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

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Acknowledgements

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Introduction

Angular momentum polarization

Photodissociation

$$\mathrm{ABC} + h\nu \longrightarrow \mathrm{A}(\mathbf{j}) + \mathrm{BC}(\mathrm{v}', \mathbf{j}')$$

Angular momentum can be polarized

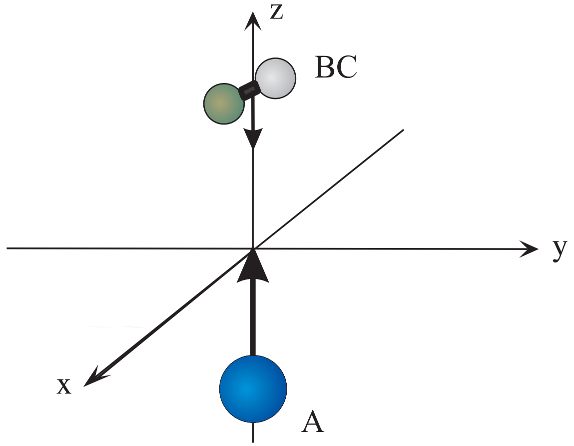
Measure angular distribution of $\mathbf{j}$ or $\mathbf{j}'$

Rotational Polarization

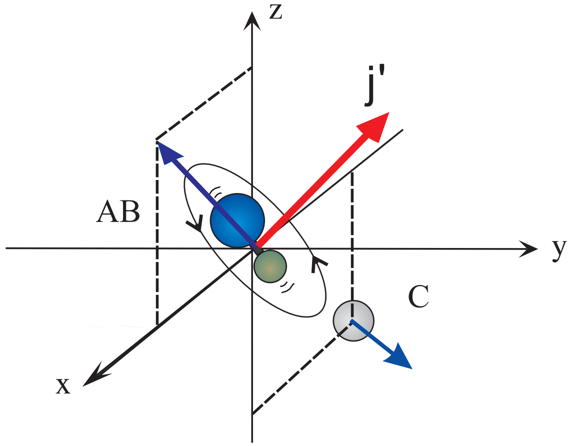
Reaction

$$\mathrm{A} + \mathrm{BC} \longrightarrow \mathrm{AB}(v', j') + \mathrm{C}(j'')$$

Reactants



Products



Torques generated on potential energy surface

Motivation

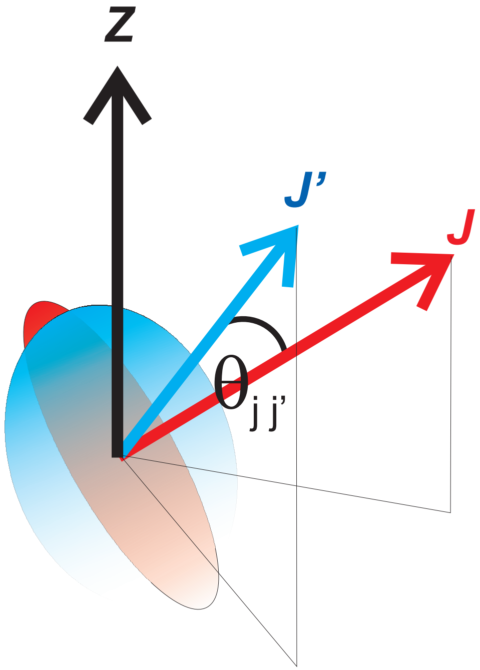
Rotational polarization

- Angular dependence of potential energy surface
- Mechanistic information

Aims

- Measure polarization using a weak magnetic field.
- Weak magnetic field effects in chemistry.
- Control of angular momentum orientation and alignment.

Collisional depolarization



- How easy is it to change the direction of **j** by collision?
- Quantified by cross-section, σ_d (also related to $a_2 = \langle P_2(\cos\theta_{\mathrm{j\,j'}})\rangle$)
- Relevant to the detection of OH(X) or NO(X) by LIF.

Zeeman quantum beat spectroscopy

OH source and detection

Pump

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

Probe

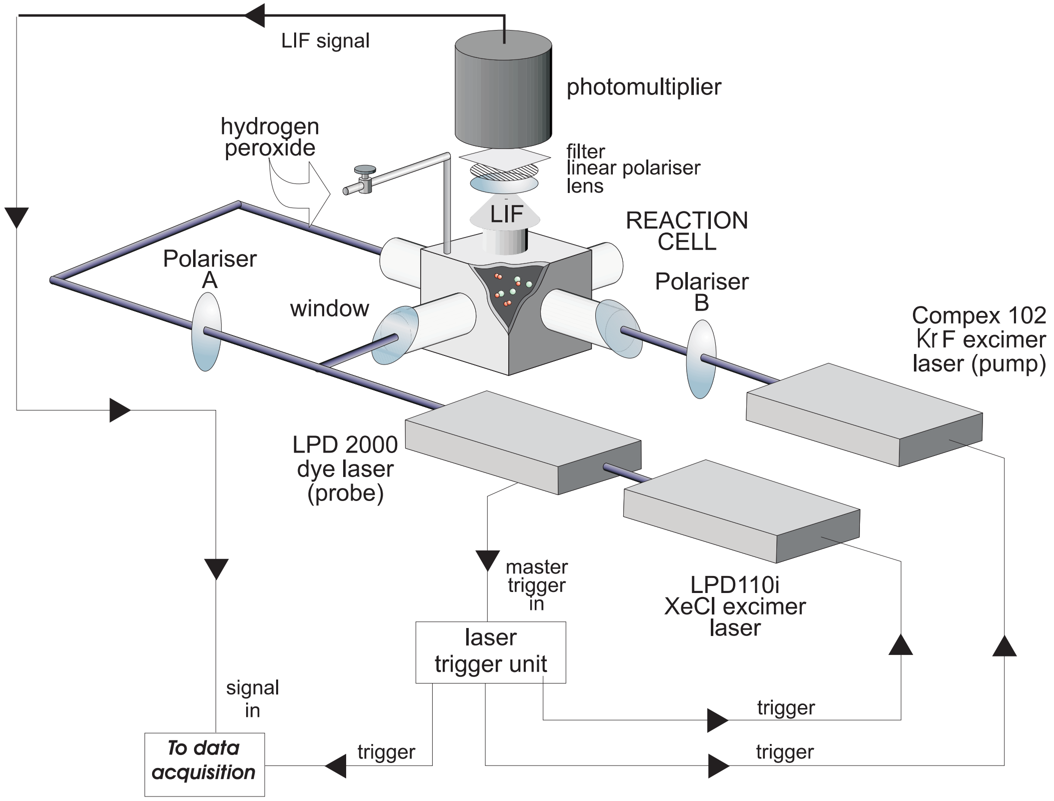
$$\mathrm{OH}(\mathrm{X}^2\Pi) + h\nu' \longrightarrow \mathrm{OH}(\mathrm{A}^2\Sigma)$$

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

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

Experiment

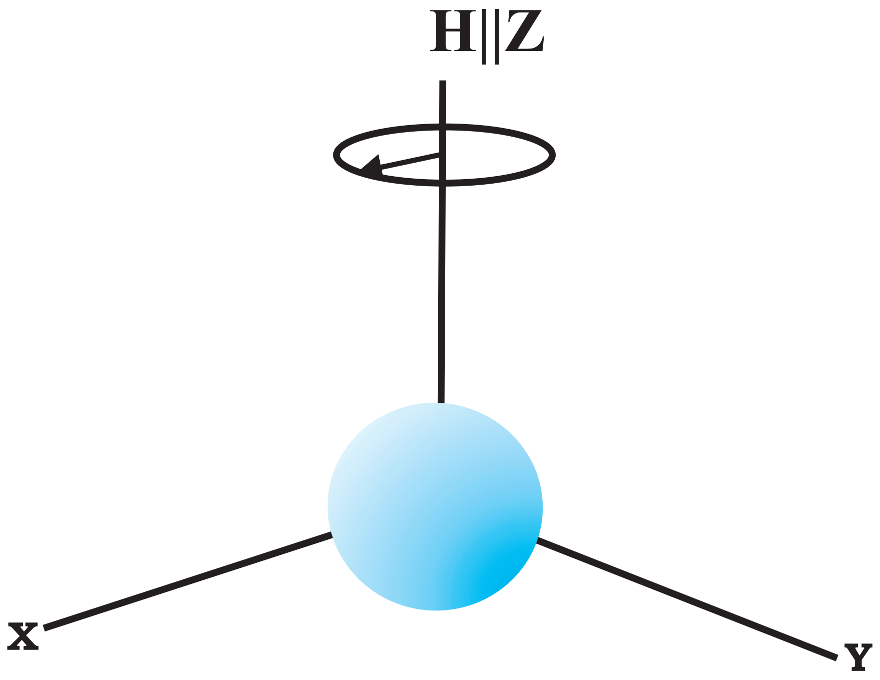
Detect OH($X^2\Pi$) by *polarized* laser induced fluorescence...



