Quantum beat studies of angular momentum polarization in chemical processes.

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Acknowledgements

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Collaborations

F. Javier Aoiz	QCT calculations
Jaçek Kłos	PES & QM calculations
Millard H. Alexander	PES & QM calculations
Marcelo P. de Miranda	Stereodynamics
Steven Stolte	He/Ar + NO(X)

Funding

EPSRC
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Plan

Quantum beat spectroscopy

Applications to:

Collisional depolarization: this talk

Molecular photodissociation: poster (Yuan-Pin Chang)

Future directions: poster (Yuan-Pin Chang)

Motivation

Rotational polarization

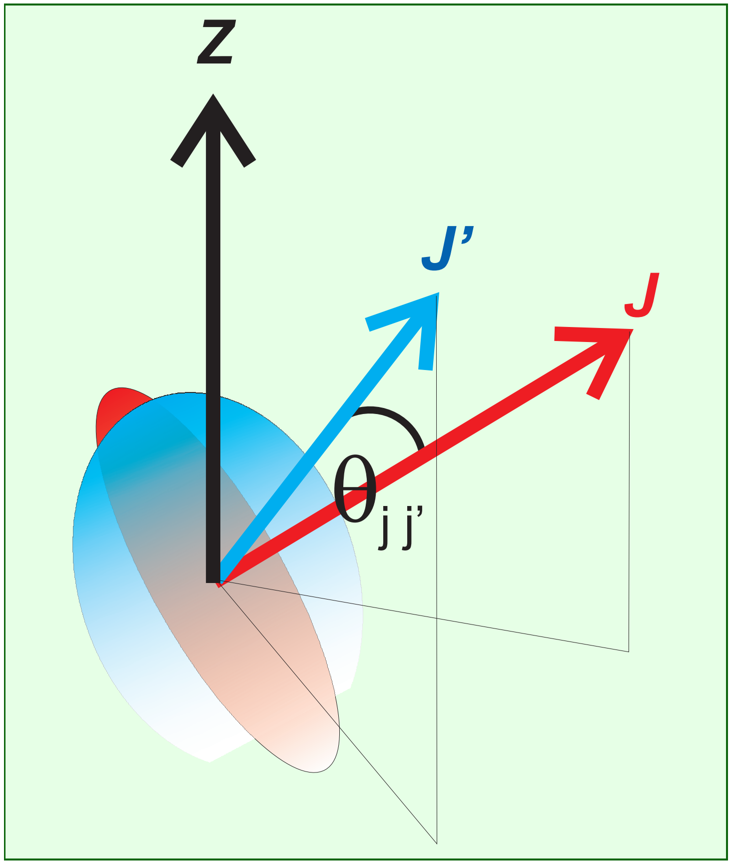
- Angular dependence of potential energy surfaces
- Mechanistic information

Aims

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

Collisional depolarization

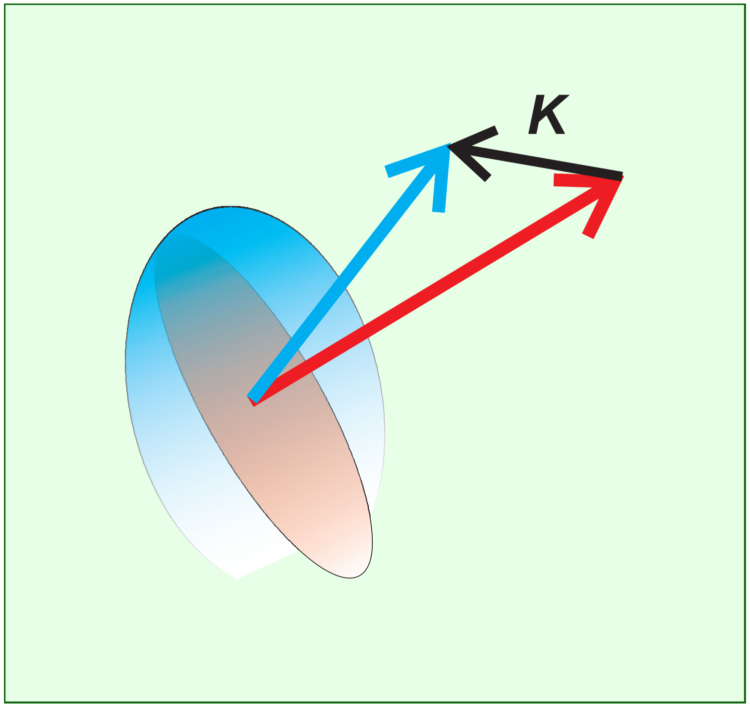
Collisional depolarization



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

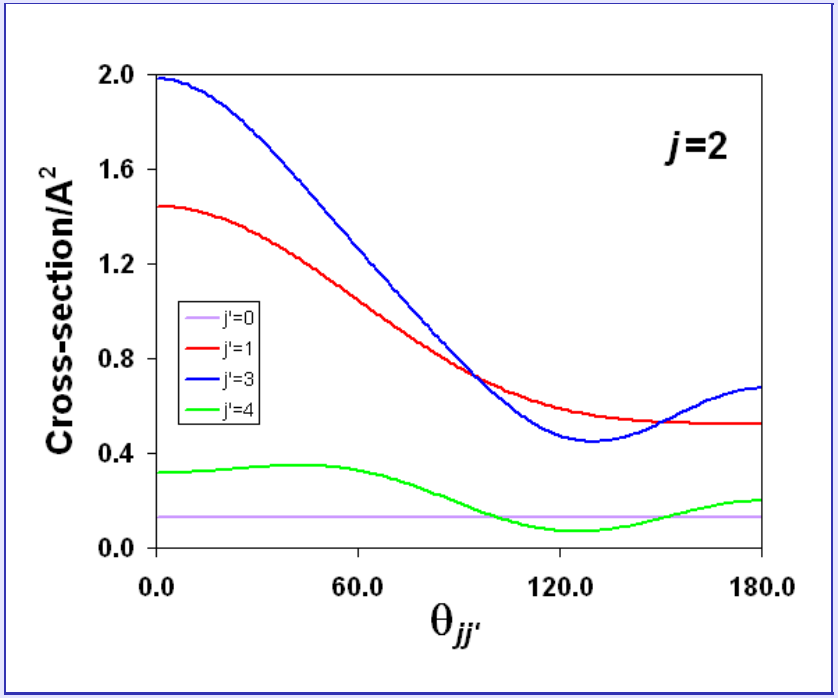


Can be characterized in terms of the angular momentum transferred, $\boldsymbol{K}$

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

Angular distribution (OH(A) + Ar)

Increasing $\boldsymbol{K}$ $\longrightarrow$



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)

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

'Disorientation' (odd terms)

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

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

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

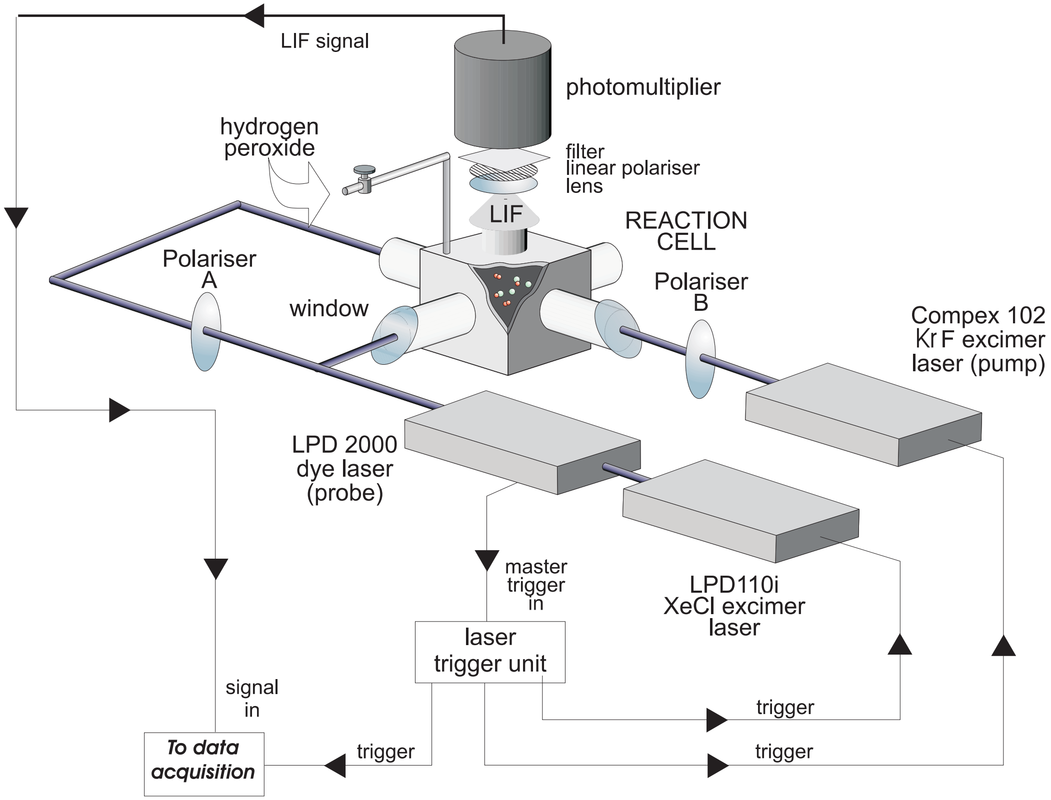
$$\left[\ \text{or}\quad \mathrm{NO}(\mathrm{X}^2\Pi) + h\nu'' \longrightarrow \mathrm{NO}(\mathrm{A}^2\Sigma^+)\ \right]$$

Use a 10 μs pump-probe laser delay.

