Quantum beat spectroscopy as a probe of angular momentum polarization in chemical processes.
The Pilling Legacy

Many thanks and happy ‘retirement’!
Acknowledgements

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Collisional depolarization
Collisional depolarization

How easy is it to change the direction of \( J \) by collision?

Relevant to the detection of OH(X) or NO(X) by LIF.
Collisional depolarization

Can be characterized in terms of the angular momentum transferred, $K$

Often assumed that $K$ is minimized in collisions
Angular distribution \((\text{OH(A)} + \text{Ar})\)

Increasing \(K\) →

QCT calculations by C.J. Eyles and F.J. Aoiz

New PES by J. Kłos and M.H. Alexander
Angular distribution

\[ \frac{d\sigma}{d\omega_{jj'}} = \sigma \left[ \sum_n \frac{(2n + 1)}{2} a_n P_n(\cos \theta_{jj'}) \right] \]

Disalignment (even terms)

\[ a_2 = \langle P_2(\cos \theta_{jj'}) \rangle \quad -0.5 \leq a_2 \leq +1.0 \]

Disorientation (odd terms)

\[ a_1 = \langle P_1(\cos \theta_{jj'}) \rangle \quad -1.0 \leq a_1 \leq +1.0 \]
Motivation

Rotational polarization

- Angular dependence of potential energy surface
- Mechanistic information

Aims

- Measure polarization using quantum beat spectroscopy.
- Weak magnetic field effects in chemistry.
- Control of angular momentum orientation and alignment.
Zeeman quantum beat spectroscopy
**OH source and detection**

**Pump**

\[ \text{H}_2\text{O}_2 + h\nu \rightarrow \text{OH}(X^2\Pi) + \text{OH}(X^2\Pi) \]

**Probe**

\[ \text{OH}(X^2\Pi) + h\nu' \rightarrow \text{OH}(A^2\Sigma^+) \]

\[ \text{or} \quad \text{NO}(X^2\Pi) + h\nu'' \rightarrow \text{NO}(A^2\Sigma^+) \]

Use a long (250 ns or 10 \(\mu\)s) pump-probe laser delay.
Experiment

Detect OH($X^2\Pi$) by *polarized* laser induced fluorescence...

...in presence of a *weak magnetic field*. 
Spatial distribution of OH($X^2\Pi$) is nearly *isotropic*.

No net magnetic moment, *no precession about the field*.
Initial OH(A) spatial distribution

Excite OH(X) with *linearly* polarized probe radiation.

**Transition probability** \[ P \propto |\hat{\mu}_{\text{OH}} \cdot \hat{e}_a|^2 \]

Generates an *aligned* ensemble of excited OH(A\(^2\Sigma^+\)) radicals.
Zeeman quantum beats

Precesses in magnetic field with *Larmor frequency*, $\omega_L$.

Observe emission through a *linear polarizer*.
Zeeman quantum beats

*Alternative picture:* $R_{11}(4) \uparrow$ transition

*Coherent excitation* of Zeeman levels.
Link with theory (linearly polarized light)

Initial aligned distribution

\[ P(\theta_j) = \frac{1}{2} \left[ 1 + A_{20} P_2(\cos \theta_j) \right] \]

Distribution after one collision

\[ P(\theta_j') = \frac{1}{2} \left[ 1 + A_{20} a_2 P_2(\cos \theta_j') \right] \]
Collisional depolarization of OH(A) and NO(A) by Ar at 300 K
Zeeman quantum beats

\[ \text{No field: } \text{OH } R_{11}(4) \uparrow \text{ transition} \]

Exponential population decay

\[ [\text{OH}^*] = [\text{OH}^*]_0 e^{-k_0 t} \]
Zeeman quantum beats

Population decay

\[ [\text{OH}^*] = [\text{OH}^*]_0 e^{-k_0 t} \]

\[ k_0 = k_{\text{rad}} + k_Q [\text{Ar}] \]

- \( k_{\text{rad}} \) - radiative decay \( (\tau_{\text{rad}} \sim 700 \text{ ns for OH(A)}) \)

- \( k_Q \) - electronic quenching \( \) (relatively small for Ar)
Zeeman quantum beats

**With field:**  $R_{11}(4) \uparrow$ transition

$H = 4$ Gauss

$$[\text{OH}^*] = [\text{OH}^*]_0 e^{-k_0 t} \left\{ 1 + C e^{-k_2 t} \sum_F \cos(2\pi \omega_L t + \phi) \right\}$$
Zeeman quantum beats

\[ \text{[OH]}^* = [\text{OH}^*]_0 e^{-k_0 t} \{ 1 + C e^{-k_2 t} \sum_F \cos(2\pi \omega_L t + \phi) \} \]

with

\[ \omega_L = g_F \mu_0 H / h \]

Oscillations at two frequencies for \( F = 5 \) and 6.
Zeeman quantum beats

Depolarization and dephasing: Beat amplitude, $C$

$$[\text{OH}^*] = [\text{OH}^*]_0 e^{-k_0 t} \left\{ 1 + C e^{-k_2 t} \sum_F \cos \left( 2\pi \omega_L t + \phi \right) \right\}$$

