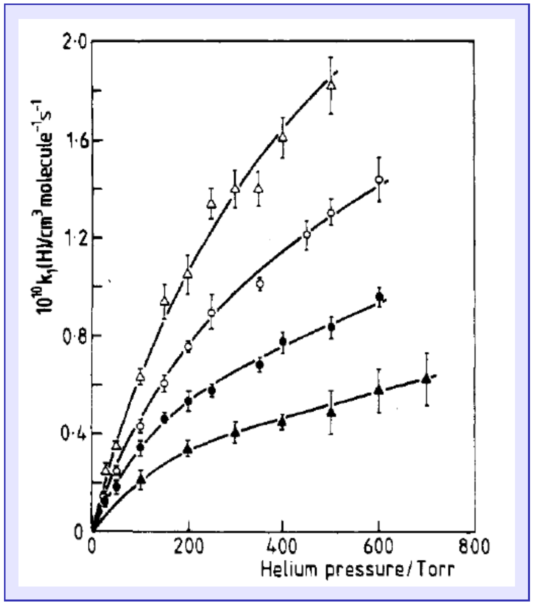
Quantum beat spectroscopy as a probe of angular momentum polarization in chemical processes.

Mark Brouard

The Department of Chemistry
Oxford University

Gas Kinetics Meeting, Leeds, September 2007

The Pilling Legacy



Many thanks and happy ‘retirement’!

Acknowledgements

The Group

Raluca Cireasa	Visiting scientist
Chris Eyles	D.Phil. student
Yuan-Pin Chang	D.Phil. student
Alessandra la Via	Part II student
Alistair Green	Part II student
David Case	Part II student
Nicholas Screen	Part II student
Alexander Bryant	Part II student

Acknowledgements

Collaborations

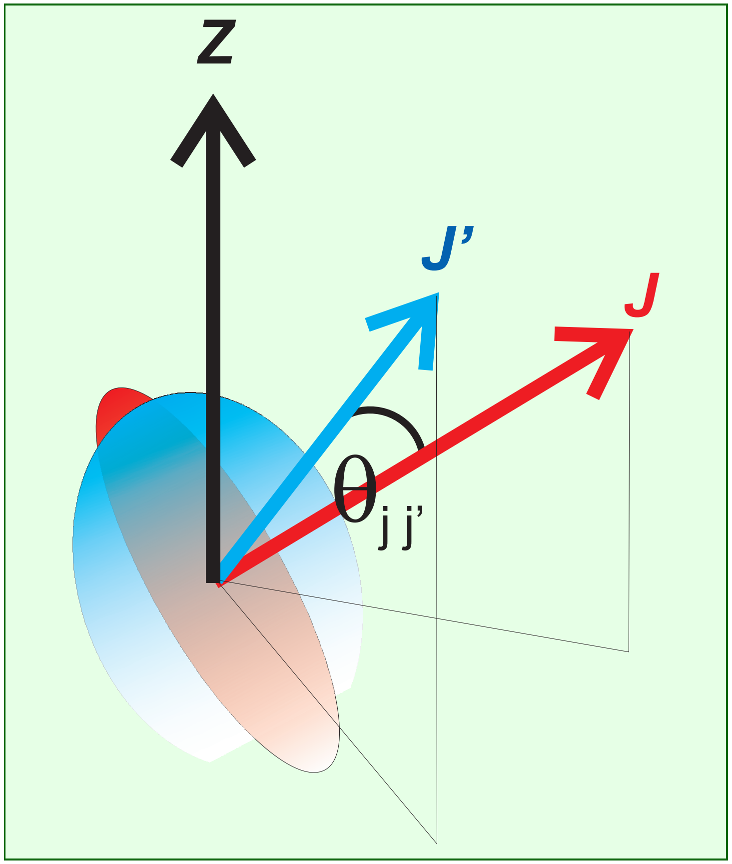
F. Javier Aoiz	QCT calculations
Jaçek Kłos	PES and QM calculations
Marcelo P. de Miranda	Stereodynamics

Funding

EPSRC
Royal Society

Collisional depolarization

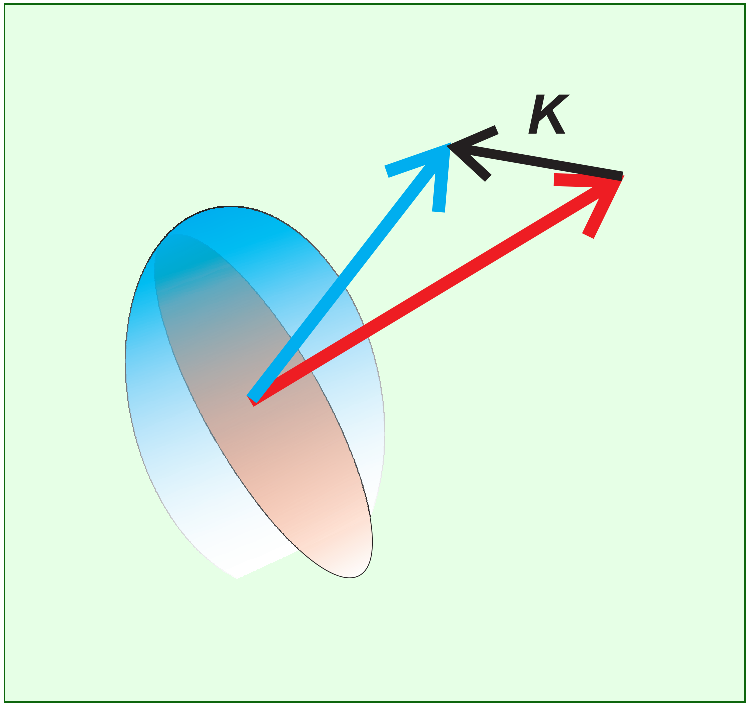
Collisional depolarization



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

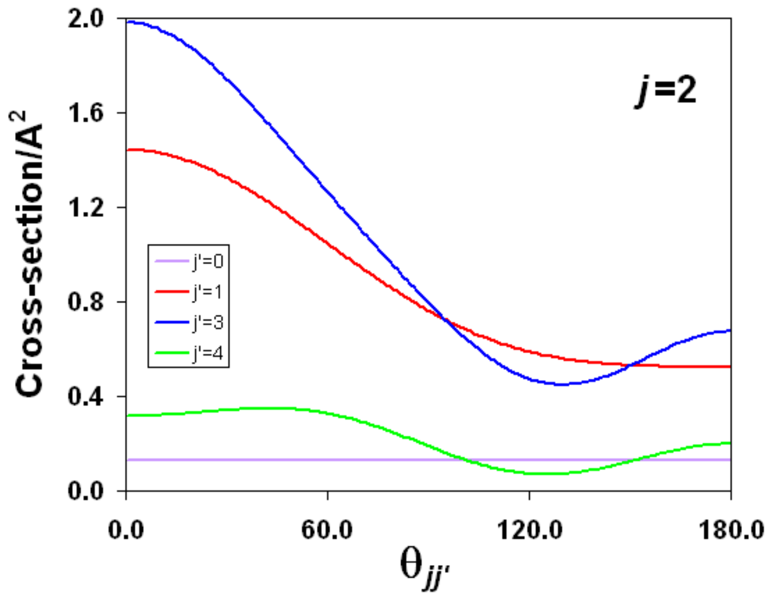


Can be characterized in terms of the angular momentum transferred, $\boldsymbol{K}$

Often assumed that $\boldsymbol{K}$ is minimized in collisions

Angular distribution (OH(A) + Ar)

Increasing K $\longrightarrow$



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

New PES by J. Kłos and M.H. Alexander

Angular distribution

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

Disalignment (even terms)

$$a_2 = \langle P_2(\cos\theta_{\mathrm{j\,j'}}) \rangle \qquad -0.5 \leq a_2 \leq +1.0$$

Disorientation (odd terms)

$$a_1 = \langle P_1(\cos\theta_{\mathrm{j\,j'}}) \rangle \qquad -1.0 \leq a_1 \leq +1.0$$