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

OH(X) spatial distribution

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

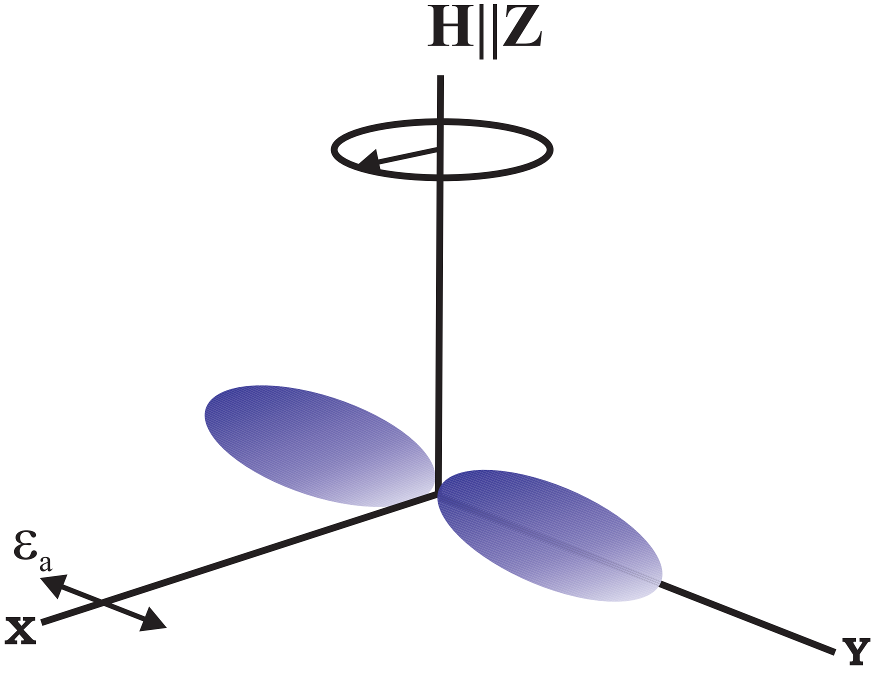


No net magnetic moment, *no precession about the field*

Initial OH(A) spatial distribution

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

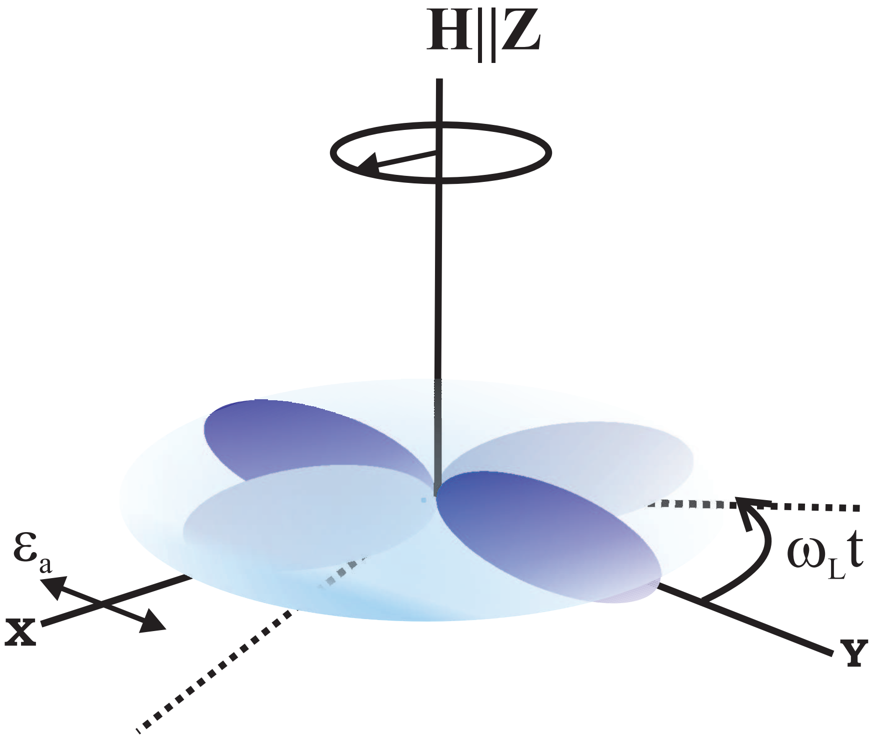
Transition probability $P \propto |\hat{\mu}_{\mathrm{OH}} \cdot \hat{\epsilon}_{\mathrm{a}}|^2$



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

Zeeman quantum beats

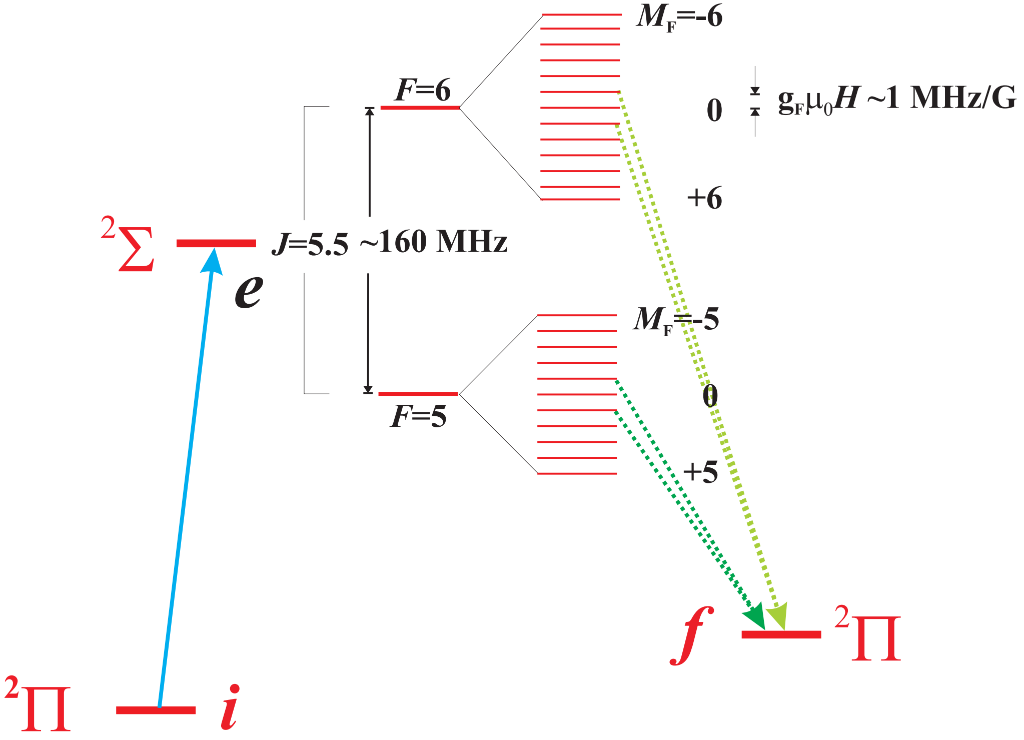
Precesses in magnetic field with *Larmor frequency*, ω_L.



Observe emission through a *linear polarizer*.

Zeeman quantum beats

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

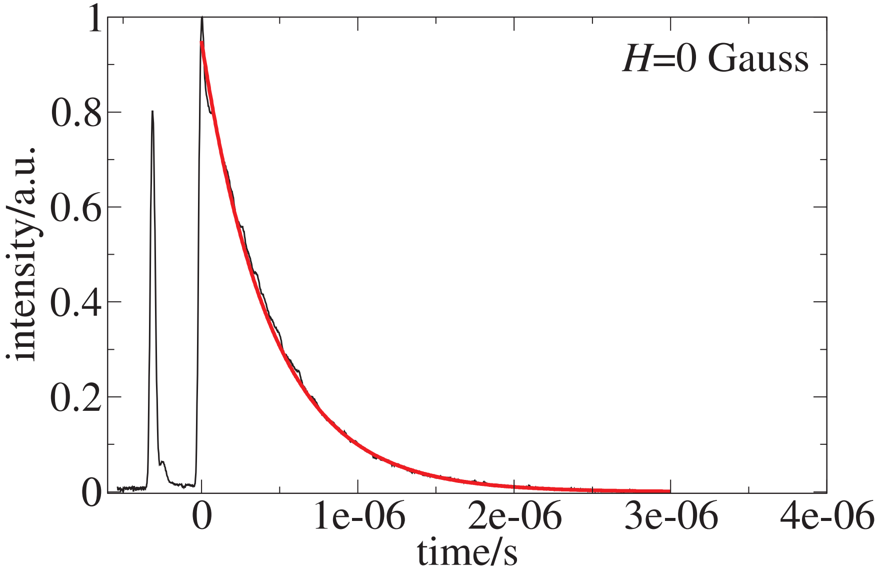


Coherent excitation of Zeeman levels.

Collisional depolarization
of
OH(A) and NO(A)

Zeeman quantum beats

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



Exponential *population* decay

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

Zeeman quantum beats

Population decay

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

$$\boxed{k_0 = k_{\mathrm{rad}} + k_{\mathrm{flyout}} + k_{\mathrm{q}}[\mathrm{H_2O}]}$$

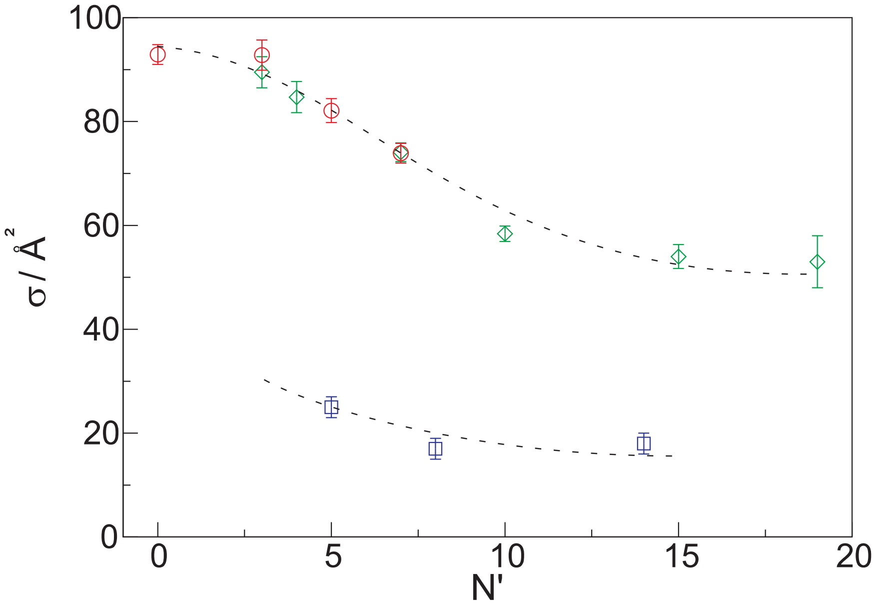
k_{rad} - *radiative decay* ($\tau_{\mathrm{rad}} \sim 700\,\mathrm{ns}$)

k_{flyout} - OH(A)* *flyout* on 1 μs timescale ($v_{\mathrm{OH}} \sim 3500\,\mathrm{m\,s^{-1}}$)

k_{q} - *electronic quenching* ($k_{\mathrm{q}} = v_{\mathrm{rel}}\,\sigma$)