Only 300 K results presented (superthermal studies also conducted).

Experiment

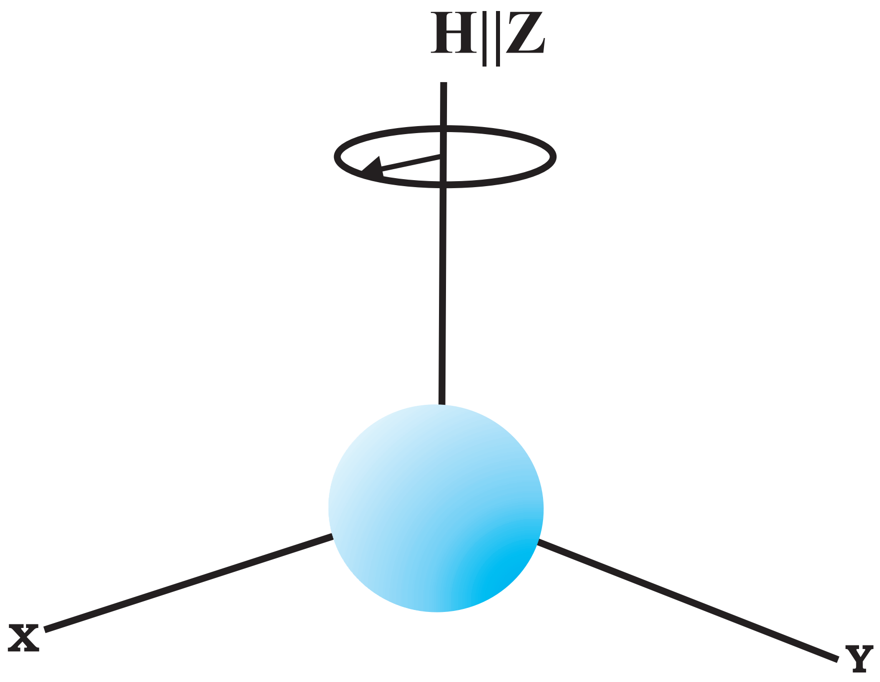
Detect OH($X^2\Pi$) by *polarized* laser induced fluorescence...



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

OH(X) spatial distribution

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

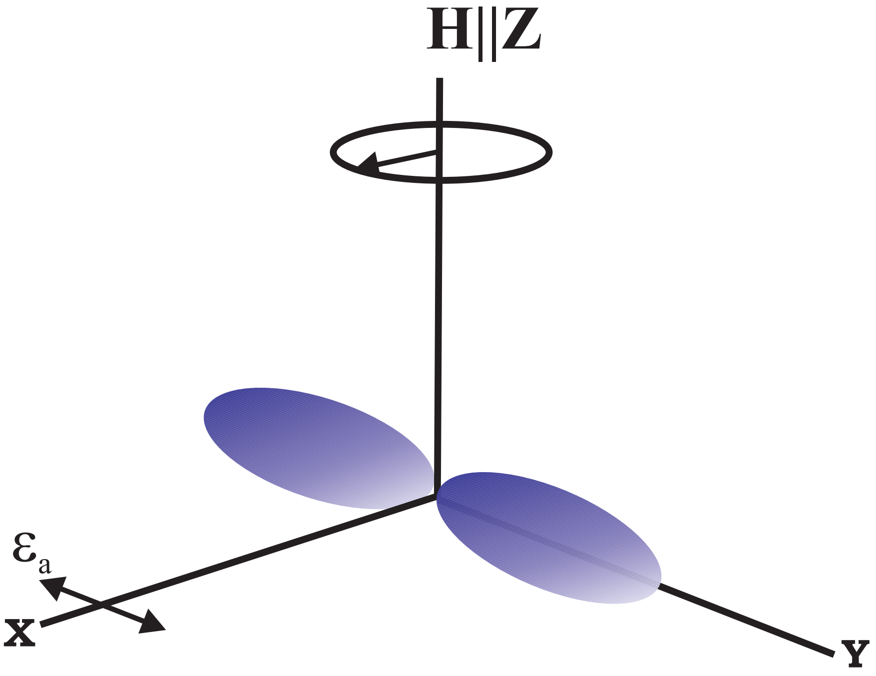


No net magnetic moment, *no precession about the field*

Initial OH(A) spatial distribution

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

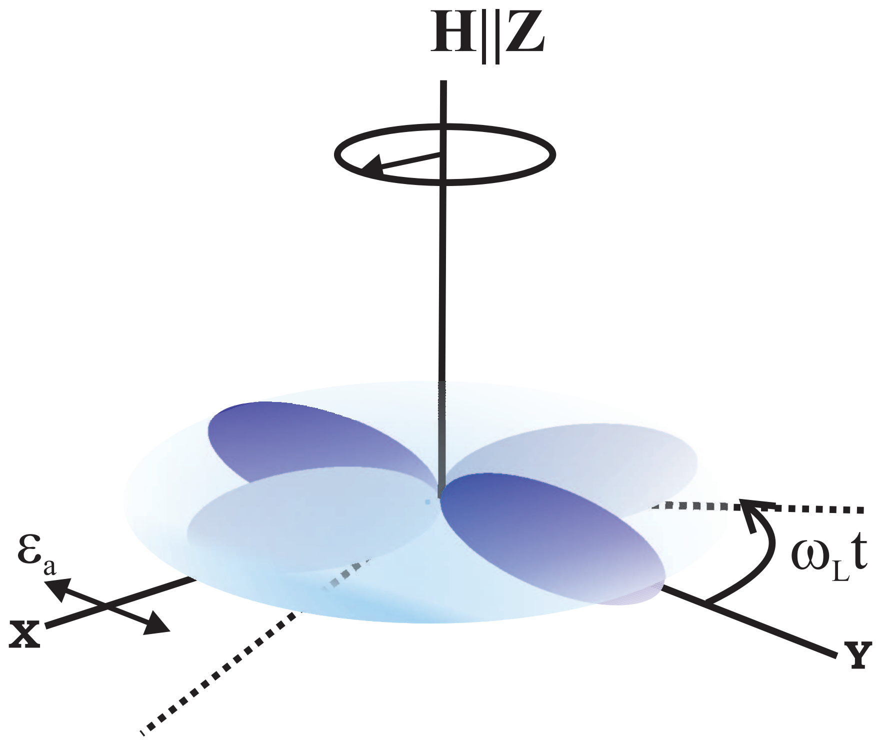
Transition probability $P \propto |\hat{\mu}_{\mathrm{OH}} \cdot \hat{\epsilon}_{\mathrm{a}}|^2$