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

$$H_2O_2 + h\nu \longrightarrow OH(X^2\Pi) + OH(X^2\Pi)$$

Probe

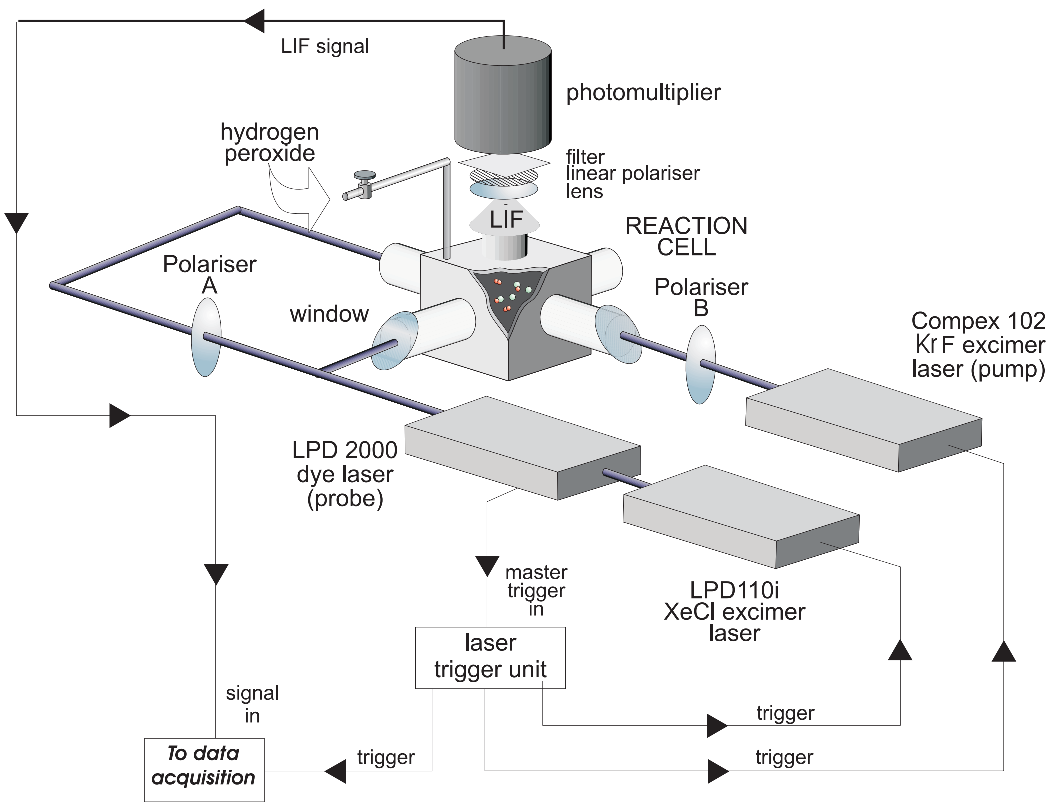
$$OH(X^2\Pi) + h\nu' \longrightarrow OH(A^2\Sigma^+)$$

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

Use a long (250 ns or 10 μs) pump-probe laser delay.

Experiment

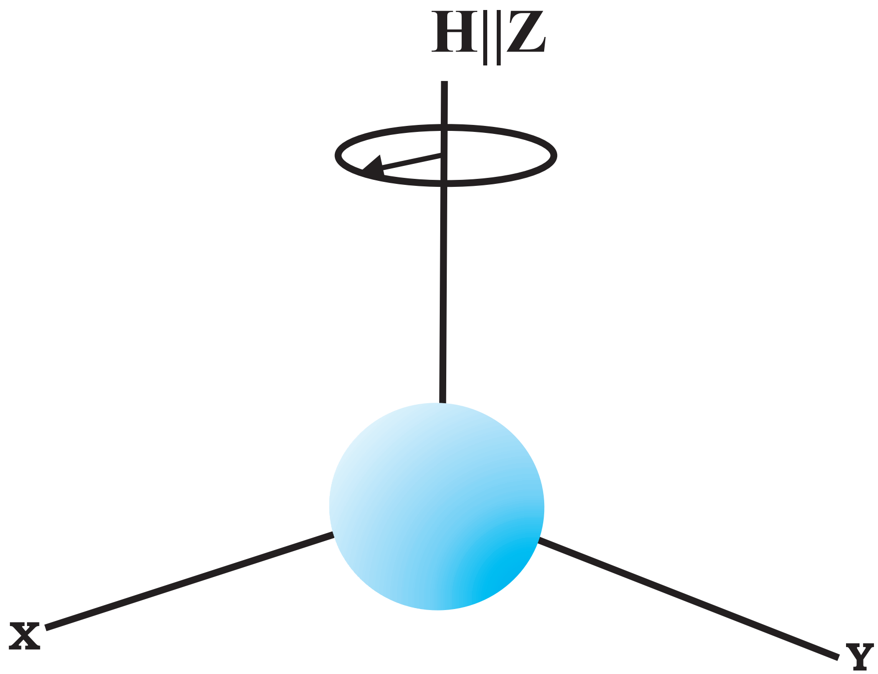
Detect $OH(X^2\Pi)$ by *polarized* laser induced fluorescence...



...in presence of a *weak magnetic field*.

OH(X) spatial distribution

Spatial distribution of OH($X^2\Pi$) is nearly *isotropic*.

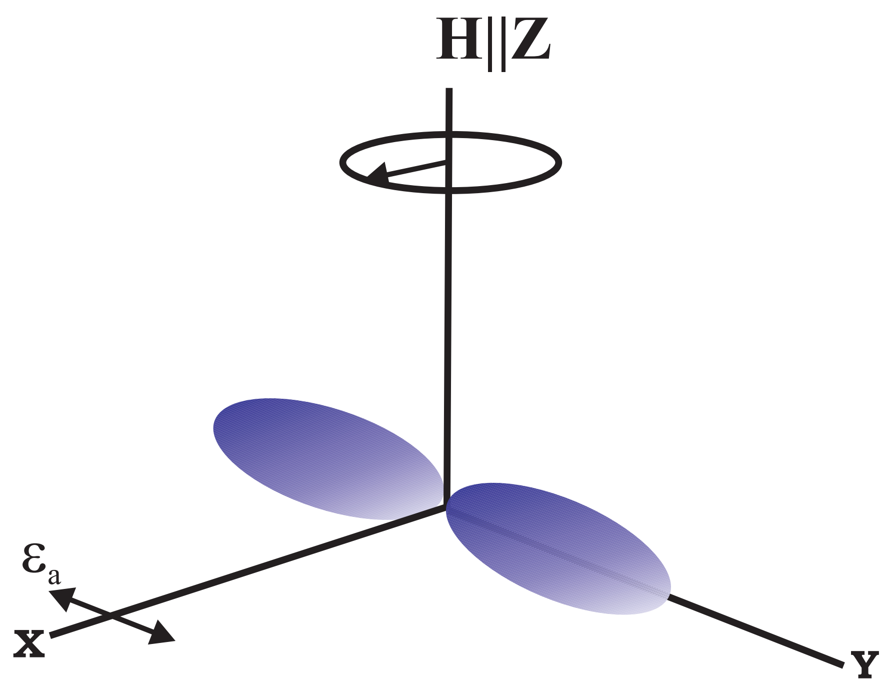


No net magnetic moment, *no precession about the field*

Initial OH(A) spatial distribution

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

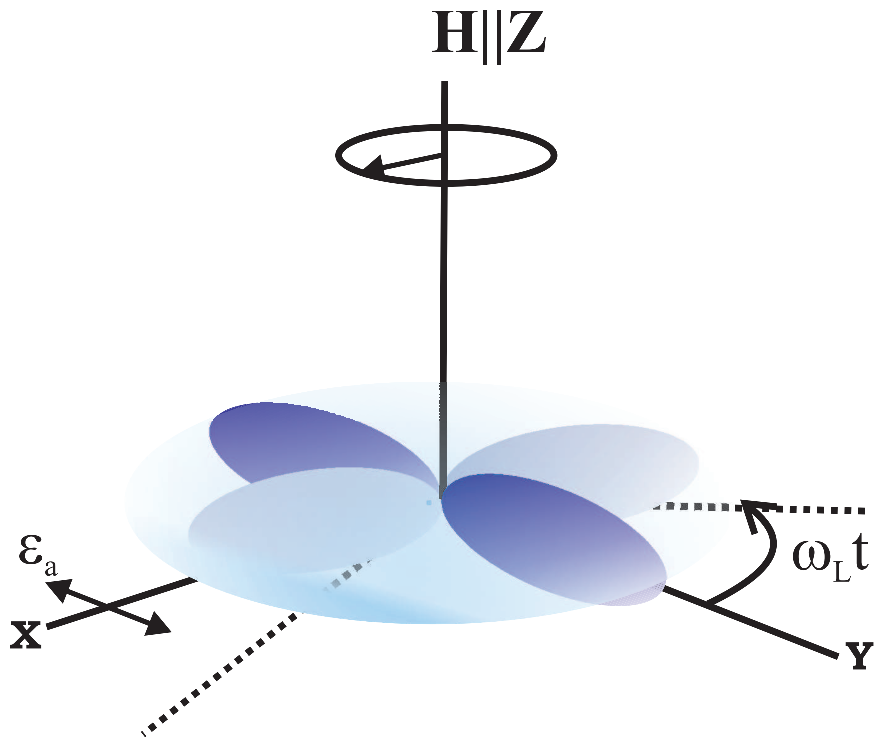
Transition probability $P \propto |\hat{\mu}_{OH} \cdot \hat{\epsilon}_a|^2$