Zeeman quantum beats

Electronic quenching by H_2O: $v_{\mathrm{rel}} \sim 3500\,\mathrm{m\,s^{-1}}$

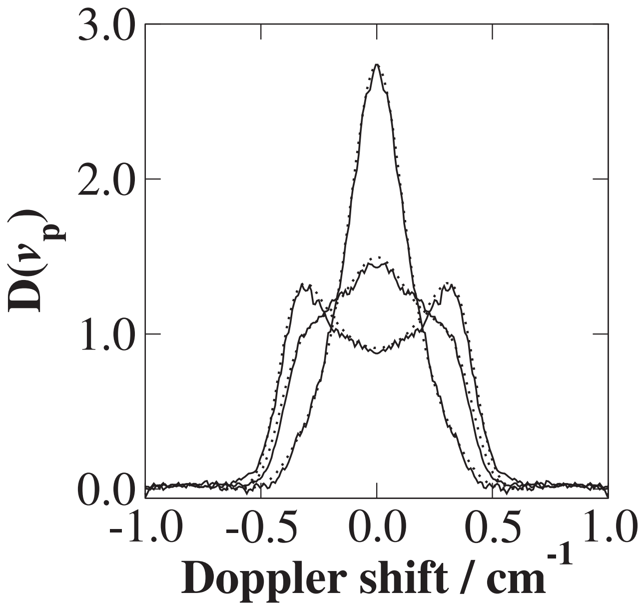


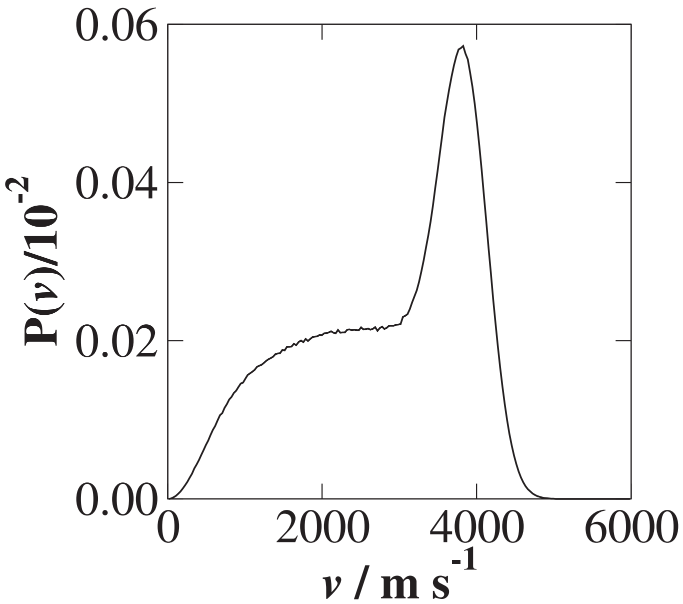
Comparison with the 300 K *measurements* of:

Cleveland and Wiesenfeld (◊) and Copeland *et al.* (●).

Zeeman quantum beats

Translational cooling of OH(X): Doppler resolved LIF





60 mTorr, 750 ns

Reveals average $v_{\mathrm{OH}} \sim 3500\,\mathrm{m\,s^{-1}}$ on 700 ns timescale.

Indicative of the likely extent of *relaxation* in OH(A).

Zeeman quantum beats

Electronic quenching by H_2O: $v_{\mathsf{rel}} \sim 3500\,\mathrm{m\,s^{-1}}$

Capture model

$$\sigma(E_{\mathsf{t}}) = \pi R_{\mathsf{H}}^2\, P_{\mathsf{H}} \left[1 \;+\; \frac{V(R_{\mathsf{H}})}{E_{\mathsf{t}}} \right]$$

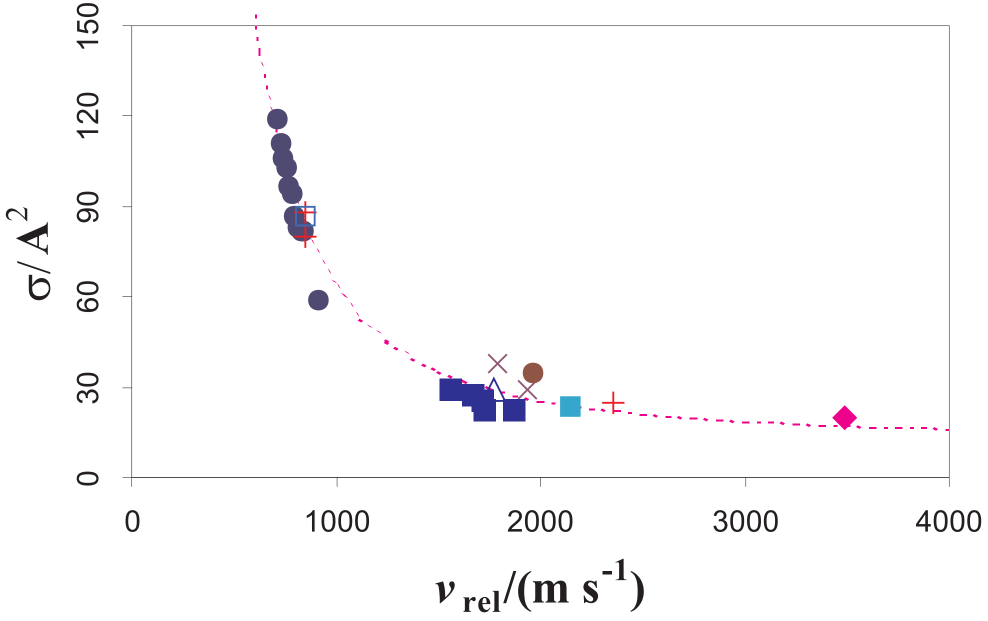
Conical intersections: Schatz and Coworkers and Lester and coworkers

Complex formation: Crosley and coworkers

Harpoon mechanism: Heard and Paul and coworkers

Zeeman quantum beats

Electronic quenching by H_2O*:* $v_{\mathrm{rel}} \sim 3500\,\mathrm{m\,s^{-1}}$



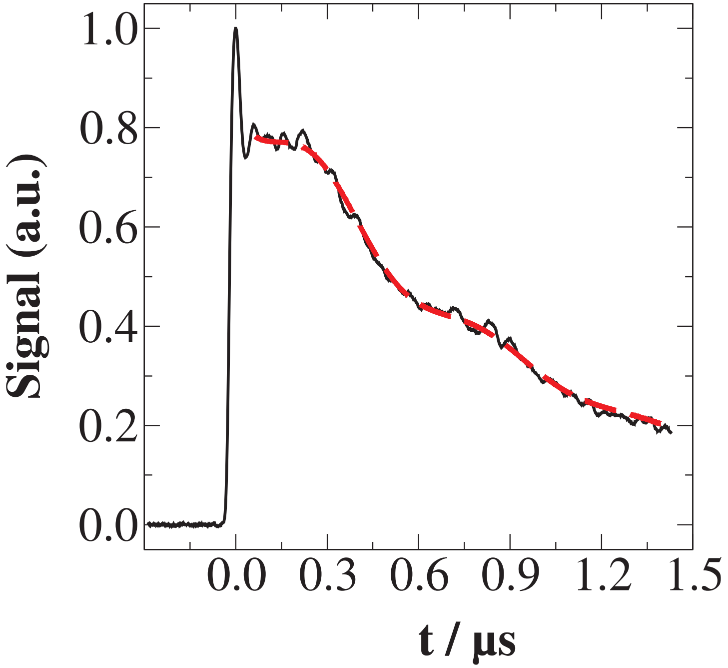
Comparison with kinetic data (this work ◆)

Heard and Paul and coworkers, *Chem. Phys. Lett.* (1999) and references therein.

Zeeman quantum beats

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

$H = 4$ Gauss



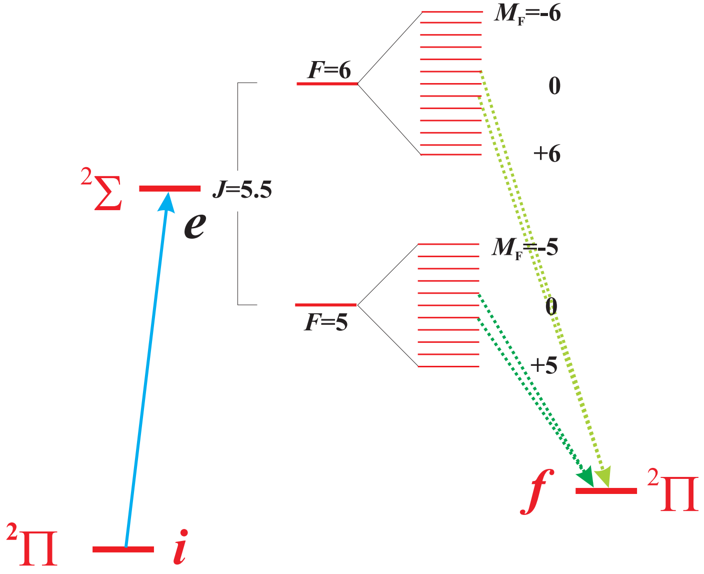
$$[\mathrm{OH}^*] = [\mathrm{OH}^*]_0\, \mathrm{e}^{-k_0 t}\{1 + C\, \mathrm{e}^{-k_2 t} \sum_F \cos\left(2\pi\omega_{\mathrm{L}} t + \phi\right)\}$$