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

Zeeman quantum beats

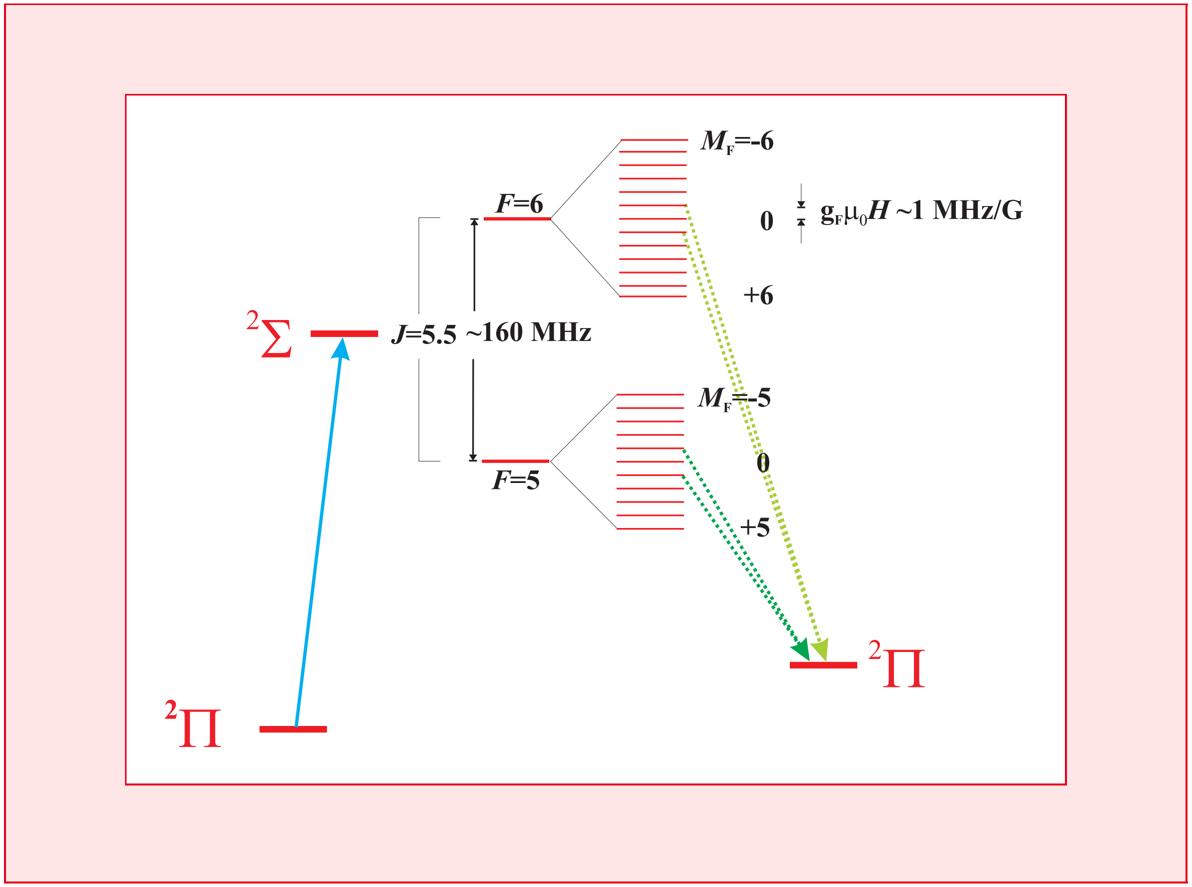
Precesses in magnetic field with *Larmor frequency*, ω_L.



Observe emission through a *linear polarizer*.

Zeeman quantum beats

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



Coherent excitation of Zeeman levels.

Link with theory (linearly polarized light)

Initial aligned distribution

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

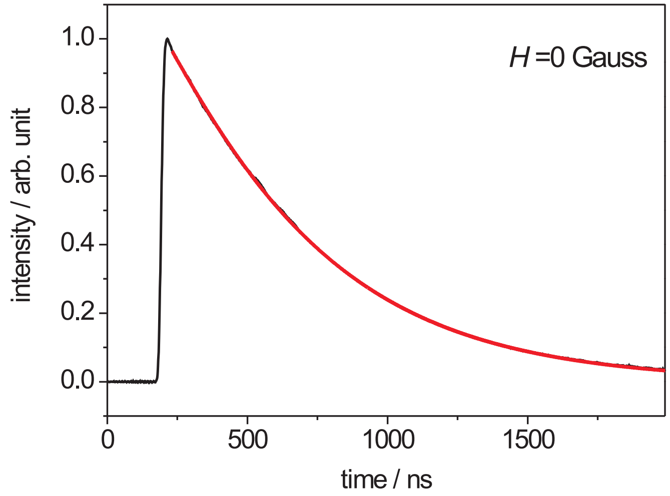
Distribution after one collision

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

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

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

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

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

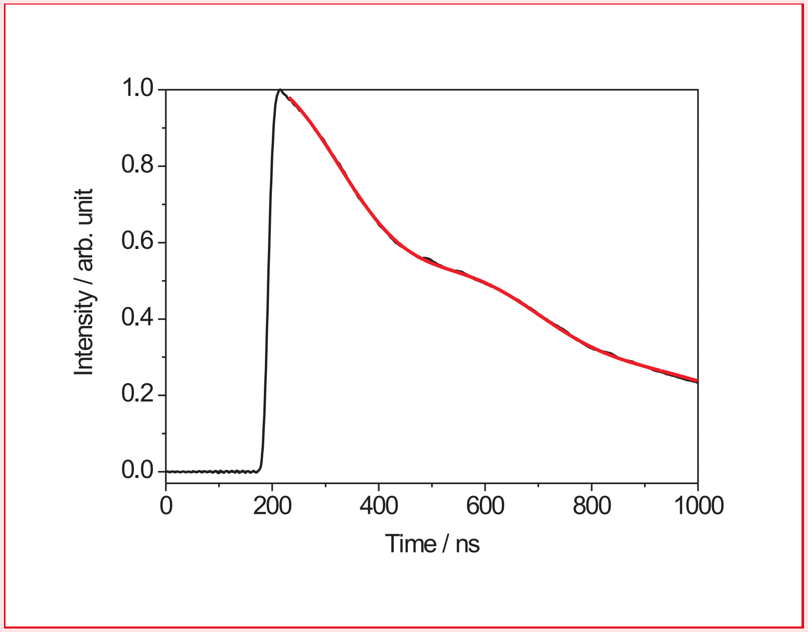
k_{rad} - *radiative decay* ($\tau_{\mathrm{rad}} \sim 700\,\mathrm{ns}$ for OH(A))

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

Zeeman quantum beats

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

$H = 4$ Gauss



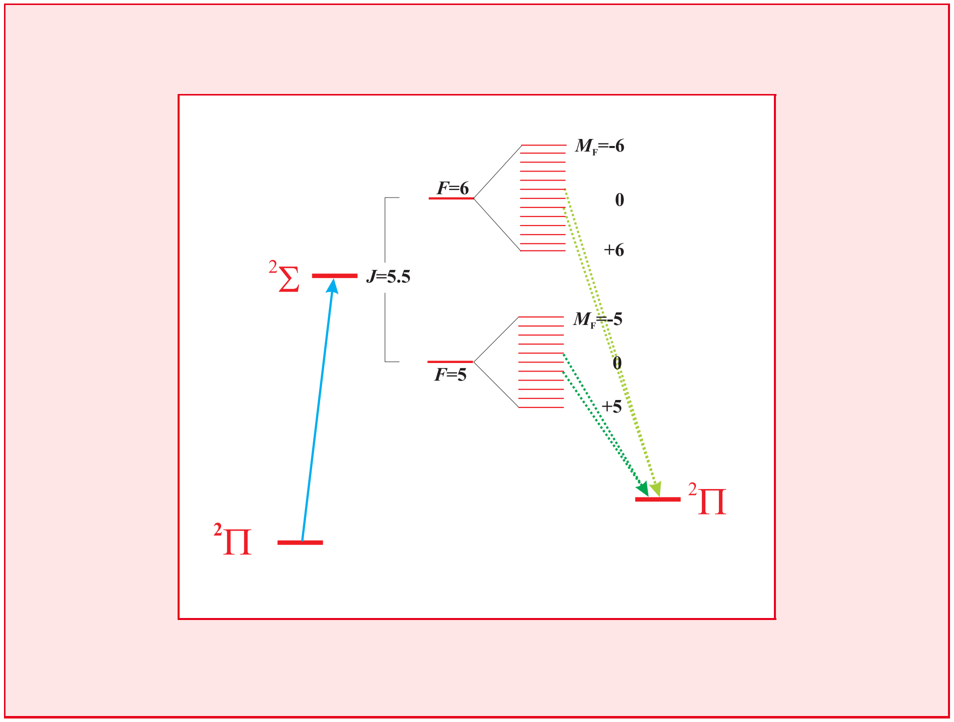
$$[\mathrm{OH}^*] \;=\; [\mathrm{OH}^*]_0\, \mathrm{e}^{-k_0 t}\{1 \;+\; C\, \mathrm{e}^{-k_2 t} \sum_F \cos\left(2\pi\omega_{\mathrm{L}} t + \phi\right)\}$$

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

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

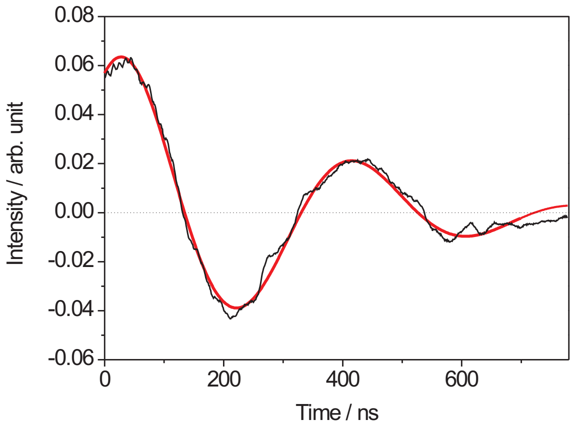


Oscillations at *two frequencies* for $F = 5$ and 6.