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

Zeeman quantum beats

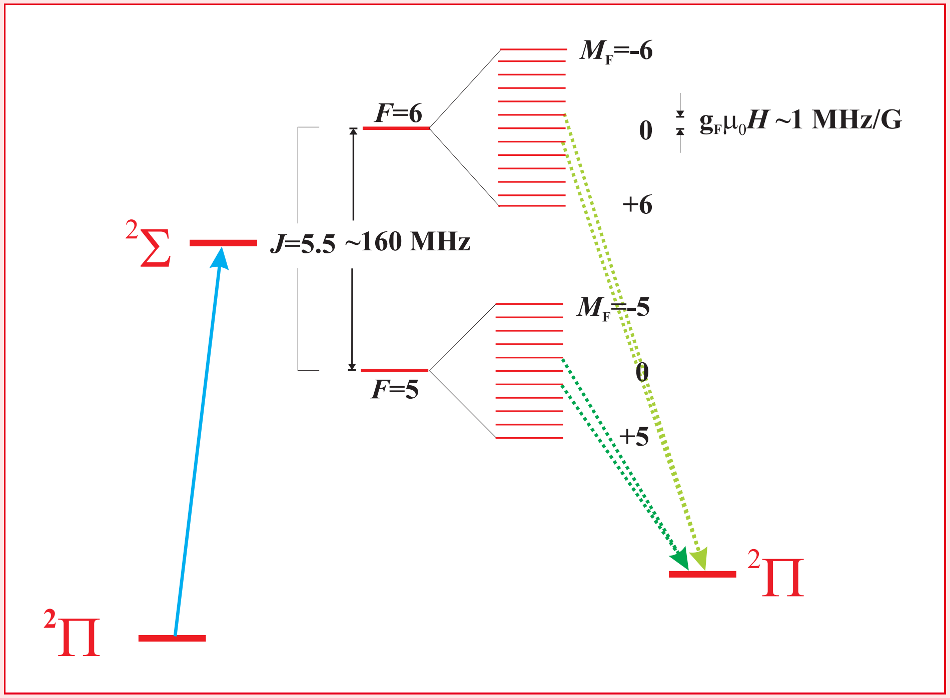
Precesses in magnetic field with *Larmor frequency*, ω_L.



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

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

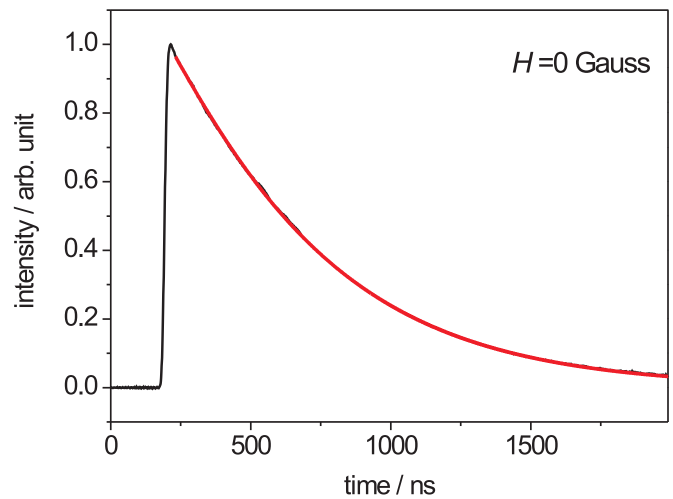
Distribution after one collision

$$P(\theta_{j'}) = \frac{1}{2}\left[1 + A_{20}\, a_2\, P_2(\cos\theta_{j'})\right]$$

Collisional depolarization of OH(A) and NO(A) by Ar at 300 K

Zeeman quantum beats

No field: OH $R_{11}(4)\uparrow$ transition



Exponential *population* decay

$$[\mathrm{OH}^*] = [\mathrm{OH}^*]_0\, \mathrm{e}^{-k_0 t}$$

Zeeman quantum beats

Population decay

$$[\mathrm{OH}^*] \;=\; [\mathrm{OH}^*]_0\,\mathrm{e}^{-k_0 t}$$

$$\boxed{k_0 = k_{\mathrm{rad}} + k_{\mathrm{Q}}[\mathrm{Ar}]}$$

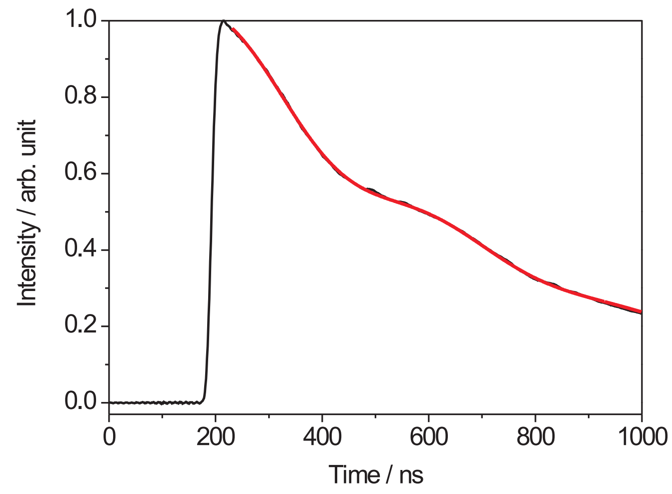
k_{rad} - *radiative decay* ($\tau_{\mathrm{rad}} \sim 700\,\mathrm{ns}$ for OH(A))

k_{Q} - *electronic quenching* (relatively small for Ar)

Zeeman quantum beats

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

$H = 4$ Gauss



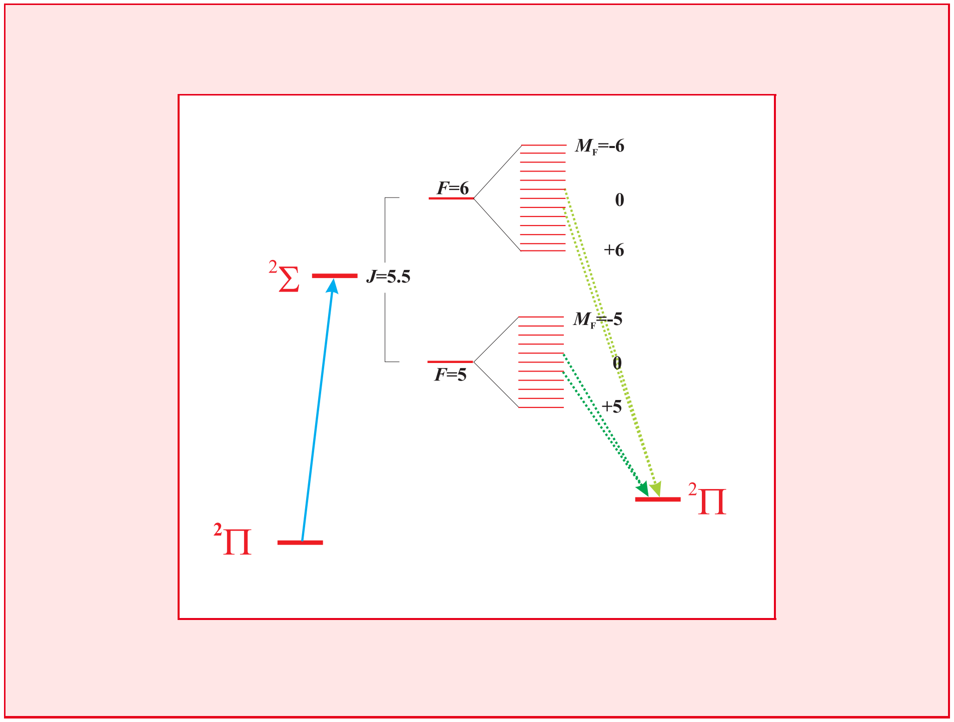
$$[\mathrm{OH}^*] \;=\; [\mathrm{OH}^*]_0\, \mathrm{e}^{-k_0 t}\{1 \;+\; C\, \mathrm{e}^{-k_2 t} \sum_F \cos\left(2\pi\omega_{\mathrm{L}} t + \phi\right)\}$$

Zeeman quantum beats

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

with

$$\omega_{\mathrm{L}} = g_F \mu_0 H / h$$

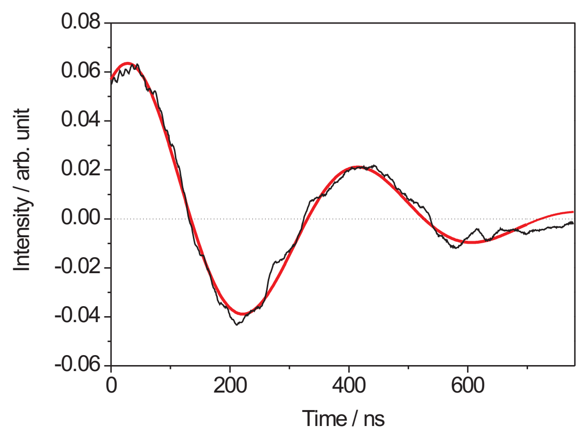


Oscillations at *two frequencies* for $F = 5$ and 6.

