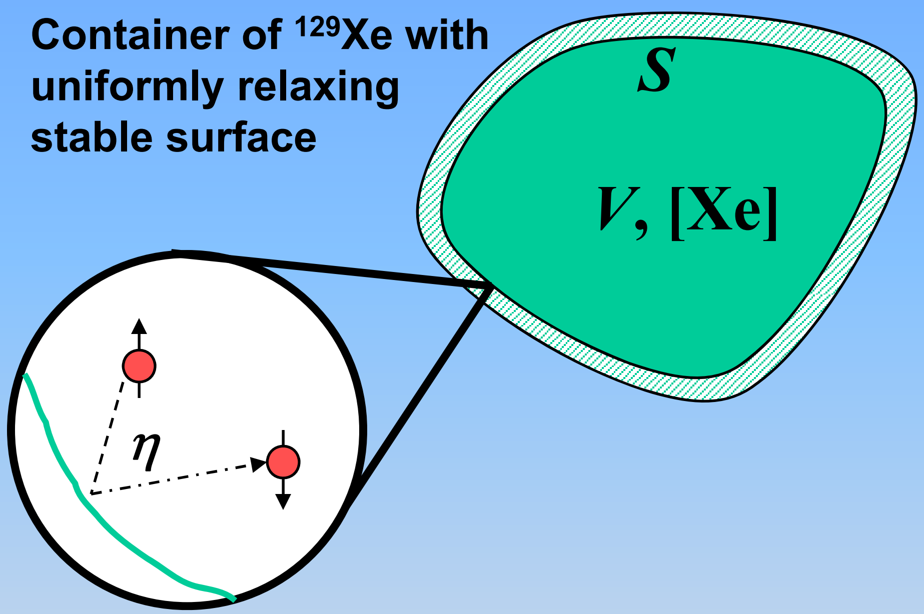
Room-Temperature Wall-Relaxation Rate vs. B_0



- Fast-fluctuation limit.
- Intrinsic relaxation rate Γ_i subtracted out.
- Lorentzian fit yields correlation time for wall interaction of ≈ 4 ns.

Simple Model for Surface Relaxation of Gases

Container of ^{129}Xe with uniformly relaxing stable surface



$\eta \propto$ surface relaxivity

$$\Gamma_{\text{wall}} = \eta\left(\frac{S}{V}\right)\bar{v}$$

$1/\Gamma_{\text{wall}}$ typically ranges from 10 to 100 min for ^{129}Xe in carefully prepared glass vessels.

For ballistic collisions with a uniformly relaxing surface, Γ_{wall} is independent of gas density [Xe].