Zeeman quantum beats

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

with

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

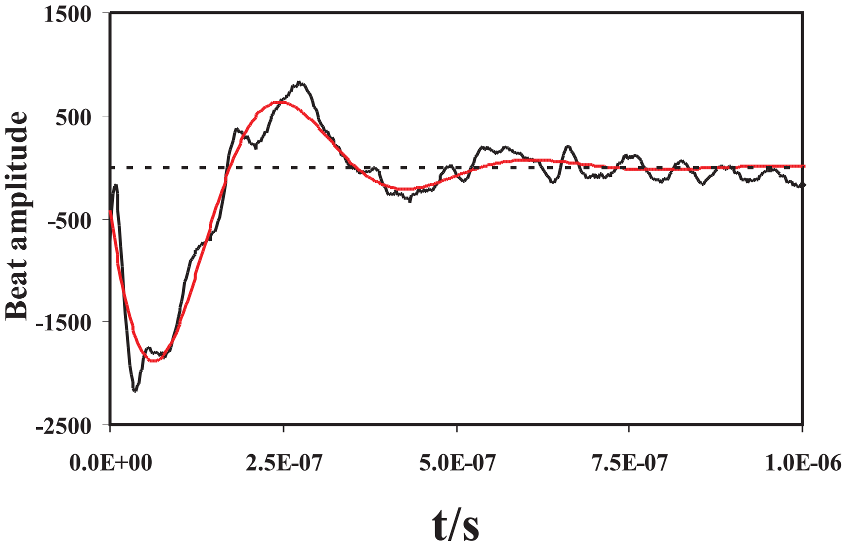


Oscillations at *two frequencies* for $F = 5$ and 6.

Zeeman quantum beats

Depolarization and dephasing: Beat amplitude, C

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

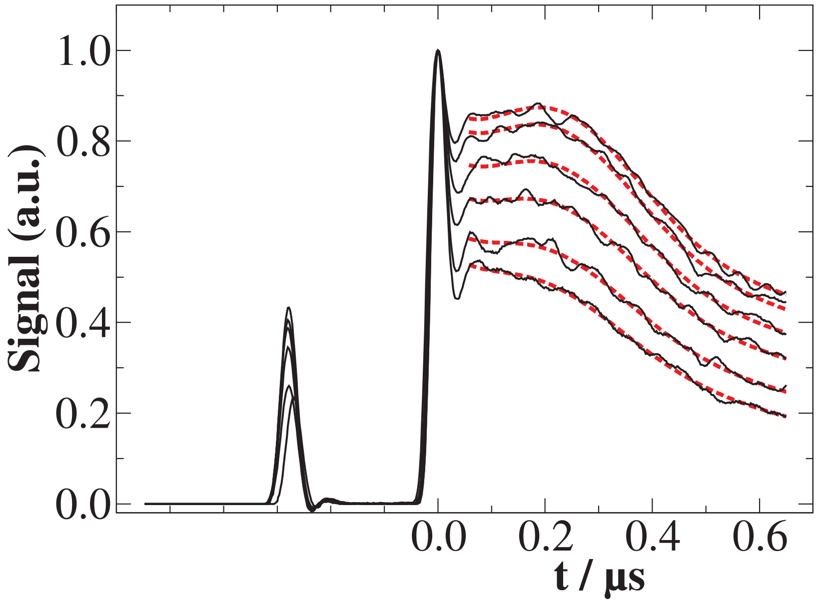


Proportional to *rotational alignment* of excited OH(A)

$C = 0.102 \pm 0.017$ (theory gives 0.096).

Zeeman quantum beats

With Field: Pressure dependence.



0 mTorr H_2O

↓

39 mTorr H_2O

Collisional *population decay* and *depolarization*

Zeeman quantum beats

Depolarization and dephasing

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

$$\boxed{k_2 = k_\mathrm{inhom} + k_\mathrm{d}\,[\mathrm{H_2O}]}$$

k_inhom - dephasing by *field inhomogeneities*

k_d - collisional depolarization, $k_\mathrm{d} = k_\mathrm{ret} + k_\mathrm{vel} \sim v_\mathrm{rel}\,\sigma_\mathrm{d}$

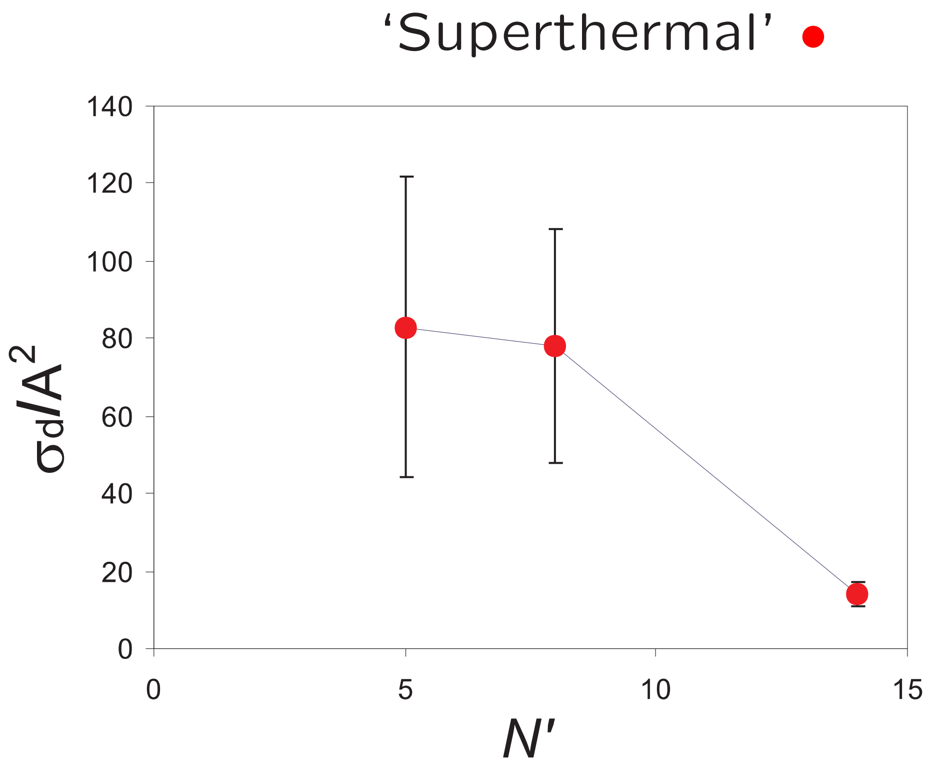
k_ret - depolarization by inelastic (*rotational energy transfer*) collisions

k_vel - depolarization by elastic (*velocity changing*) collisions

Zeeman quantum beats

Trends in depolarization cross-sections:

$OH(A) + H_2O$

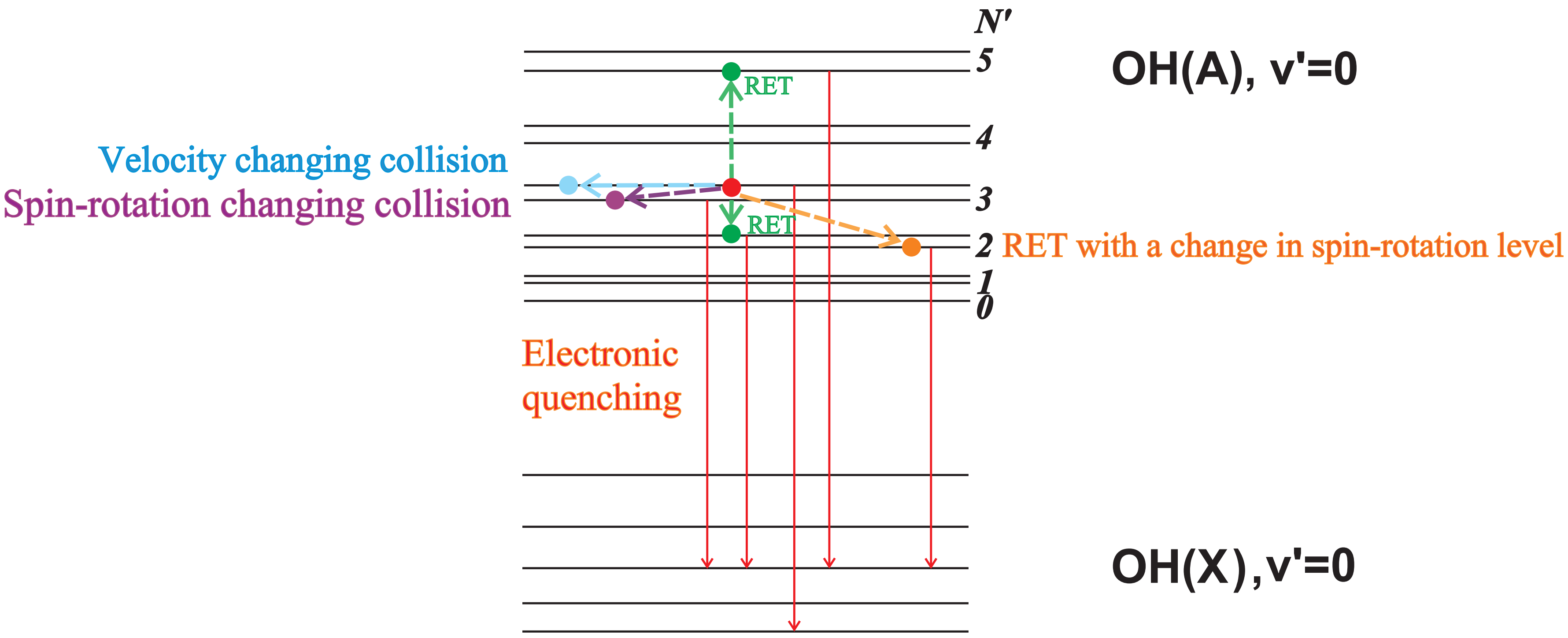


Cross-sections are *large* (long range interaction).