Proportional to rotational alignment of excited OH(A)
Zeeman quantum beats

**With Field:** Pressure dependence.

Collisional *population decay* and *depolarization*
Zeeman quantum beats

Depolarization and dephasing

\[
[\text{OH}^*] = [\text{OH}^*]_0 e^{-k_0 t} \{ 1 + C e^{-k_2 t} \sum_F \cos(2\pi \omega_L t + \phi) \}
\]

\[k_2 = k_{\text{inhom}} + k_d [\text{Ar}]\]

\(k_{\text{inhom}}\) - dephasing by field inhomogeneities

\(k_d\) - collisional depolarization by Ar \((k_d \sim v_{\text{rel}} \sigma_d)\)
Depolarization rate constant, \( k_d \sim v_{rel} \sigma_d \)

\[
k_d = k_c (1 - a_2)
\]

where \( k_c \) is the collision rate constant (e.g., for energy transfer)

Three cases:

1. \( a_2 = +1.0 \) \( k_d = 0 \) no depolarization
2. \( a_2 = 0.0 \) \( k_d = k_c \) depolarization rate same as collision rate
3. \( a_2 = -0.5 \) \( k_d = 1.5k_c \) depolarization faster than the collision rate
Zeeman quantum beats

**Trends in depolarization cross-sections:**

OH(A) + Ar (300 K)

Cross-sections are *large* (long range interaction).

Cross-sections *decrease* with $N'$ (angular momentum conservation).
Zeeman quantum beats

Collisional processes leading to depolarization

Inelastic depolarization (rotational energy transfer)

Elastic depolarization (velocity changing)
**Zeeman quantum beats**

**Comparison with rotational energy transfer:**

\[ \text{OH(A)} + \text{Ar (300 K)} \]

Depolarization *more efficient* than RET \( (a_2 \lesssim 0 \text{ for this system}) \)

Elastic contribution to \( \sigma_d \sim 20 \text{ Å}^2 \) for \( N = 4 \)

Zeeman quantum beats

Caveat: we detect unresolved OH(A) emission

- Populated levels have different $g_F$ values - leads to a dephasing
- Important for spin-rotation changing collisions
- Effects can be accounted for, although better to resolve emission
Comparison with hyperfine quantum beats: NO(A)

Coherent superposition of hyperfine levels (Low $N'$)

Observe two of the three Hyperfine beat frequencies.
Hyperfine quantum beats: NO(A)

Initial distribution of $J$

Nuclear spin, $I$, initially unpolarized.
Hyperfine quantum beats: NO(A)

Alignment of $J$ reduced

Nuclear spin, $I$, becomes aligned.
Hyperfine quantum beats: NO(A)

Alignment of $J$ and $I$ cycle in time

Hyperfine quantum beats: NO(A)

Beat signal

\[ S_{21}(0) \uparrow \] \hspace{1cm} \[ R_{22}(4) \uparrow \]

Amplitude decreases rapidly with \( J \).
Hyperfine quantum beats: NO(A)

Depolarization cross-sections

NO(A) + Ar (300 K)

Reasonable agreement between hyperfine and Zeeman beat data

Depolarization is *less efficient* than RET ($a_2 > 0$ for NO(A) + Ar)
Trends in depolarization cross-sections

OH(A) + Ar versus NO(A) + Ar at 300 K

Well-depth for NO(A)+Ar is one tenth that of OH(A) + Ar

Balanced by kinematic/energetic factors
**OH(A) + Ar potential**

*Strongly attractive and highly anisotropic PES*

J. Kłos and M.H. Alexander,  
*in preparation* (2007)

Well depth $\sim 1600 \text{ cm}^{-1}$
NO(A) + Ar potential

Very weakly attractive PES

N. Shafizadeh et al.,

$D_0 \sim 44 \text{ cm}^{-1}$ ‡

Role of electron and nuclear spin

Spin is a spectator in $^2\Sigma^+$ radicals

\[
f_2 : \quad J = N - S \quad \uparrow
\]
\[
f_1 : \quad J = N + S
\]

Spin-rotation changing collisions only occur if $N$ is strongly depolarized.
OH(A) + Ar and spin-rotation changing collisions

Play an important role for OH(A) + Ar

QCT calculations by C.J. Eyles and F.J. Aoiz

QM and new PES by J. Kłos and M.H. Alexander
Spin-rotation changing collisions require large $K$

These are enhanced for OH(A) + Ar by the deep well
OH(A) + Ar and rotational energy transfer

‘Disalignment’ coefficients

QCT calculations by C.J. Eyles and F.J. Aoiz

New PES by J. Kłos and M.H. Alexander
Final thought

‘Disorientation’ coefficients?

Use circularly polarized light

Provides a means of measuring $a_1 = \langle P_1(\cos(\theta)) \rangle$
Zeeman quantum beats

**Collisional depolarization:** Some conclusions.

- Less efficient at high $N'$ - *angular momentum conservation*.
- Attractive long-range interaction plays crucial role.
- Both elastic and inelastic depolarization can be important.
- Depolarization efficiency relative to RET is very system dependent.
- For $2\Sigma^+$ radicals $S$ and $I$ are spectators in the collision.
- $\sigma_d$ is large for spin-rotation and hyperfine state-changing collisions.
The End