Zeeman quantum beats

Depolarization and dephasing: Beat amplitude, C

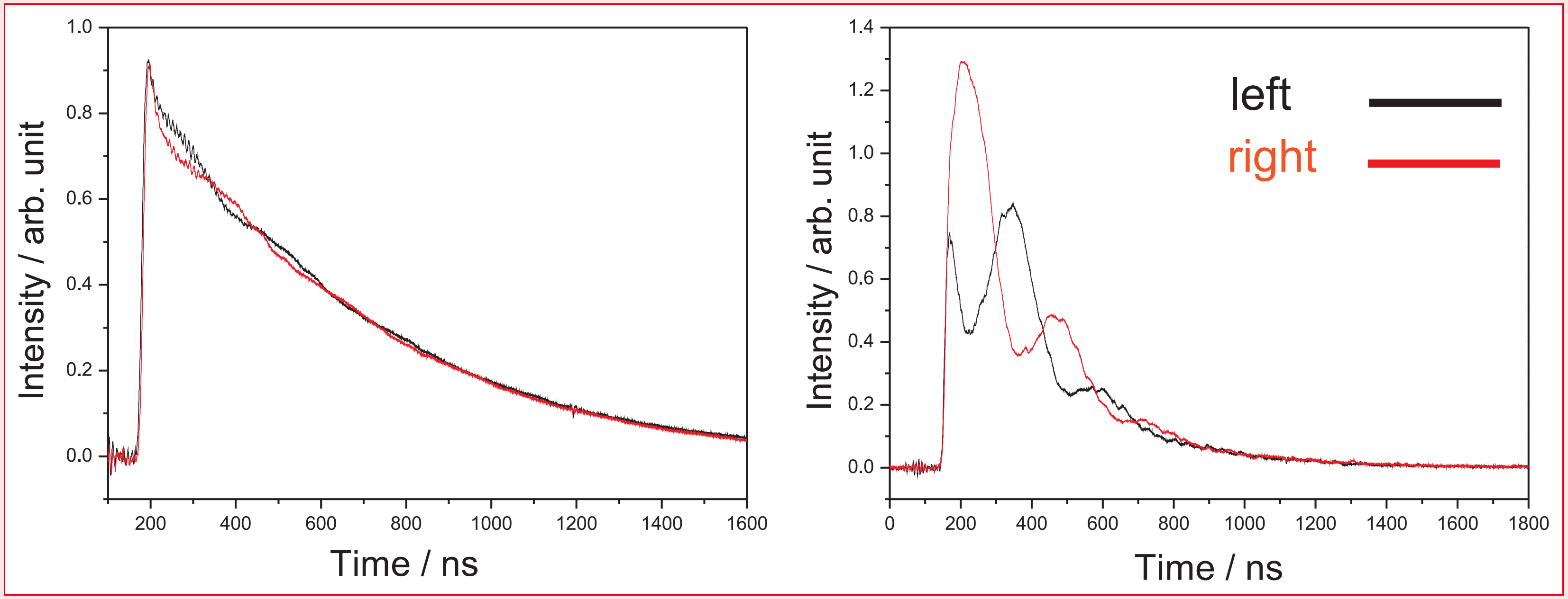
$$[\mathrm{OH}^*] \;=\; [\mathrm{OH}^*]_0\,\mathrm{e}^{-k_0 t}\{1 \;+\; C\,\mathrm{e}^{-k_2 t}\sum_F \cos\left(2\pi\omega_{\mathrm{L}} t + \phi\right)\}$$



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

Zeeman quantum beats

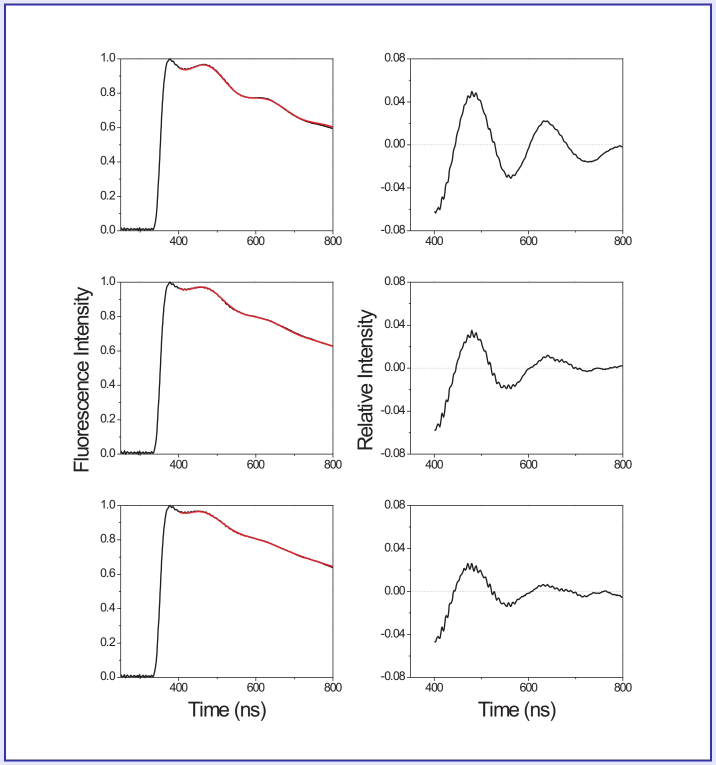
Orientation signal with resolved emission branch:



Proportional to *rotational orientation* 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

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

$$\boxed{k_2 = k_{\mathrm{inhom}} + k_{\mathrm{d}}^{(2)}\,[\mathrm{Ar}]}$$

k_{inhom} - dephasing by *field inhomogeneities*

$k_{\mathrm{d}}^{(2)}$ - collisional depolarization by Ar ($k_{\mathrm{d}}^{(2)} \sim v_{\mathrm{rel}}\sigma_{\mathrm{d}}^{(2)}$)

Link with theory - e.g., for disalignment

Depolarization rate constant, $k_{\mathrm{d}}^{(2)} \sim v_{\mathrm{rel}} \sigma_{\mathrm{d}}^{(2)}$

$$\boxed{k_{\mathrm{d}}^{(2)} = k_{\mathrm{c}} (1 - a_2)}$$

where k_{c} is the collision rate constant (e.g., for energy transfer)