Zeeman quantum beats

Depolarization and dephasing: Beat amplitude, C

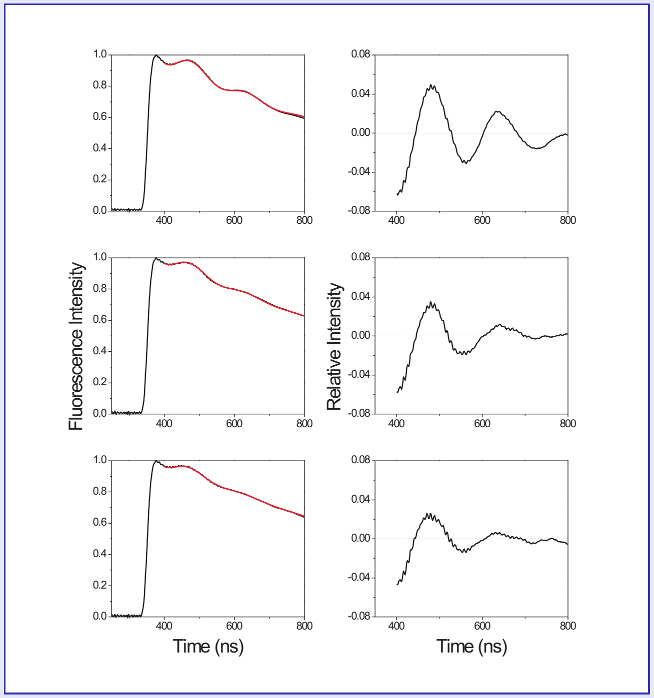
$$[\mathrm{OH}^*] = [\mathrm{OH}^*]_0\, \mathrm{e}^{-k_0 t}\{1 + C\, \mathrm{e}^{-k_2 t} \sum_F \cos(2\pi\omega_{\mathrm{L}} t + \phi)\}$$



Proportional to *rotational alignment* of excited OH(A)

Zeeman quantum beats

With Field: Pressure dependence.



50 mTorr Ar

↓

250 mTorr Ar

Collisional *population decay* and *depolarization*

Zeeman quantum beats

Depolarization and dephasing

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

$$k_2 = k_{\mathrm{inhom}} + k_{\mathrm{d}}\,[\mathrm{Ar}]$$

k_{inhom} - dephasing by *field inhomogeneities*

k_{d} - collisional depolarization by Ar ($k_{\mathrm{d}} \sim v_{\mathrm{rel}}\sigma_{\mathrm{d}}$)

Link with theory

Depolarization rate constant, $k_\mathrm{d} \sim v_\mathrm{rel}\sigma_\mathrm{d}$

$$k_\mathrm{d} = k_\mathrm{c}\,(1 - a_2)$$

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

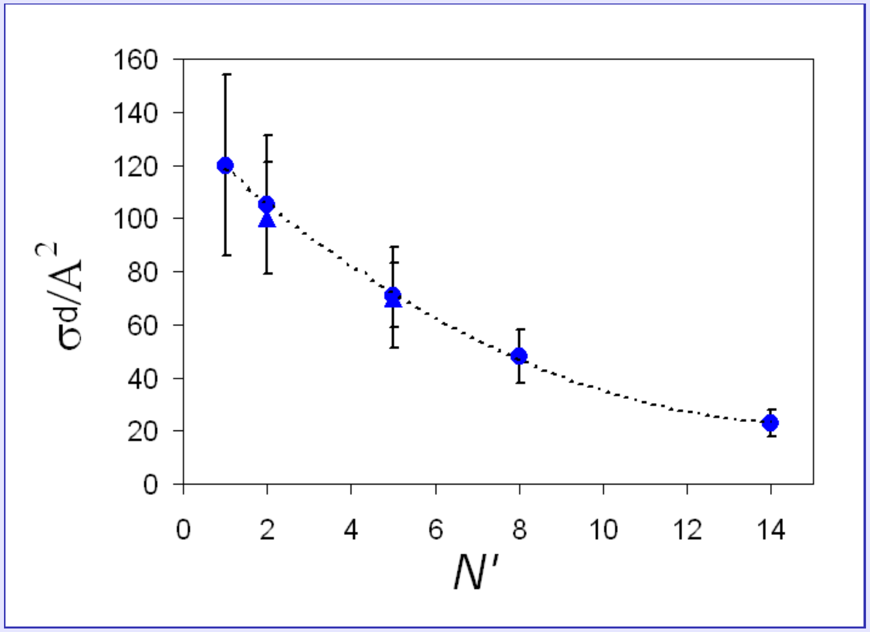
Three cases:

1. $a_2 = +1.0 \quad k_\mathrm{d} = 0$ — no depolarization
2. $a_2 = 0.0 \quad k_\mathrm{d} = k_\mathrm{c}$ — depolarization rate same as collision rate
3. $a_2 = -0.5 \quad k_\mathrm{d} = 1.5k_\mathrm{c}$ — depolarization faster than the collision rate

Zeeman quantum beats

Trends in depolarization cross-sections:

OH(A) + Ar (300 K)

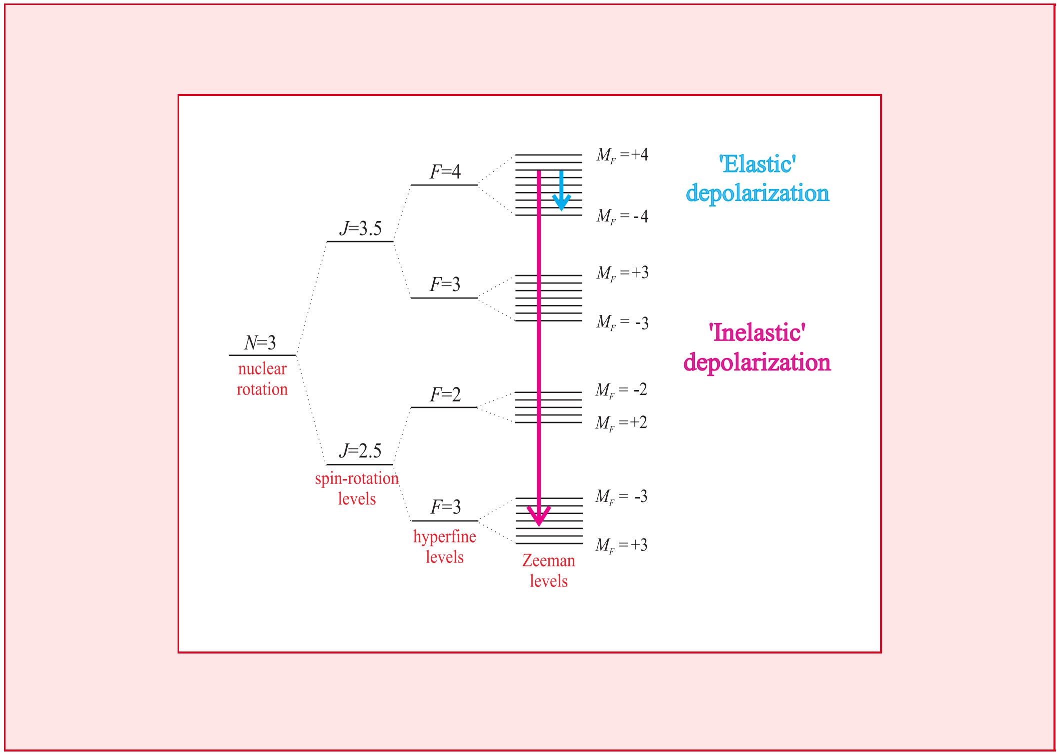


Cross-sections are *large* (long range interaction).

Cross-sections *decrease* with N' (angular momentum conservation).

Zeeman quantum beats

Collisional processes leading to depolarization



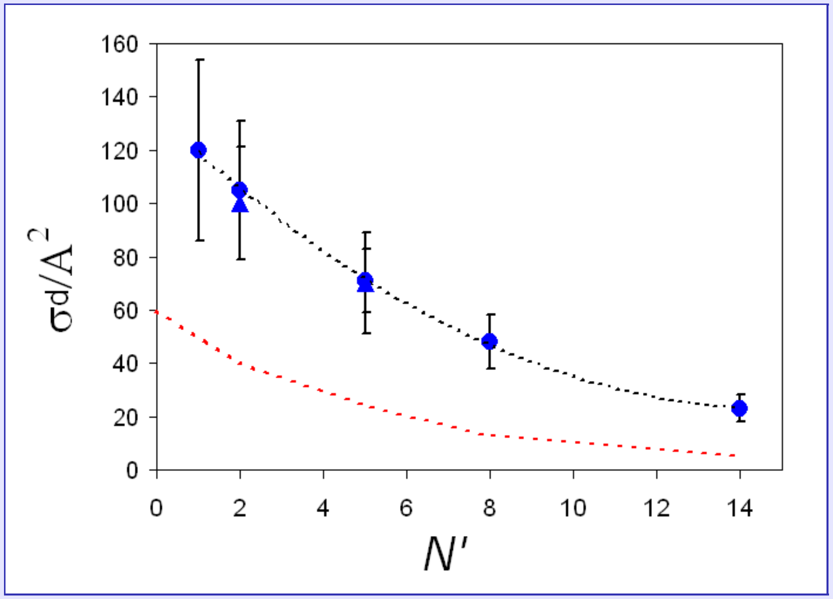
Inelastic depolarization (*rotational energy transfer*)