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

Zeeman quantum beats

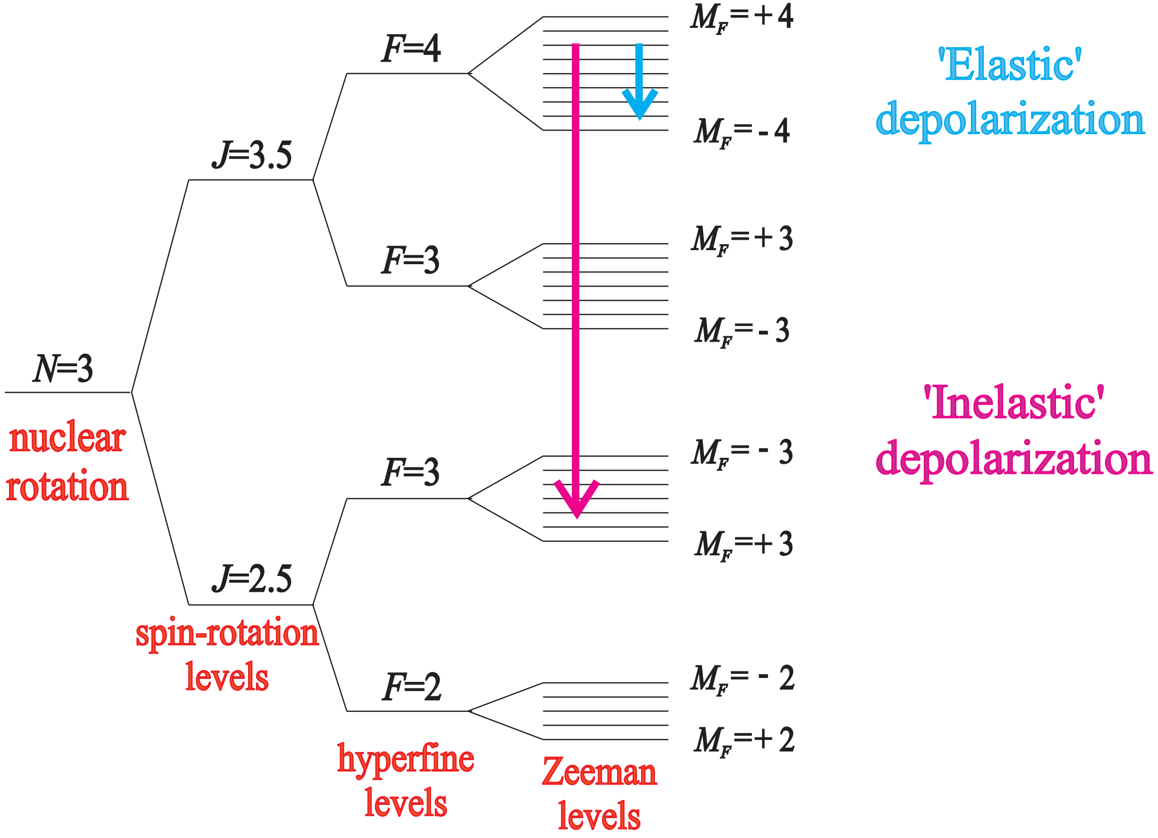
Collisional processes leading to depolarization



Both elastic and inelastic processes contribute to k_{d}

Zeeman quantum beats

Examples of collisional depolarization

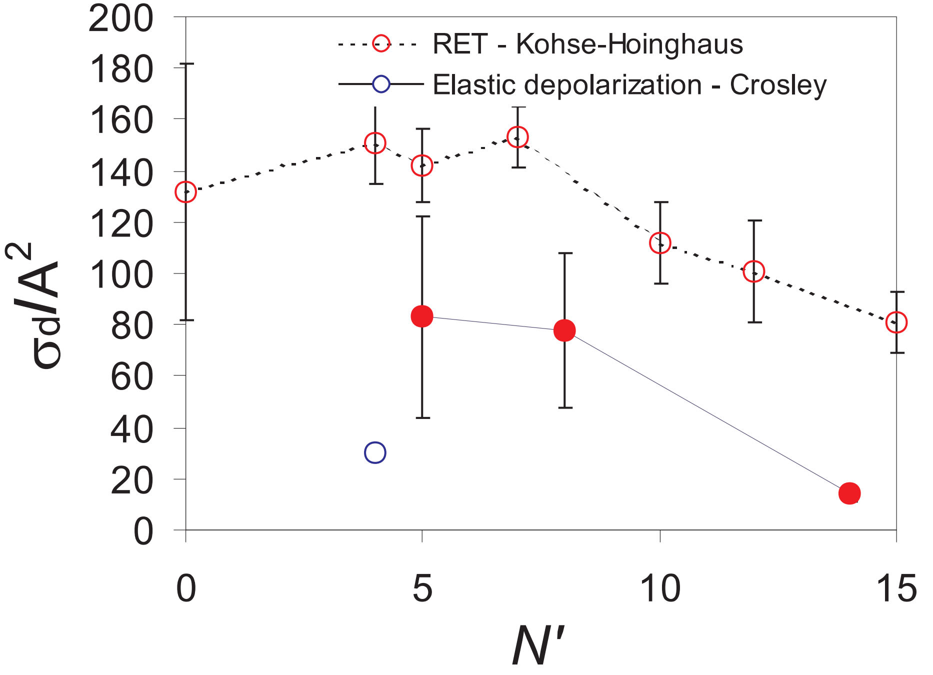


Zeeman quantum beats

Comparison with rotational energy transfer:

$OH(A) + H_2O$

'Superthermal' ●

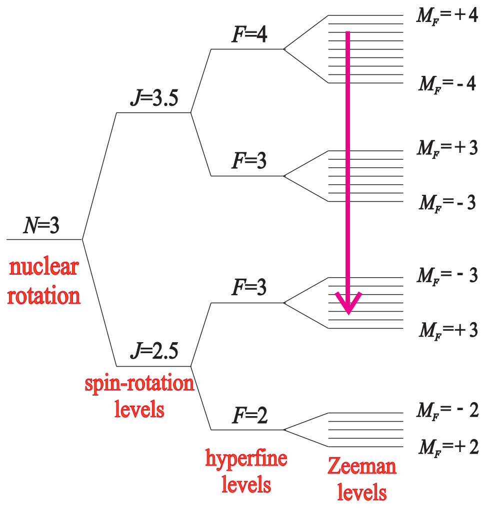


Depolarization *less efficient* than RET (for this system).

Both *elastic and inelastic* depolarization play a role.

Zeeman quantum beats

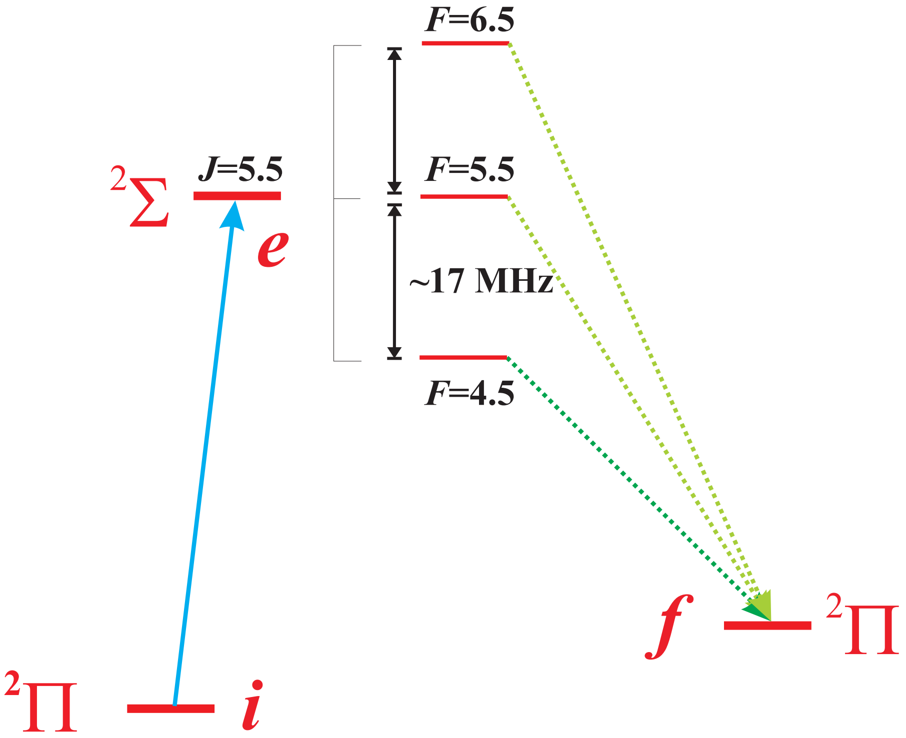
Caveat: we detect unresolved OH(A) emission



- 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)

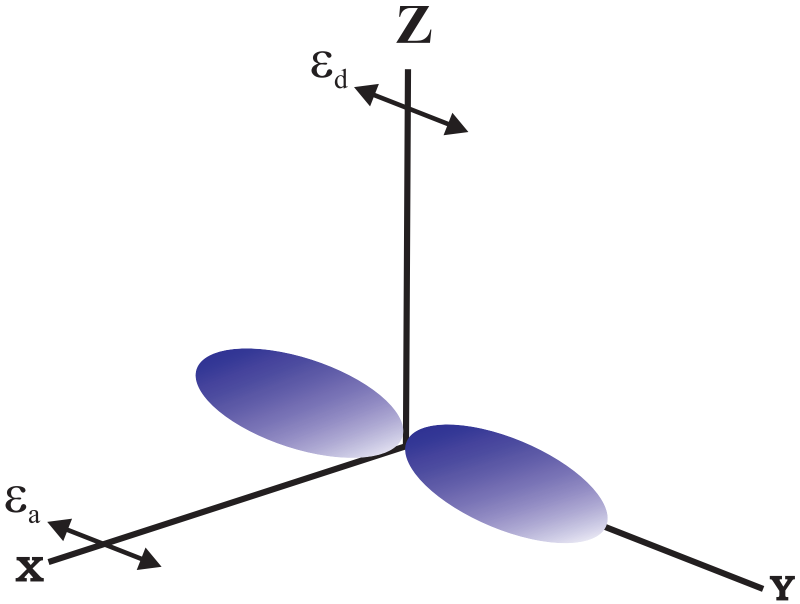
Coherent superposition of hyperfine levels (Low N')



Observe two of the three Hyperfine beat frequencies.