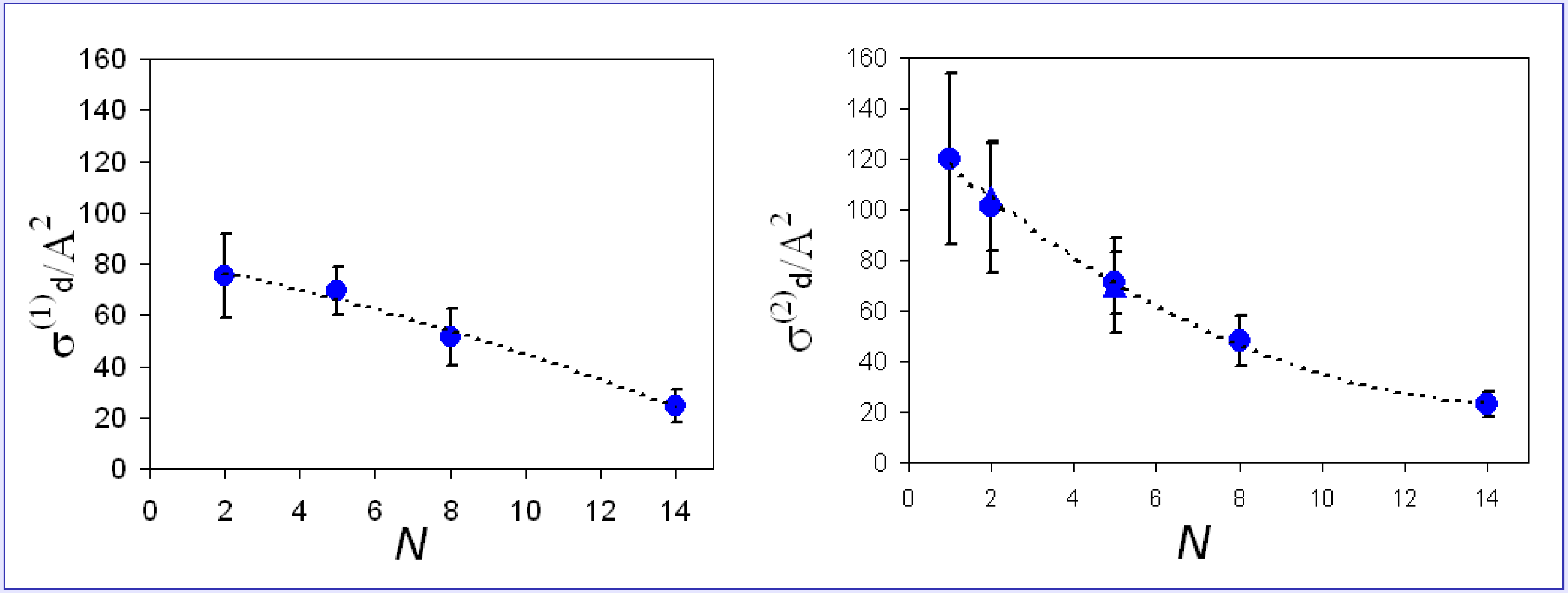
Three cases:

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

Trends in depolarization cross-sections

OH(A) + Ar (300 K)

‘Disorientation’ ‘Disalignment’



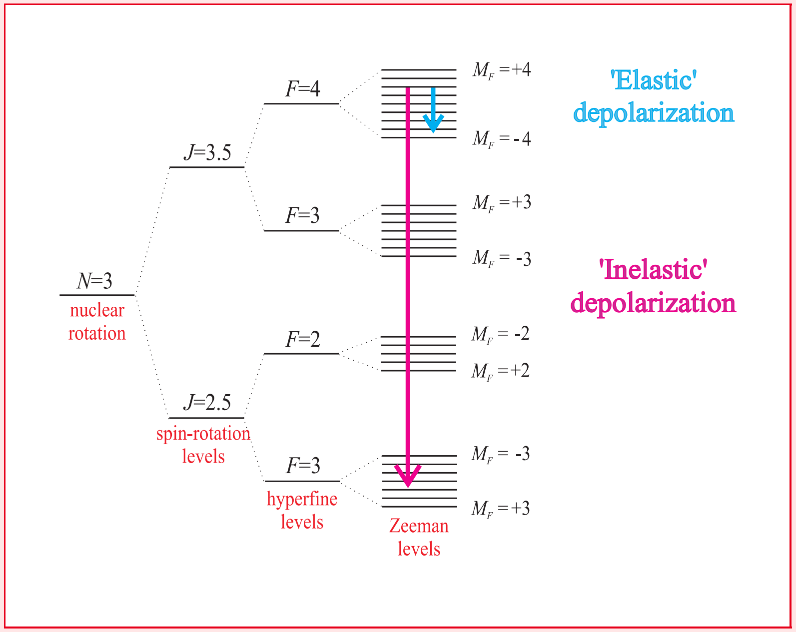
Cross-sections are *large* (long range interaction).

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

‘Disalignment’ more probable than (‘disorientation’).

Zeeman quantum beats

Collisional processes leading to depolarization



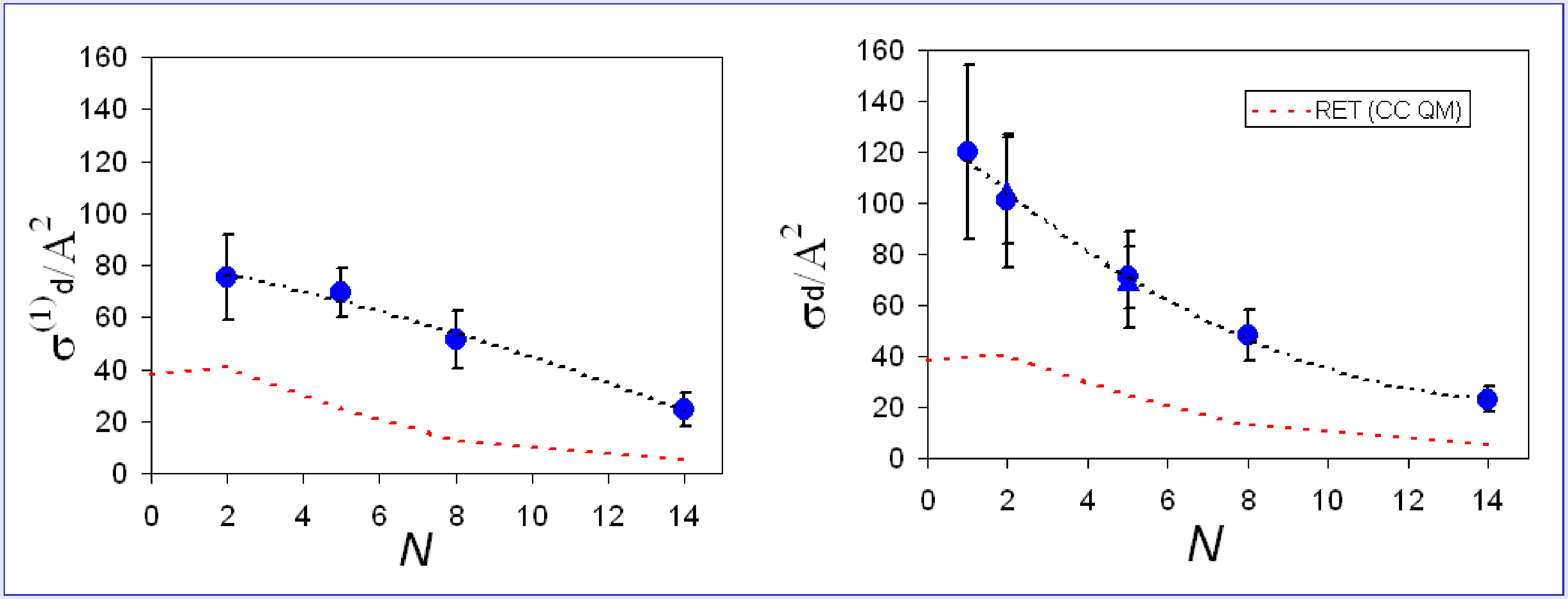
Inelastic depolarization (*rotational energy transfer*)

Elastic depolarization (M_j-*changing*)

Comparison with rotational energy transfer

OH(A) + Ar (300 K)

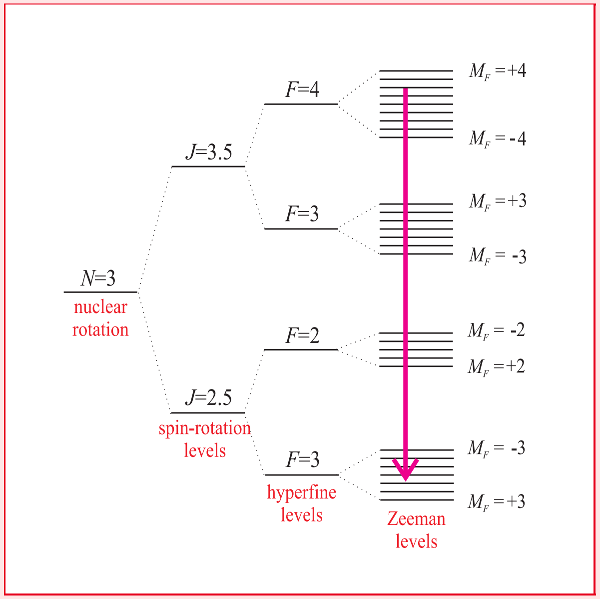
‘Disorientation’ ‘Disalignment’



