Gas-phase spin relaxation of $^{129}$Xe

$T_1 = 100$ hours!

Workshop on Physics & Applications of Polarized Noble Gases
University of Virginia, 19 May 2009
Filling the Polarization Bucket

To maximize $P_{Xe}$, we want $\gamma_{se} >> \Gamma$ AND $\langle P_{Rb} \rangle \approx 1$.

- $\gamma_{se}$ limited by available laser light.
- Goal: understand and minimize $\Gamma$.

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

\[
\gamma_{se} = [Rb] \langle \sigma_{se} v \rangle
\]
Longitudinal Spin Relaxation in Noble Gases

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

\[ \Gamma_{\text{gradient}} = D \left| \nabla \perp B \right|^2 \frac{1}{B_0^2} \]

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

Density independent!

Negligible in our experiments.

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

Spin-rotation interaction:

\[ C_k(R) \text{ N} \cdot \text{K} \]

Occurs during binary collision AND during the lifetime of a molecule.
Early Studies of Intrinsic $^{129}$Xe Relaxation

Γ ∝ [Xe]

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

\[ \Gamma_{\text{intrinsic}} = \Gamma_t + \Gamma_p \]

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

**Persistent Dimers**
- Form/break up in 3-body collisions.
- Last for lifetime \( \tau_p \approx 1 \text{ ns} \) (until next collision).
- \( \Gamma_t \) is independent of [Xe] (for fixed gas composition).
Mean-squared spin-rotation interaction energy.

Power spectrum $J(\omega)$ for field fluctuations
- $\tau_p \sim 10^{-9}$ seconds for $[\text{Xe}] = 1$ amagat.
- $\omega/2\pi = 11.8$ MHz for $B_0 = 1$ T.
- Can often assume $\Omega^2 \tau_p^2 << 1$ (fast-fluctuation limit).

Fraction of atoms bound in molecules, assumes $[\text{Xe}_2] \ll [\text{Xe}]$.

Key point for SEOP regime, where $\Omega^2 \tau_p^2 << 1$:

$$[\text{Xe}] \propto \frac{1}{\tau_p} \quad \Rightarrow \quad \Gamma_p \text{ is independent of } [\text{Xe}]; \text{ looks like wall relaxation!}$$

Low-field (2 mT) Results*

\[
\Gamma_p = \left( \frac{4K \langle c_K^2 N^2 \rangle}{3\hbar^2} \right) [\text{Xe}] \tau_p = \left( \frac{4K \langle c_K^2 N^2 \rangle}{3\hbar^2} \right) \left( \frac{1}{k_{Xe}} \right) \left( \frac{1}{1 + r_B ([B]/[Xe])} \right)
\]

\( \Gamma_{vdW}^\text{Xe} = \) pure-Xe rate  \hspace{1cm} \text{Correction for 2nd gas}

\[
\frac{1}{\tau_p} = k_{Xe} [\text{Xe}] + k_B [B] + \cdots
\]

With:

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

High-field Experiments: Theory

\[ \Gamma_p = \left( \frac{2}{3} \frac{\langle c_K^2 N^2 \rangle}{\hbar^2} \right) \left( \frac{\tau_p}{1 + \Omega^2 \tau_p^2} \right) \left( 2K[Xe] \right) \]

Magnetic-field decoupling term important for large \( \Omega \), small \( \tau_p \).

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

\[ M^{sr} + M^{csa} \]

\[ \Gamma_p = \left( M^{sr} + M^{csa} \right) \left( \frac{\tau_p}{1 + \Omega^2 \tau_p^2} \right) \left( 2K[Xe] \right) \]
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.
$\Gamma_p = \left( M^{\text{sr}} + M^{\text{csa}} \right) \left( \frac{\tau_p}{1 + \Omega^2 \tau_p^2} \right) (2\kappa[Xe])$

reparam.

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

Total gas density: $[G] = [Xe] + [N_2]$

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

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

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

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

- Inferred wall relaxation time: $T_1 \text{ (wall)} = 175 \text{ h!!}$
- Obeys the Driehuys Axiom concerning HP xenon.
Quadratic Dependence on Applied Field

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

Combined interaction strength of SR and CSA

- Data consistent with CSA interaction strength \( M^\text{csa} \) proportional to \( B_0^2 \).
- Intercept is proportional to SR interaction strength \( M^\text{sr} \).
- Characteristic crossover field \( B_0 \approx 16 \) T.
So what about \([\text{Xe}] = 1 \text{ amagat}; B_0 = 30 \text{ G}\)?

<table>
<thead>
<tr>
<th>Cell</th>
<th>([\text{Xe}])</th>
<th>(T_1) 293 K</th>
<th>(T_1) 373 K</th>
<th>(T_1) (wall) 293 K</th>
<th>(T_1) (wall) 373 K</th>
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</thead>
<tbody>
<tr>
<td>105B</td>
<td>1.5(1)</td>
<td>2.40(5)</td>
<td>3.66(11)</td>
<td>5.8(8)</td>
<td>8.7(1.1)</td>
</tr>
<tr>
<td>113A</td>
<td>(\approx 1.5)</td>
<td>1.30(4)</td>
<td>2.45(5)</td>
<td>1.9(1)</td>
<td>4.0(2)</td>
</tr>
<tr>
<td>113B</td>
<td>1.1(1)</td>
<td>2.57(15)</td>
<td>4.53(13)</td>
<td>6.6(1.3)</td>
<td>14.5(3.0)</td>
</tr>
<tr>
<td>139</td>
<td>0.7(1)</td>
<td>3.40(22)</td>
<td>(5.75(23))</td>
<td>16(7)</td>
<td>35(18)</td>
</tr>
</tbody>
</table>


- We’ve measured \(T_1 = 5.75 \text{ h}\) 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 ($\approx 1$ m long $\times$ 4 cm diam).
- $[\text{Xe}] \leq 1$ amagat; use spectrally narrowed diode-laser array.
- Counterpropagation of gas and laser light.
- Cryogenic (LN$_2$) freeze out, separation, and storage of xenon ($T_1 \approx 2.5$ h @ 77 K).

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

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

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

- 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 $\Gamma_p$.

- 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.
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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 $\Gamma_i$ subtracted out.
- Lorentzian fit yields correlation time for wall interaction of $\approx 4$ ns.
Simple Model for Surface Relaxation of Gases

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

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

$\eta \propto$ 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.