Hyperfine quantum beats: NO(A)

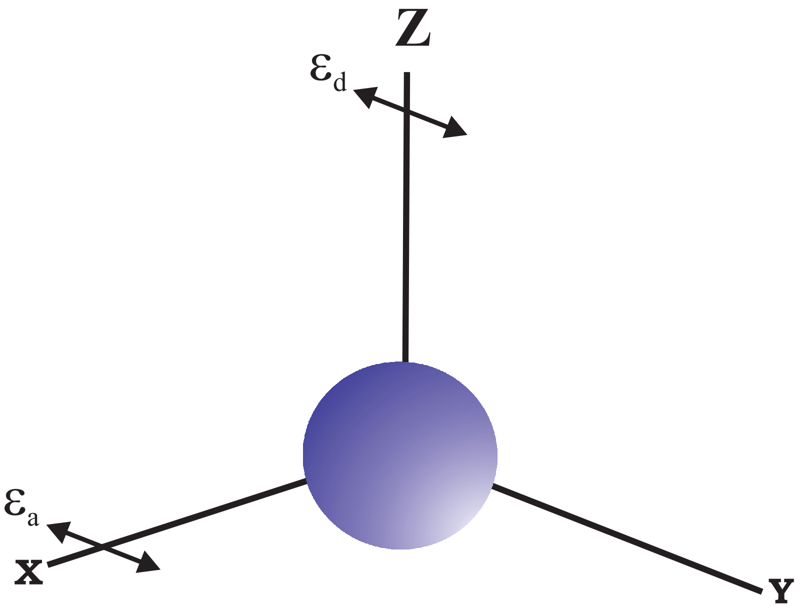
Initial distribution of **J**



Nuclear spin, **I**, initially unpolarized.

Hyperfine quantum beats: NO(A)

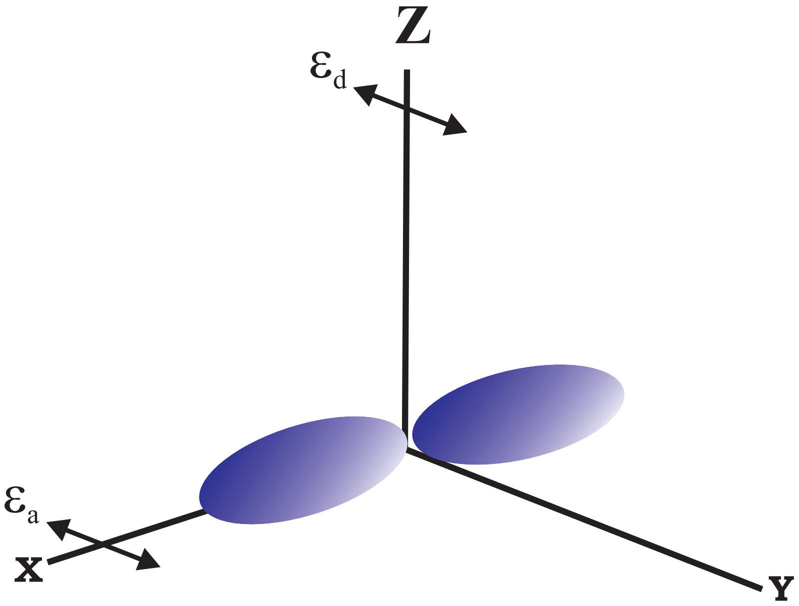
Alignment of **J** *reduced*



Nuclear spin, **I**, becomes aligned.

Hyperfine quantum beats: NO(A)

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

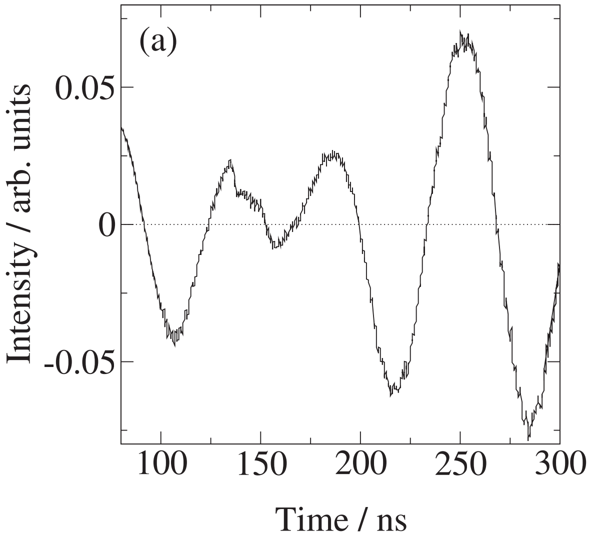


See T.P. Rakitzis, *Phys. Rev. Lett.* (2005)

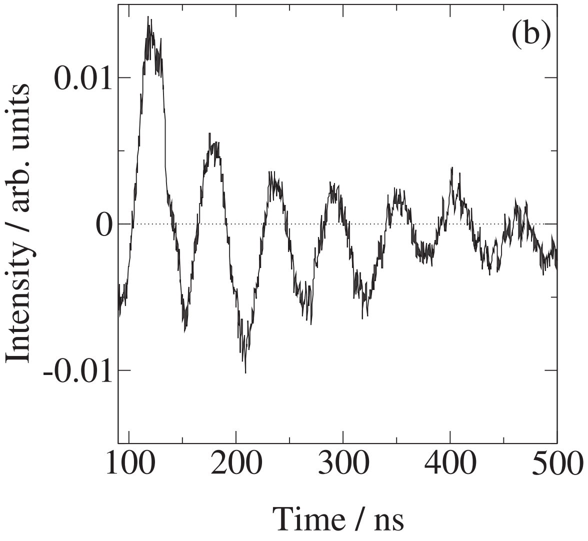
Hyperfine quantum beats: NO(A)

Beat signal

$S_{21}(0) \uparrow$



$R_{22}(4) \uparrow$

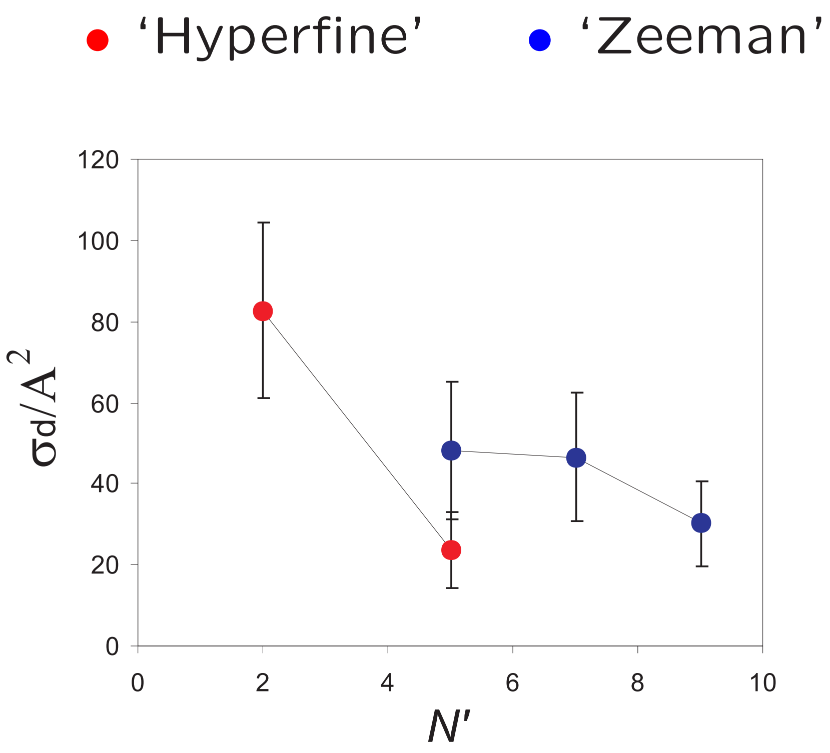


Amplitude decreases rapidly with J.