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

Zeeman quantum beats

Caveat: we detect unresolved OH(A) emission



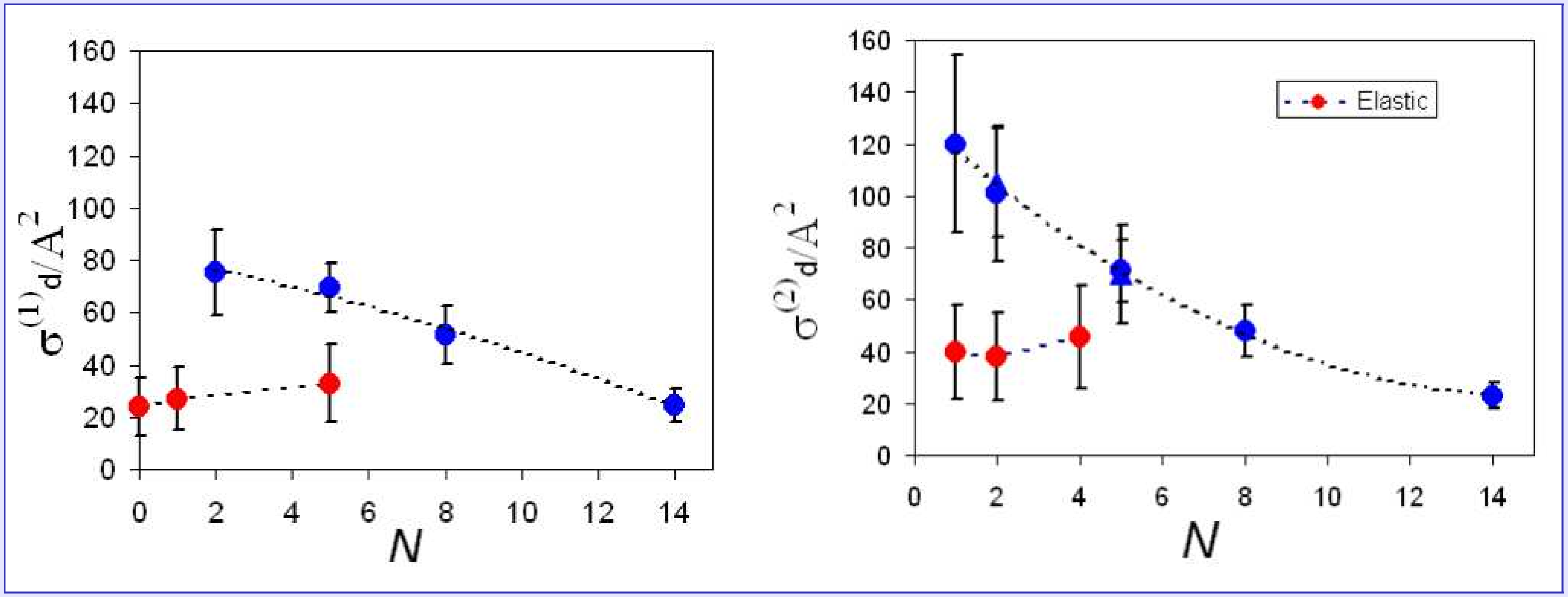
- Populated levels have different g_F values - leads to a dephasing
- Important for spin-rotation changing collisions
- Effects can be accounted for, although better to resolve emission

Elastic depolarization

Employ higher resolution emission

OH(A) + Ar (300 K)

‘Disorientation’ ‘Disalignment’

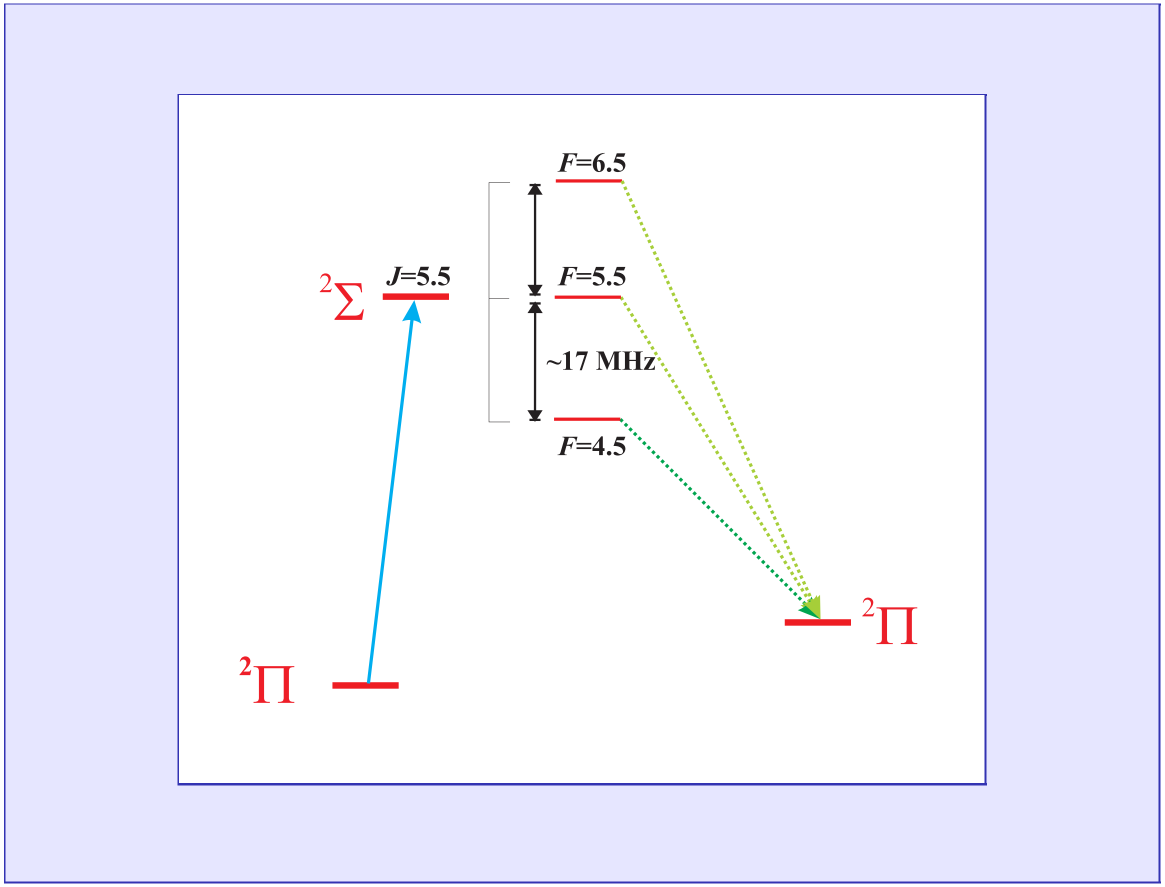


Previous work: elastic contribution to $\sigma_{\mathrm{d}}^{(2)} \sim 20\,\text{Å}^2$ for $N = 4$ [‡]

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

Comparison with hyperfine quantum beats: NO(A)

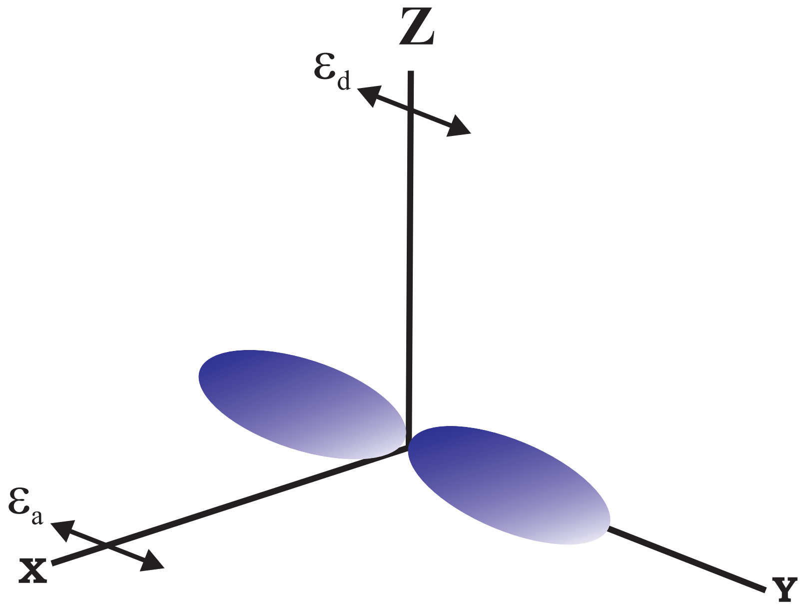
Coherent superposition of hyperfine levels (Low N)



Observe two of the three Hyperfine beat frequencies.