Elastic depolarization (*velocity changing*)

Zeeman quantum beats

Comparison with rotational energy transfer:

OH(A) + Ar (300 K)



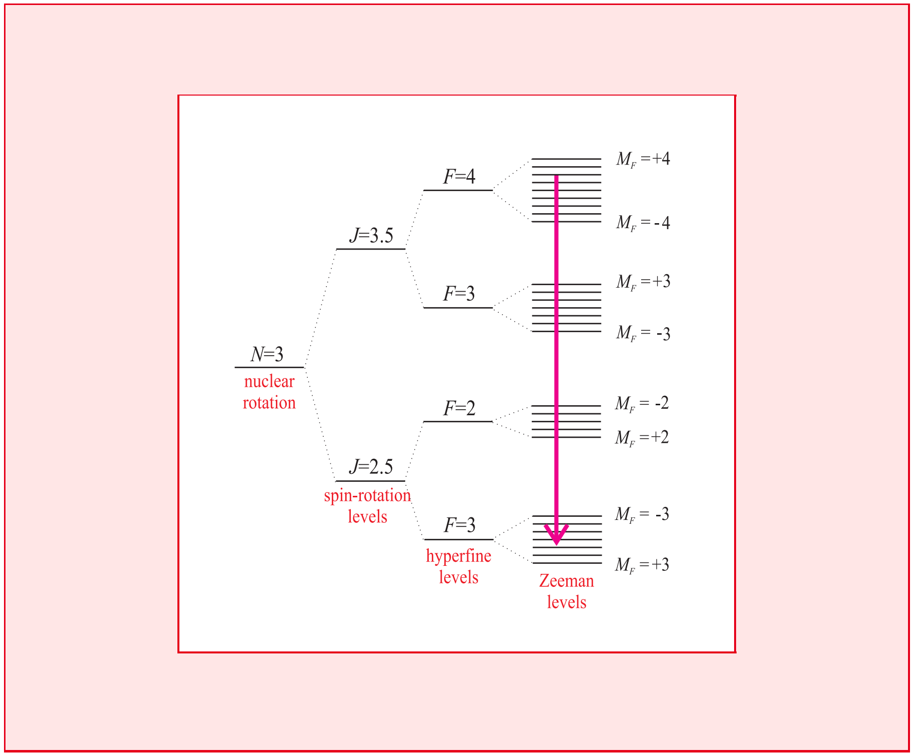
Depolarization *more efficient* than RET ($a_2 \lesssim 0$ for this system)

Elastic contribution to $\sigma_\mathrm{d} \sim 20\,\text{Å}^2$ for $N = 4$ ‡

‡ E.A. Brinkman and D.R. Crosley *J. Chem. Phys.* (2004)

Zeeman quantum beats

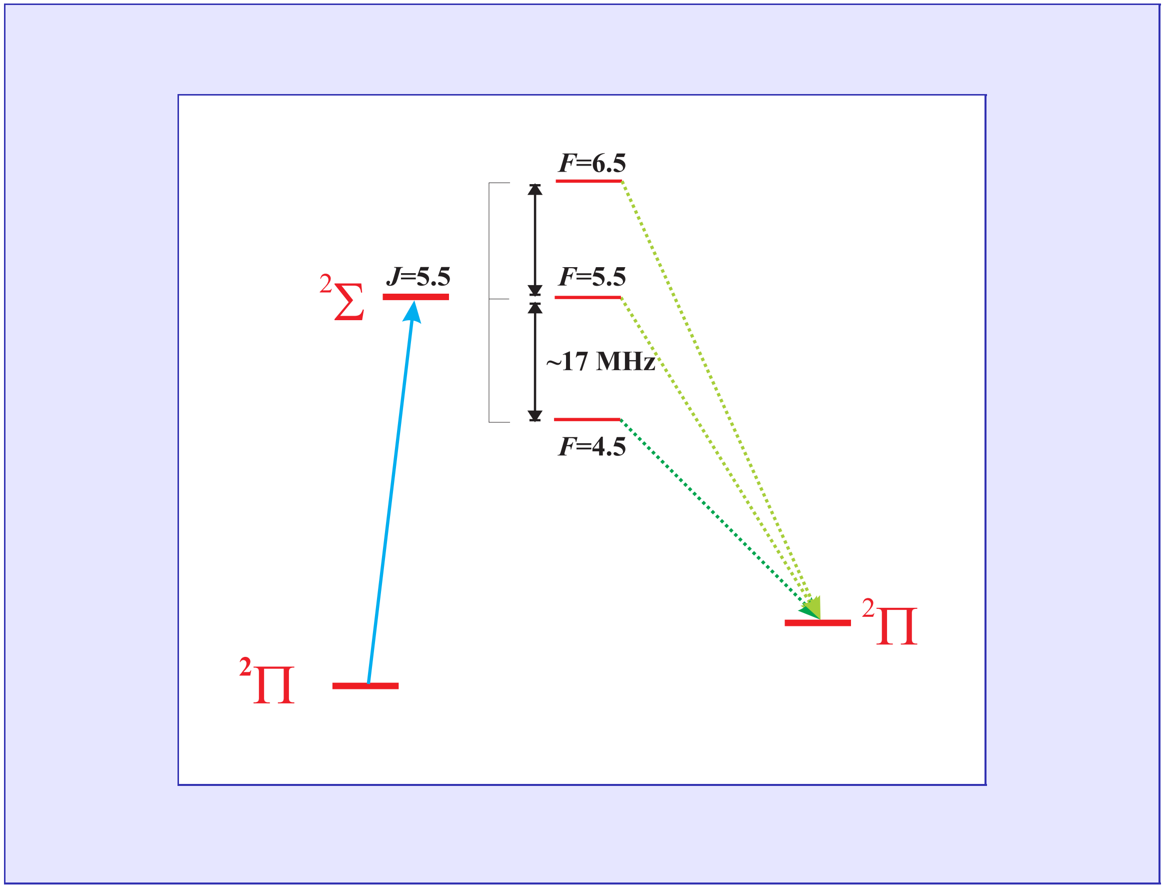
Caveat: we detect unresolved OH(A) emission



- 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)

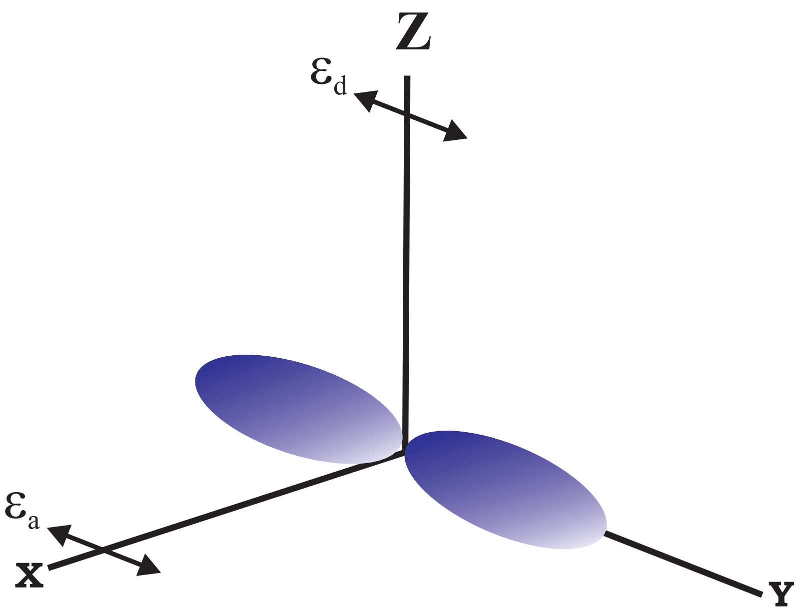
Coherent superposition of hyperfine levels (Low N')



Observe two of the three Hyperfine beat frequencies.

Hyperfine quantum beats: NO(A)

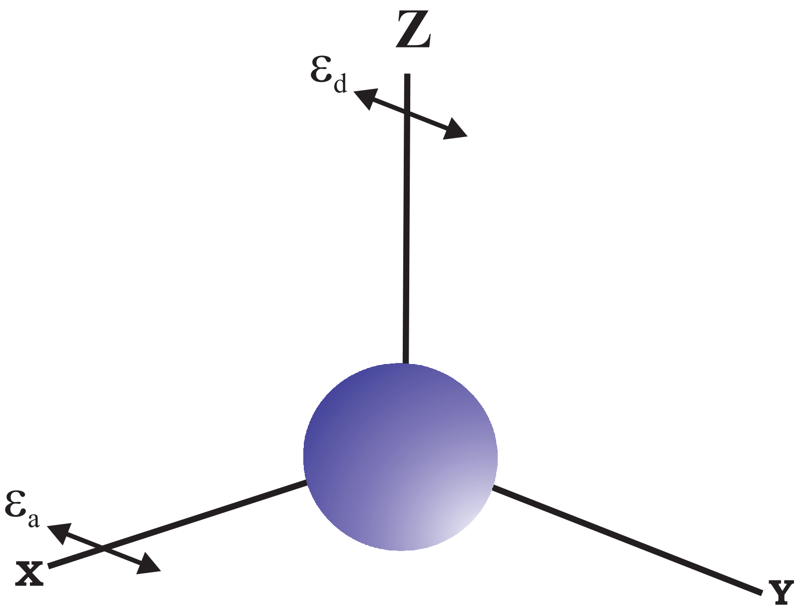
Initial distribution of $\boldsymbol{J}$



Nuclear spin, $\boldsymbol{I}$, initially unpolarized.