Hyperfine quantum beats: NO(A)

Depolarization cross-sections

$NO(A) + N_2$

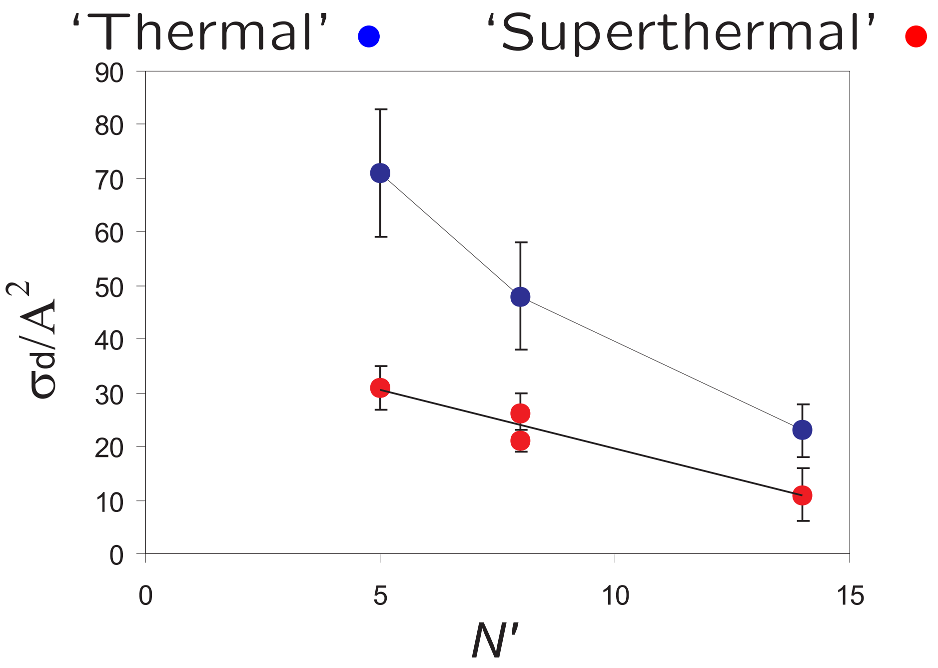


Reasonable agreement with Zeeman beat data.

Zeeman quantum beats

Trends in depolarization cross-sections

OH(A) + Ar



Ar is much *less efficient* at depolarizing than water.

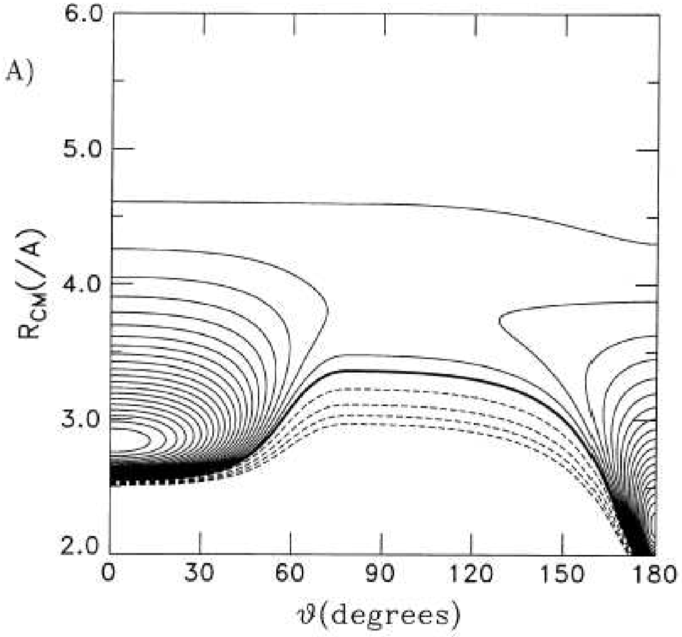
Thermal cross-sections *much larger* than 'superthermal' cross-sections.

Long range interactions important (cf. electronic quenching).

Zeeman quantum beats

Depolarization cross-sections

OH(A) + Ar



Relatively attractive and highly *anisotropic* PES.

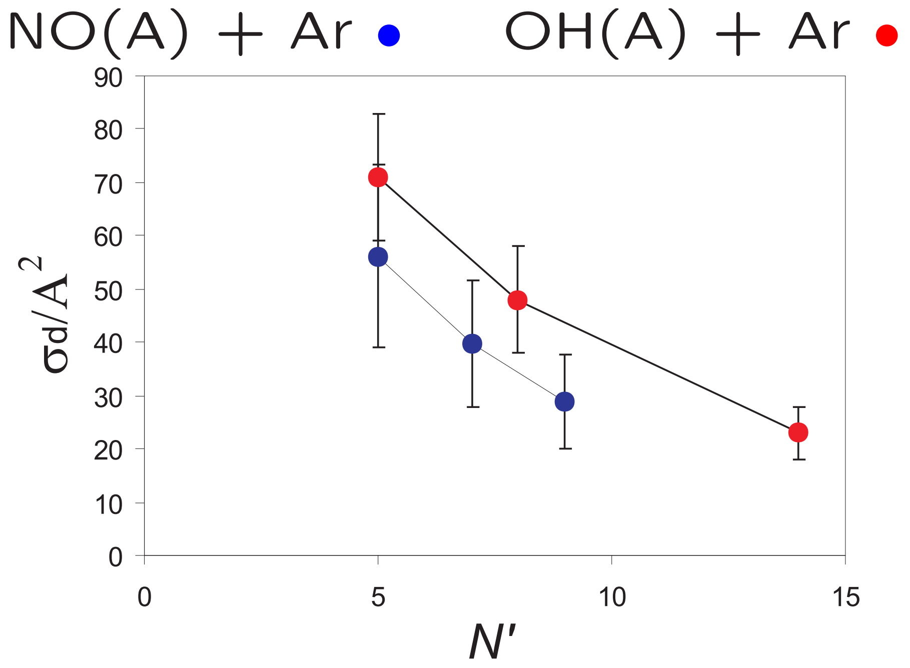
Well depth about 1000 cm^{-1}.

T.A. Miller and coworkers, *J. Mol. Struct.* (2000).

Zeeman quantum beats

Trends in depolarization cross-sections

OH(A)/NO(A) + Ar



Ar depolarizes NO(A) *less efficiently* than it does OH(A).

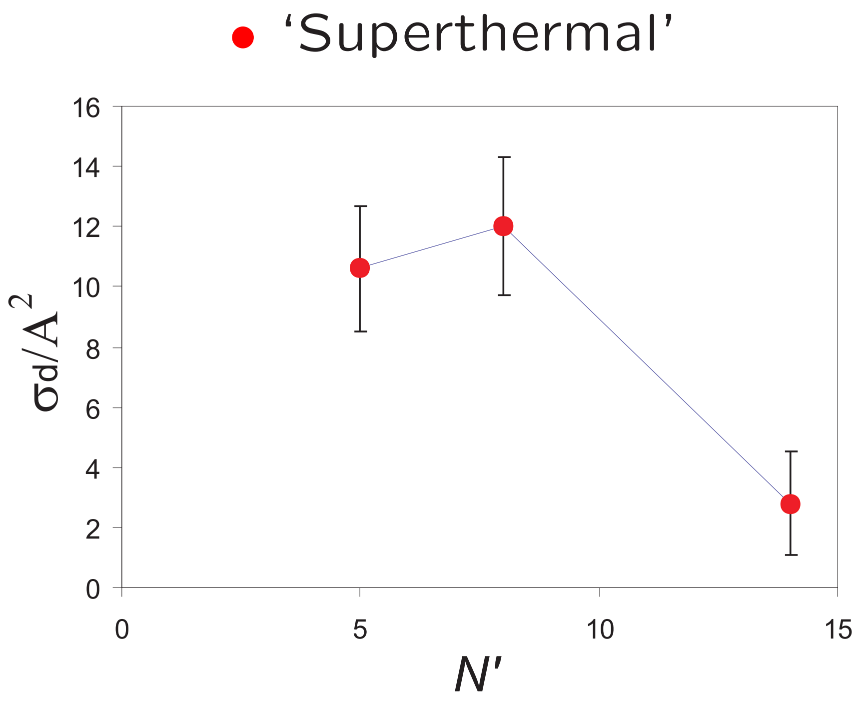
Well-depth for NO(A)+Ar is about *one tenth* that of OH(A)+Ar.

Kinematic/energetic differences may also be important.

Zeeman quantum beats

Depolarization cross-sections: potentially reactive system

$\mathrm{OH(A)} + \mathrm{H_2}$



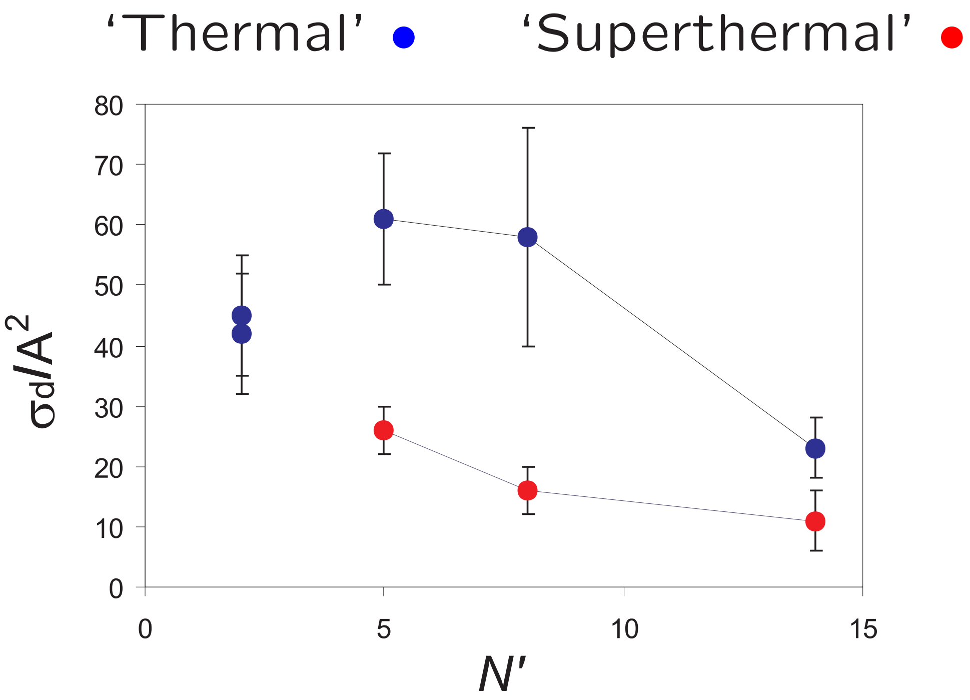
$\mathrm{H_2}$ *behaves similarly* to non-reactive systems.