Hyperfine quantum beats: NO(A)

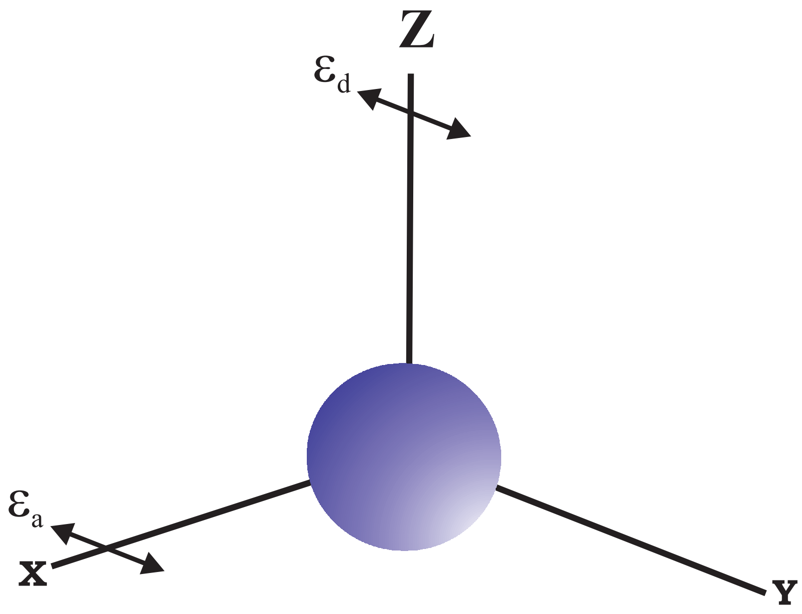
Initial distribution of $\boldsymbol{J}$



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

Hyperfine quantum beats: NO(A)

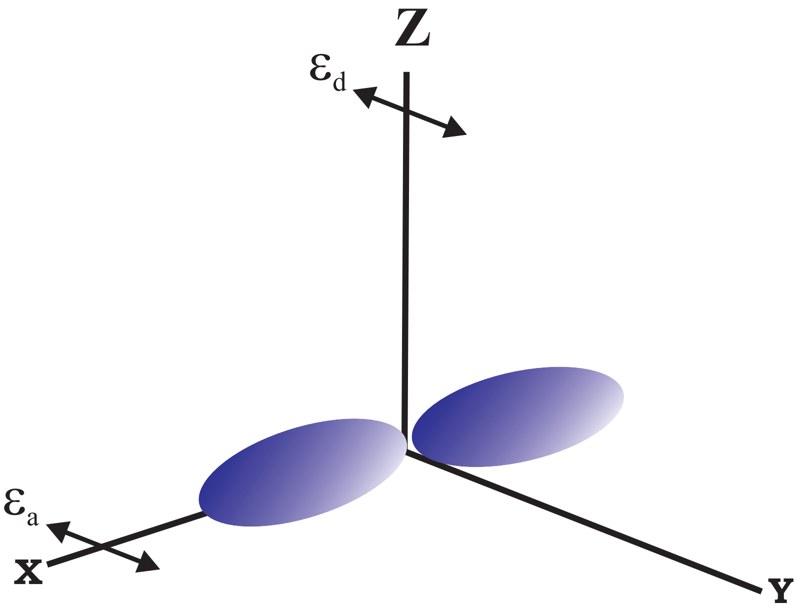
Alignment of $\boldsymbol{J}$ reduced



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

Hyperfine quantum beats: NO(A)

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

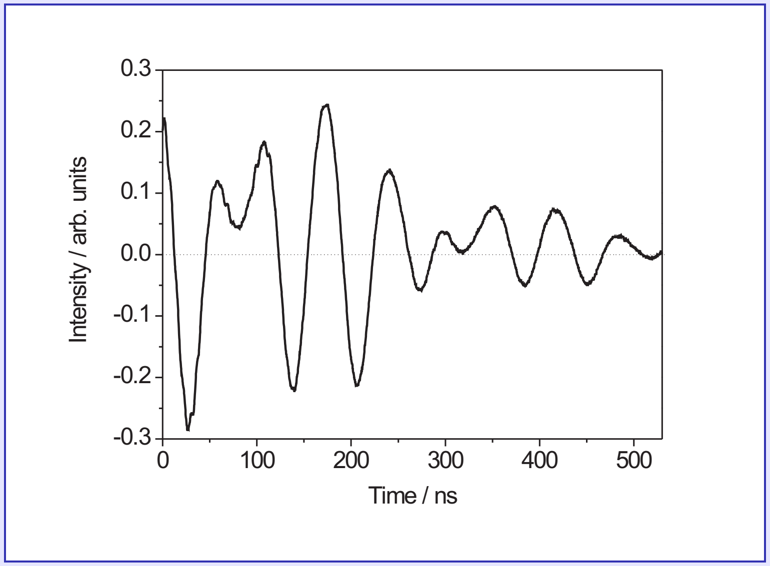


See T.P. Rakitzis, *Phys. Rev. Lett.* (2005)

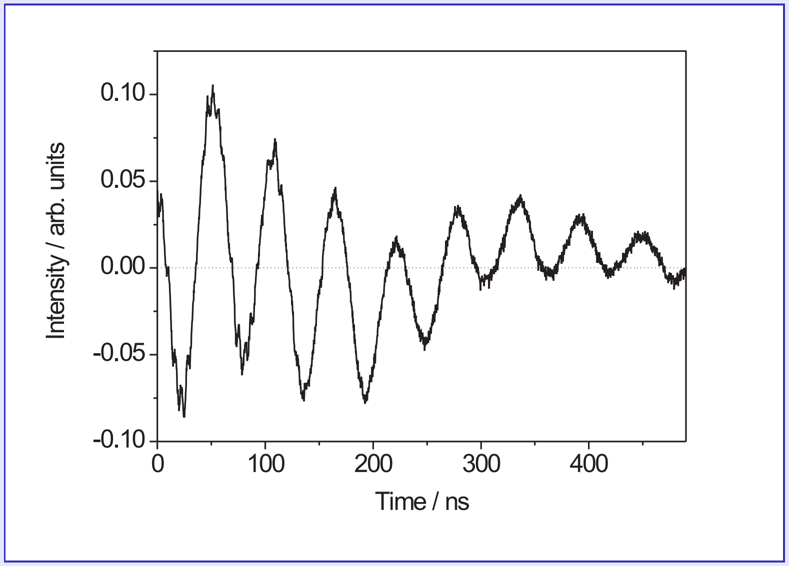
Hyperfine quantum beats: NO(A)

Beat signal

$S_{21}(0) \uparrow$



$R_{22}(4) \uparrow$



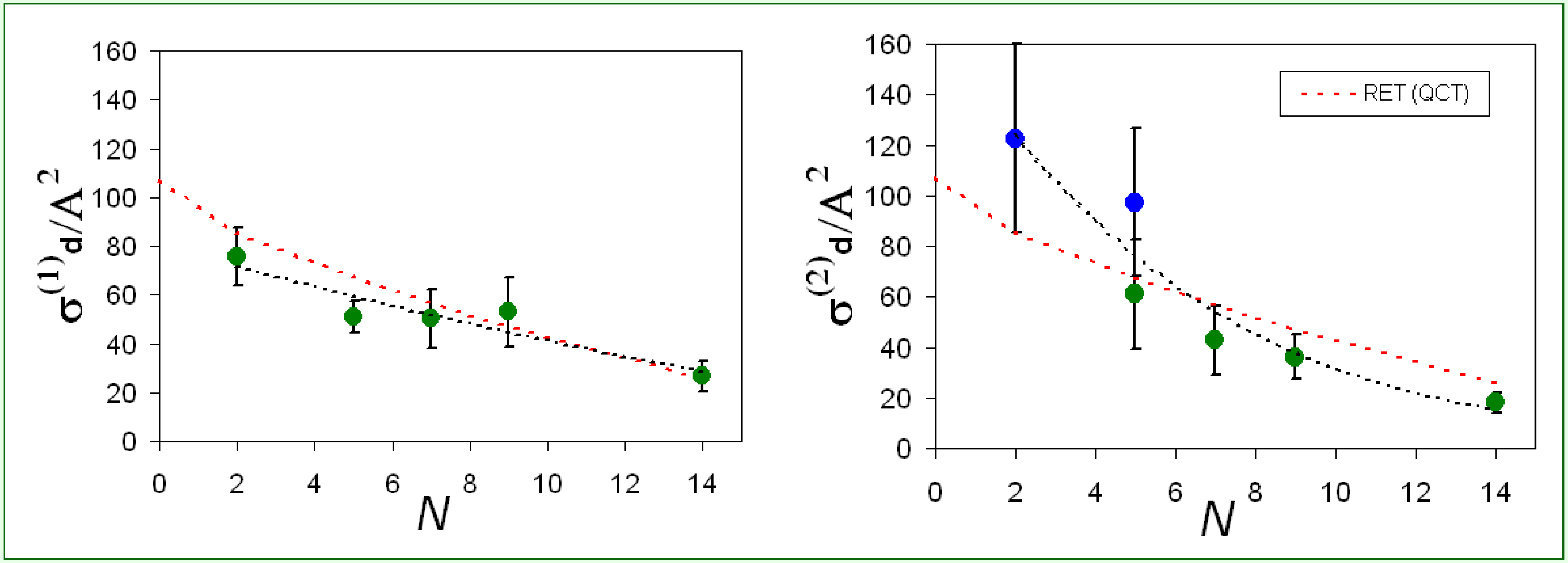
Amplitude decreases rapidly with J.