Hyperfine quantum beats: NO(A)

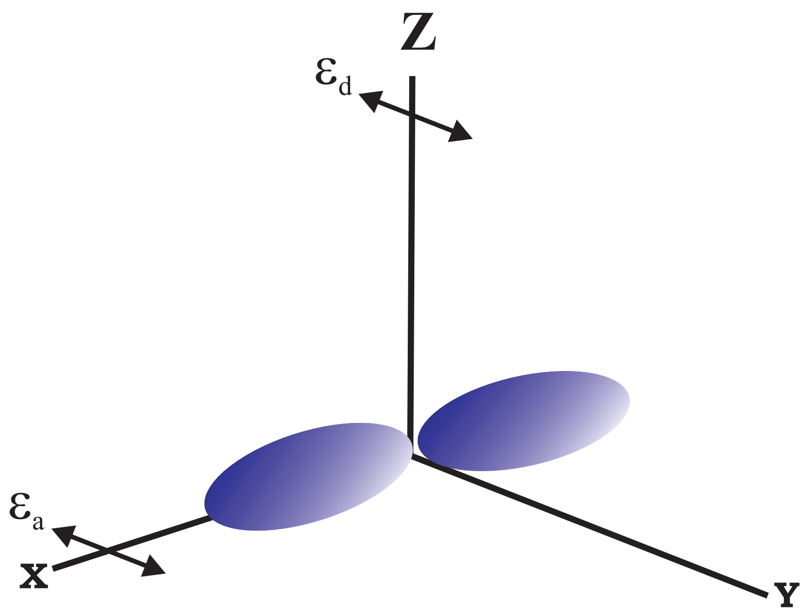
Alignment of $\boldsymbol{J}$ *reduced*



Nuclear spin, $\boldsymbol{I}$, becomes aligned.

Hyperfine quantum beats: NO(A)

Alignment of $\boldsymbol{J}$ *and* $\boldsymbol{I}$ *cycle in time*

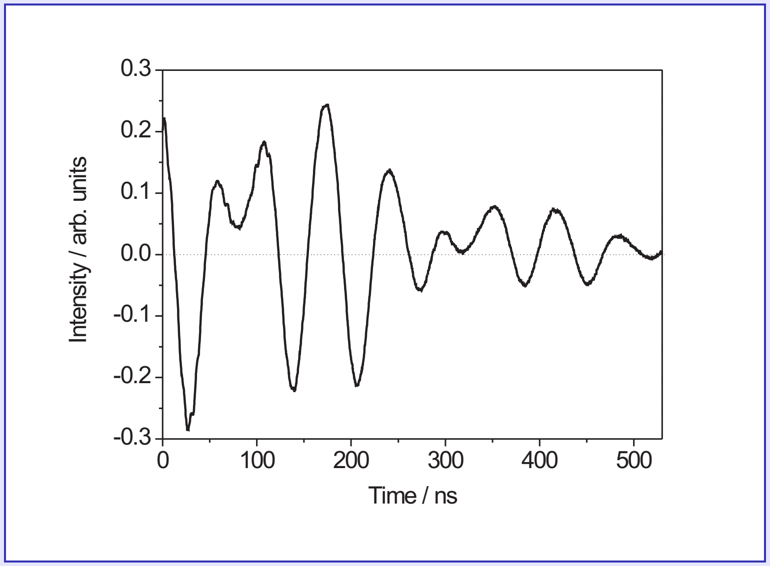


See T.P. Rakitzis, *Phys. Rev. Lett.* (2005)

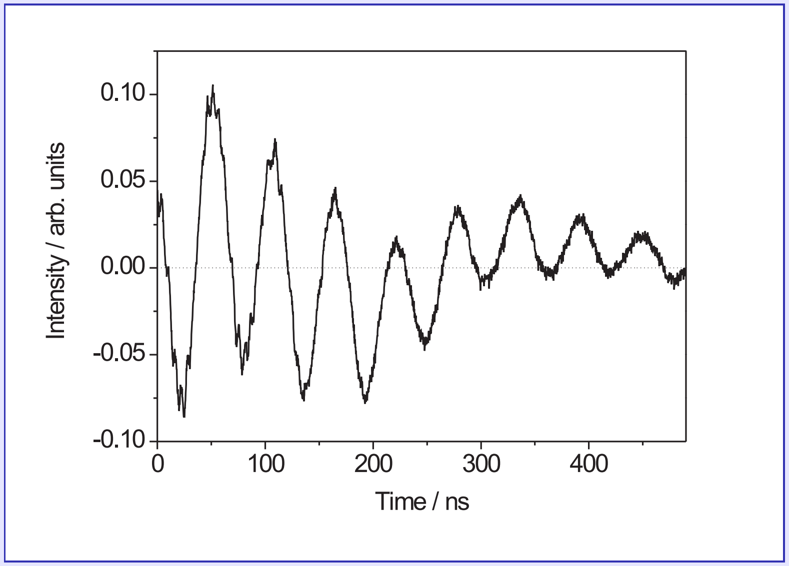
Hyperfine quantum beats: NO(A)

Beat signal

$S_{21}(0)\uparrow$



$R_{22}(4)\uparrow$

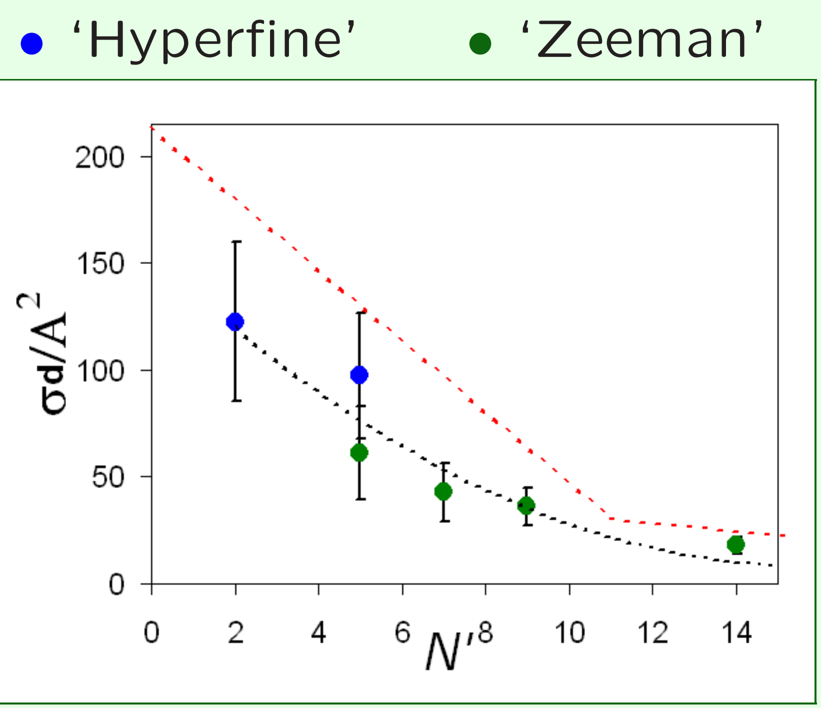


Amplitude decreases rapidly with J.

Hyperfine quantum beats: NO(A)

Depolarization cross-sections

NO(A) + Ar (300 K)



Reasonable agreement between hyperfine and Zeeman beat data

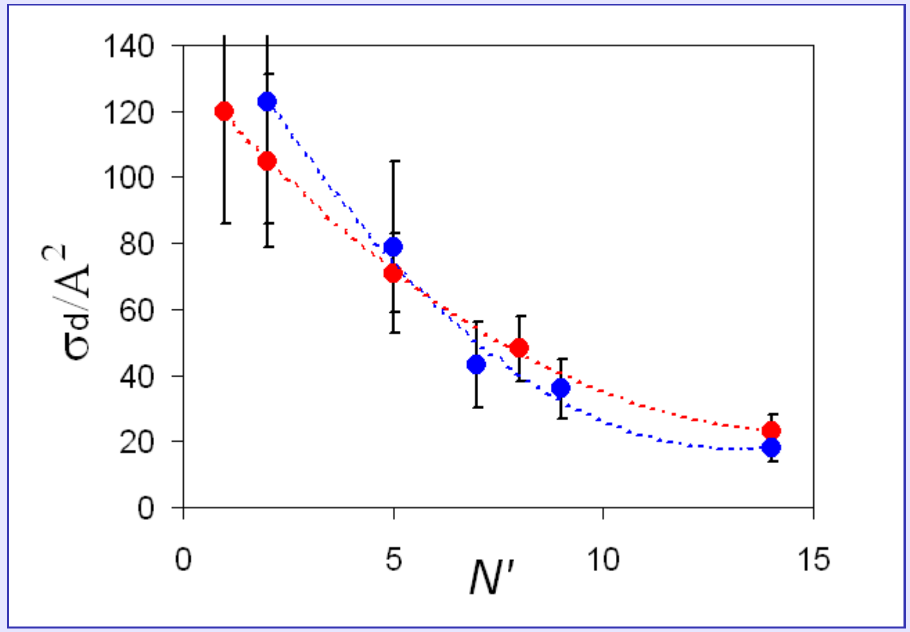
Depolarization is *less efficient* than RET ($a_2 > 0$ for NO(A) + Ar)