Reactive region of the potential not important for depolarization.

Zeeman quantum beats

Depolarization cross-sections: potentially reactive system

$OH(A) + N_2$



Ar and N_2 *behave similarly* although OH(A) can *react* with N_2.

The *lowest rotational levels* appear to behave differently.

Zeeman quantum beats

Collisional depolarization: Some conclusions.

- Less efficient at high N' - *angular momentum conservation*.
- Seems to involve a long-range interaction - *cf., RET*.
- Both elastic and inelastic depolarization play a role.
- Depolarization efficiency relative to RET is very system dependent.
- For OH(A) + H_2/N_2 - *reactive channel not sampled*.

Zeeman quantum beats

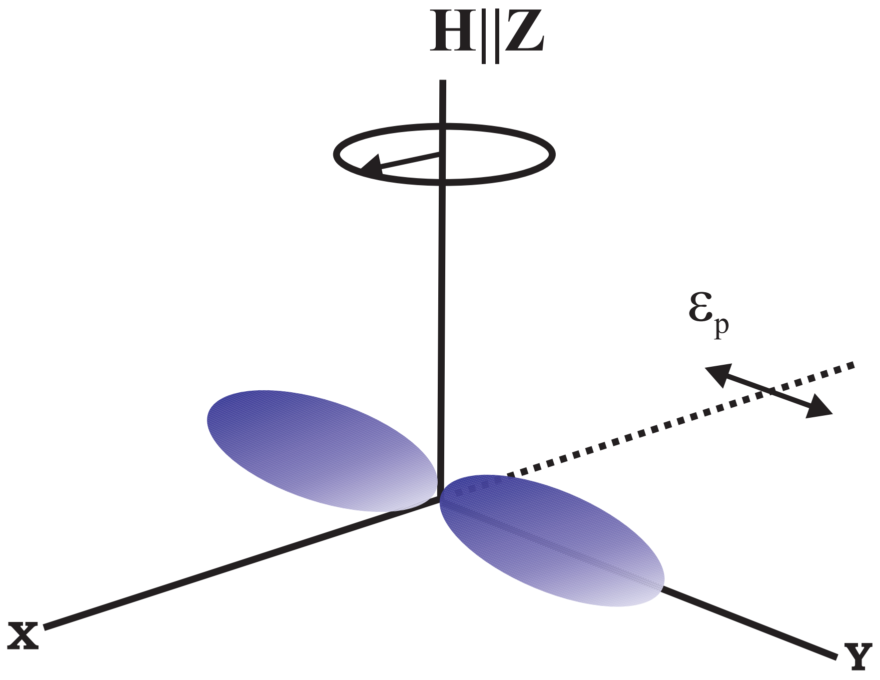
Collisional depolarization: Future directions.

- QM or QCT scattering calculations (in progress).
- Resolve emission (significantly increases beat amplitude).
- What happens at low N', where electron spin is significant?
- Measurement of polarization in OH(X) or NO(X).
- Control of angular momentum polarization.

Future work: probing OH(X) polarization

Faraday rotation

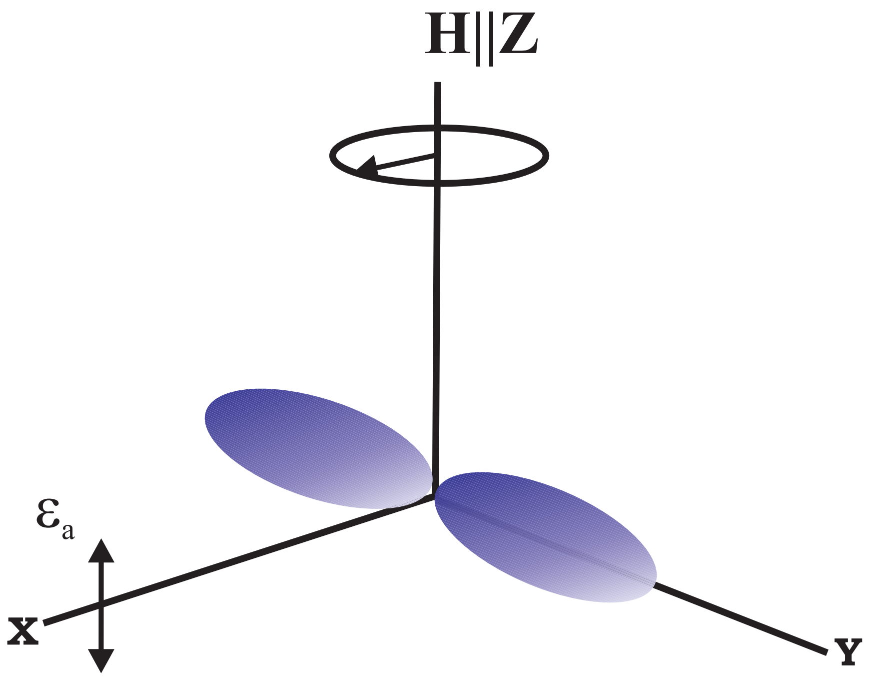
$$e.g., \qquad \mathrm{H_2O_2} + h\nu \longrightarrow \mathrm{OH(^2\Pi)} + \mathrm{OH(^2\Pi)}$$



Generates *aligned* distribution of $\mathrm{OH(^2\Pi)}$ radicals.

Faraday rotation

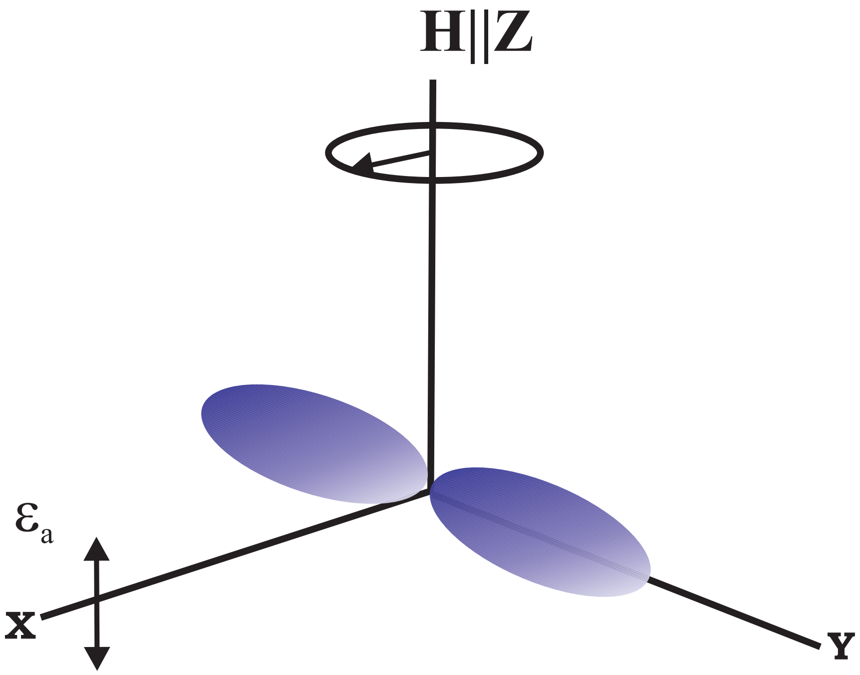
Use short pump-probe laser delay



Excite OH($^2\Pi$) with *vertically* polarized probe radiation.

Faraday rotation

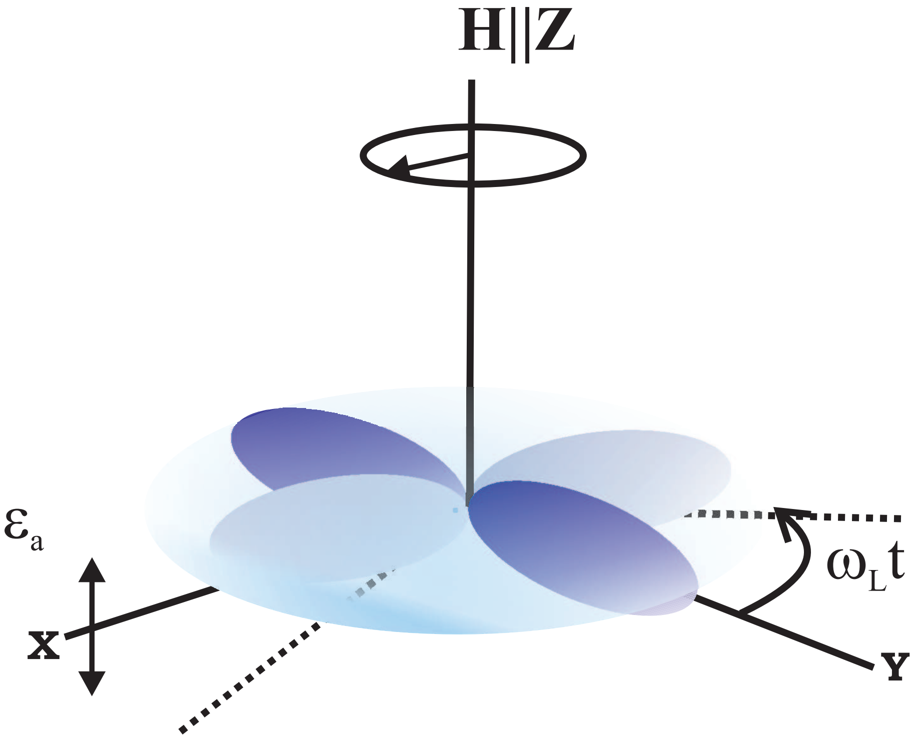
Generate *aligned* ensemble of excited OH($^2\Sigma$) radicals.



Alignment in ground state OH($^2\Pi$) is mapped onto OH($^2\Sigma$).

Faraday rotation

Precesses in magnetic field with *Larmor frequency*, ω_L



Observe emission through a *linear polarizer*.

The end