Trends in depolarization cross-sections

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

NO(A) + Ar ●

OH(A) + Ar ●



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

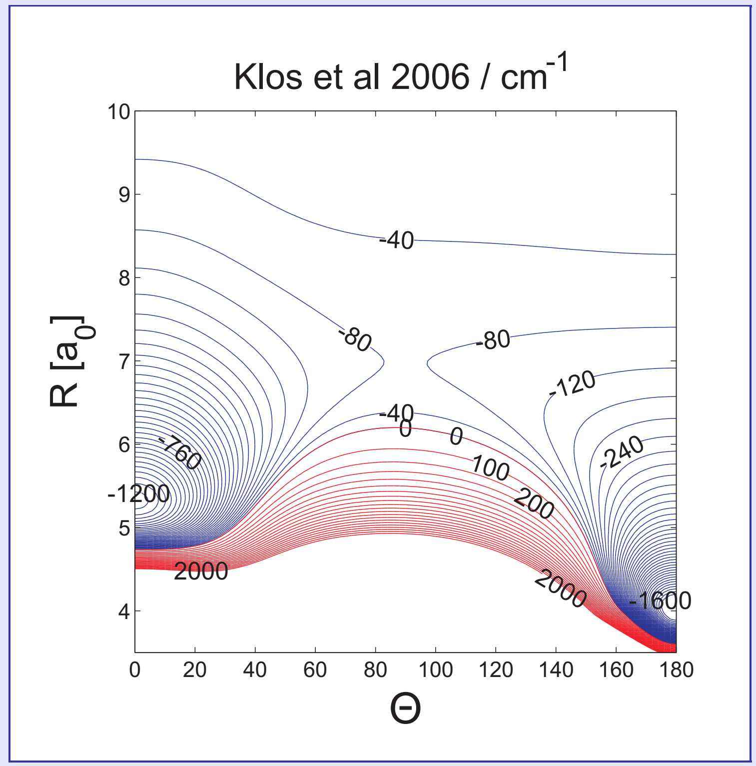
Balanced by kinematic/energetic factors

OH(A) + Ar potential

Strongly attractive and highly anisotropic PES

J. Kłos and M.H. Alexander,

in preparation (2007)



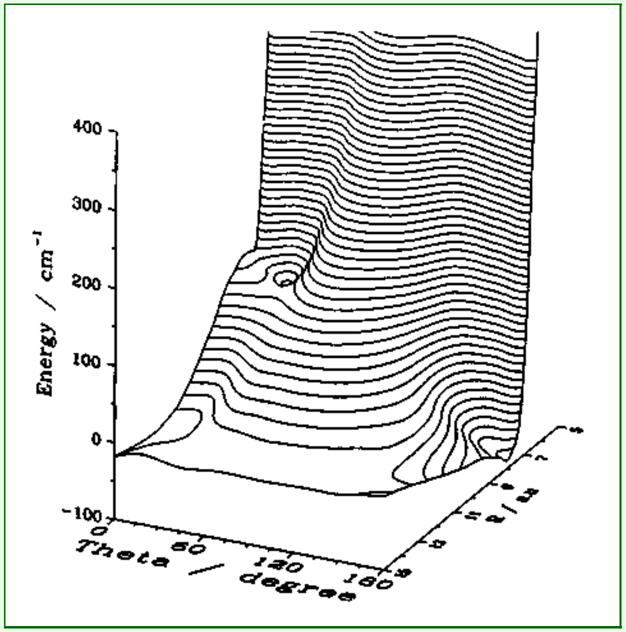
Well depth ~1600 cm^{-1}

NO(A) + Ar potential

Very weakly attractive PES

N. Shafizadeh *et al.*,

J. Chem. Phys (1998)



$D_0 \sim 44\,\mathrm{cm}^{-1}$ ‡

‡ T.G. Wright and coworkers, *J. Chem. Phys.* (2000)

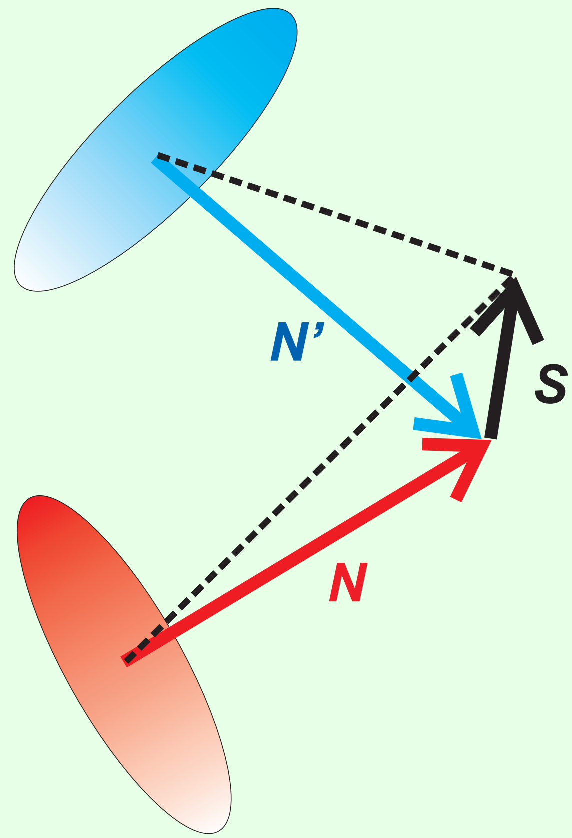
Role of electron and nuclear spin

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

$$f_2: \quad J = N - S$$

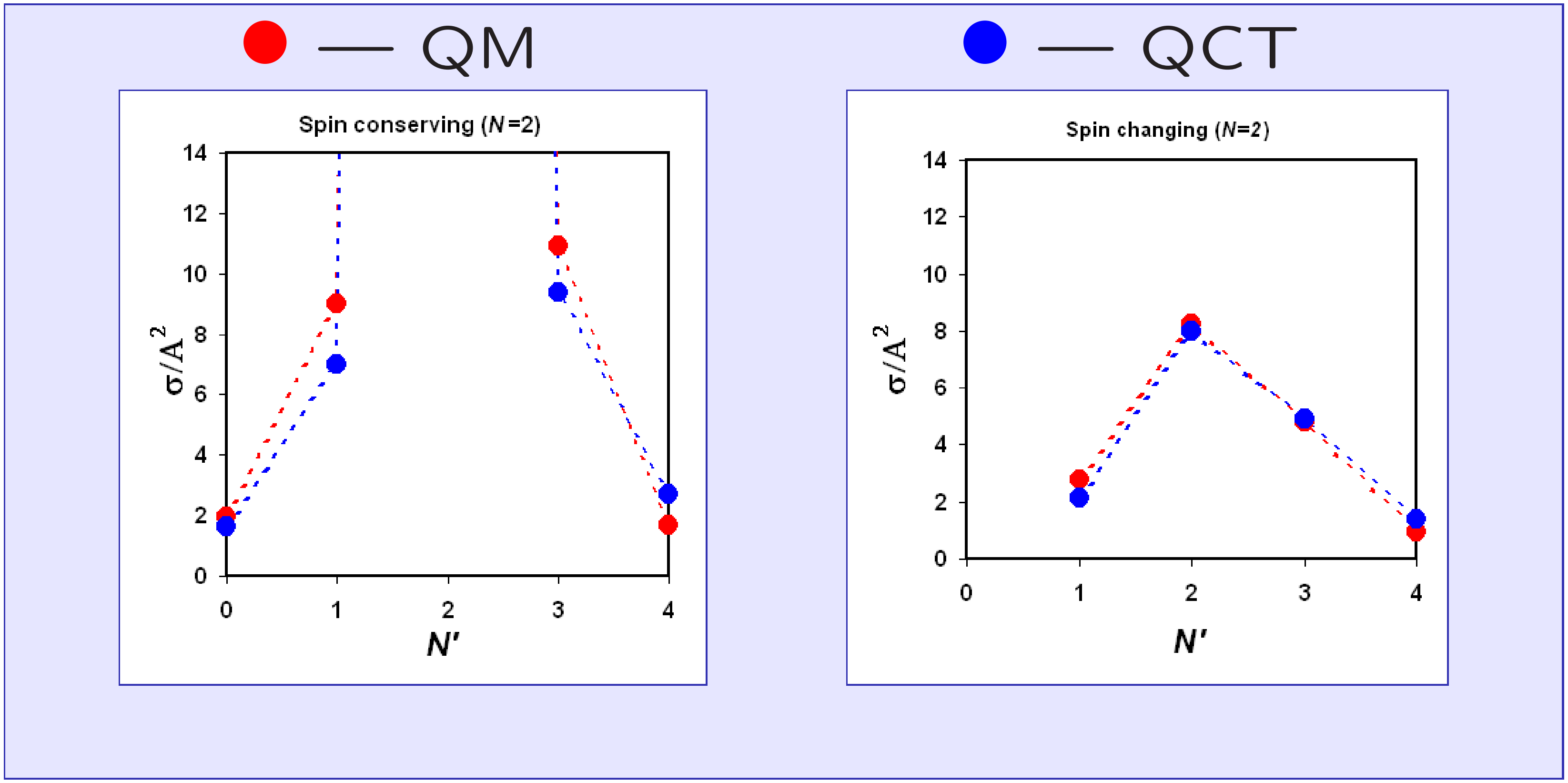
$$\uparrow$$

$$f_1: \quad J = N + S$$



Spin-rotation changing collisions only occur if $\boldsymbol{N}$ 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

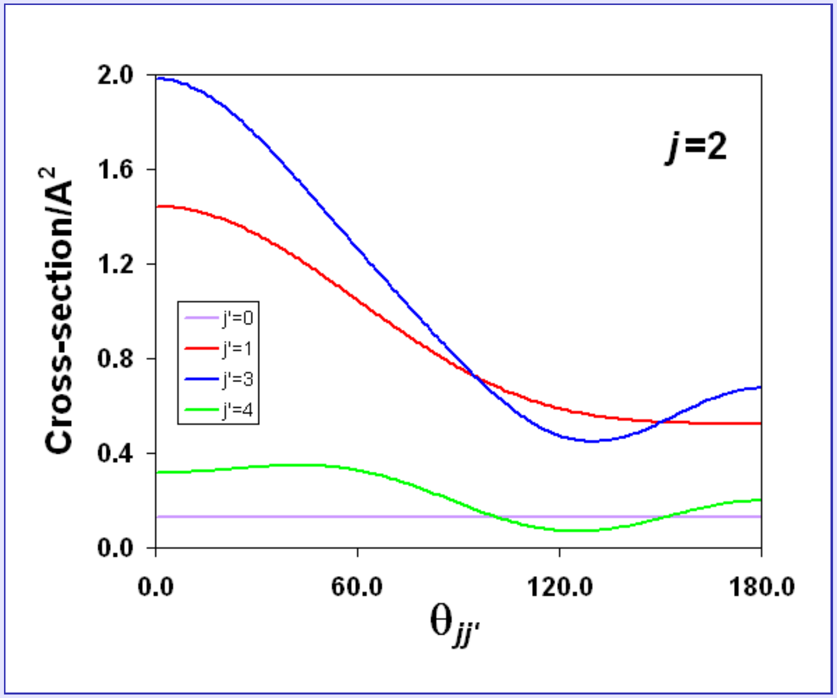
QM and new PES by J. Kłos and M.H. Alexander

OH(A) + Ar and spin-rotation changing collisions

Increasing K $\longrightarrow$

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

New PES by J. Kłos and M.H. Alexander

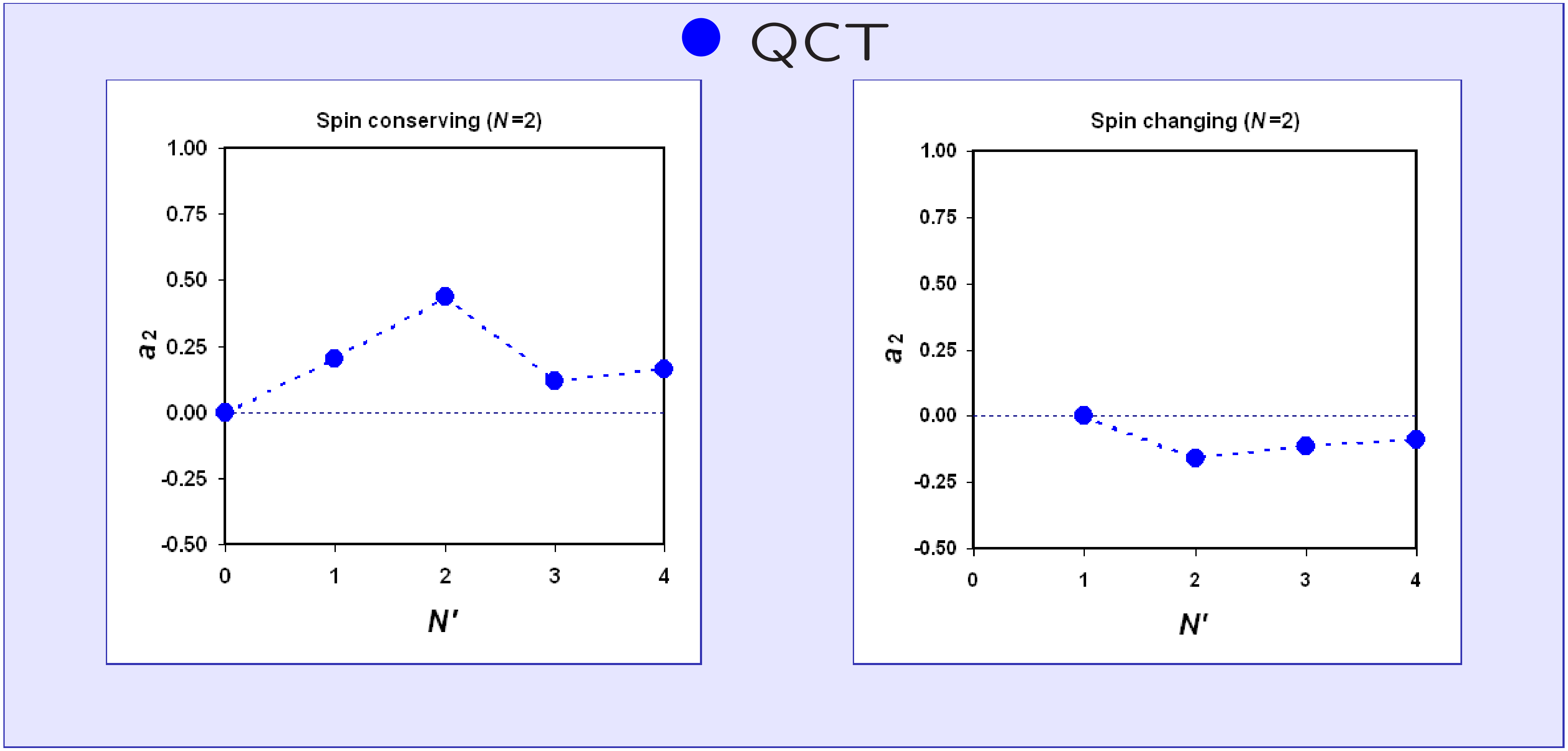


Spin-rotation changing collisions require large K

These are enhanced for OH(A) + Ar by the deep well

OH(A) + Ar and rotational energy transfer

'Disalignment' coefficients



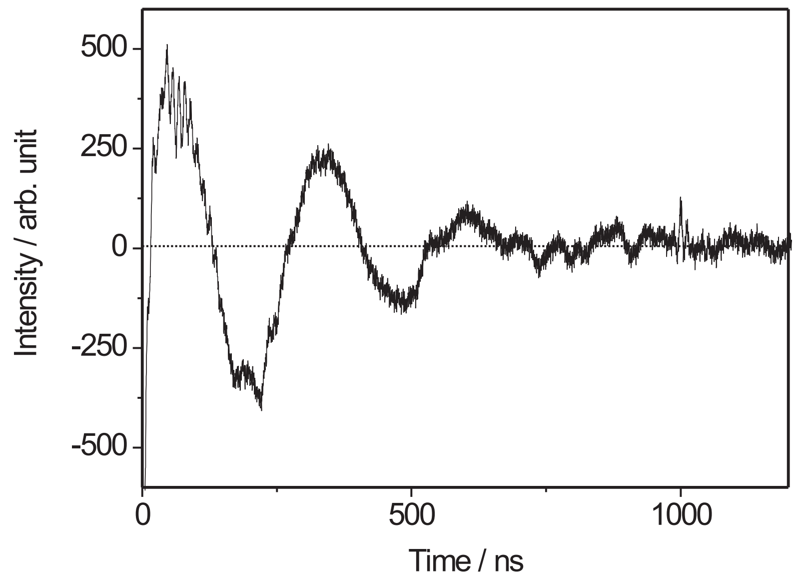
QCT calculations by C.J. Eyles and F.J. Aoiz

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 $\boldsymbol{S}$ and $\boldsymbol{I}$ are spectators in the collision.
- σ_{d} is large for spin-rotation and hyperfine state-changing collisions.

The End