Hyperfine quantum beats: NO(A)

Depolarization cross-sections

NO(A) + Ar (300 K)

● ‘Hyperfine’ ● ‘Zeeman’



Reasonable agreement between hyperfine and Zeeman beat data

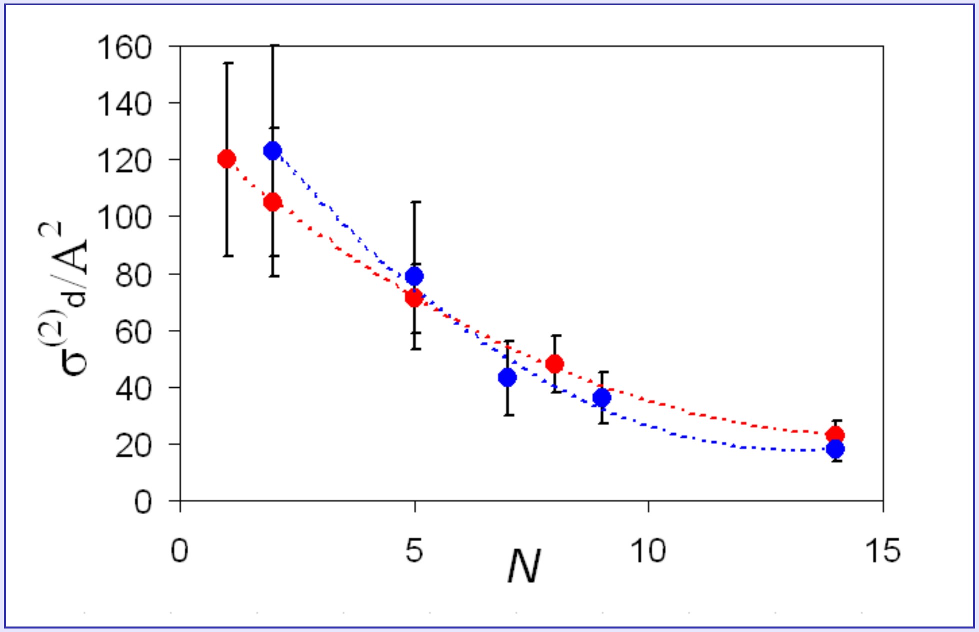
Depolarization has similar efficiency to RET ($a_2 \gtrsim 0$).

Trends in depolarization cross-sections

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

NO(A) + Ar ●

OH(A) + Ar ●



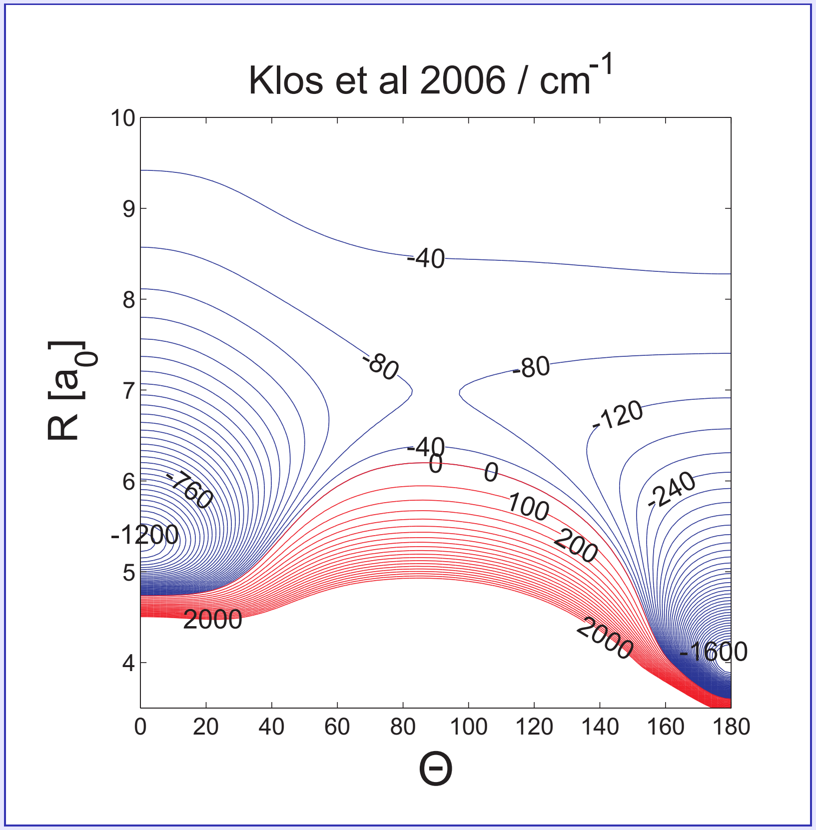
Well-depth for NO(A)+Ar is *one tenth* that of OH(A) + Ar

Balanced by kinematic/energetic factors and differences in a_k parameters

OH(A) + Ar potential

Strongly attractive and highly anisotropic PES

J. Kłos and M.H. Alexander *et al., J. Chem. Phys.* (2008)

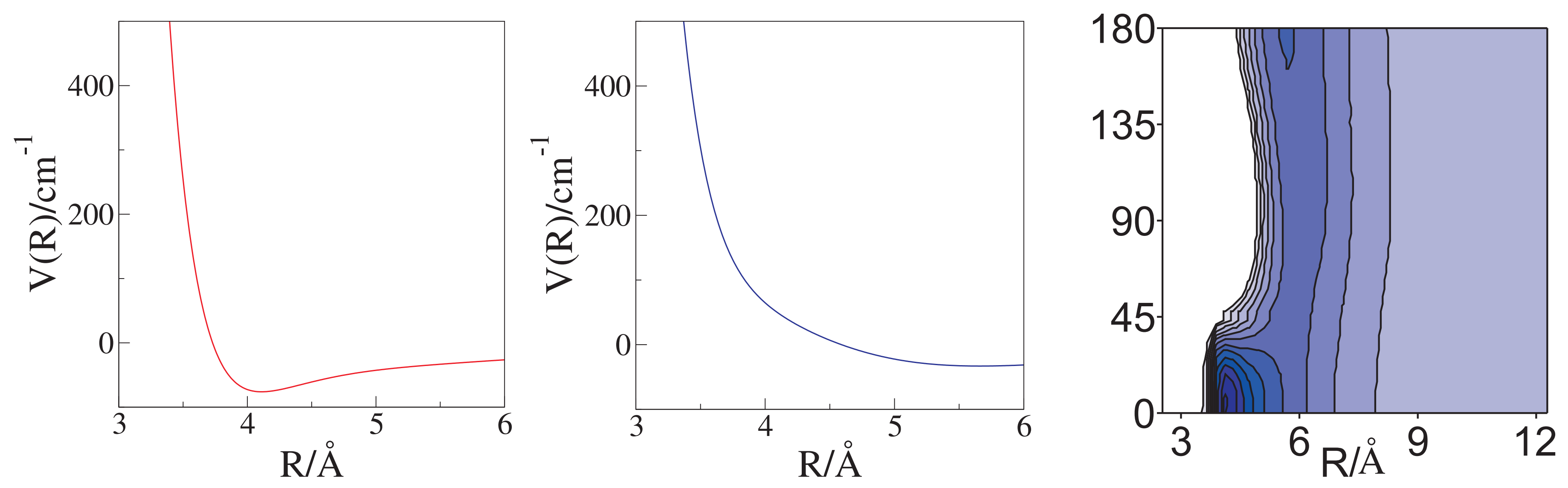


Well depth $\sim 1600\,\mathrm{cm}^{-1}$

NO(A) + Ar potential

Very weakly attractive PES

Kłos *et al.*, in preparation *(2008)*



$D_0 \sim 44\,\mathrm{cm}^{-1}$ ‡

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

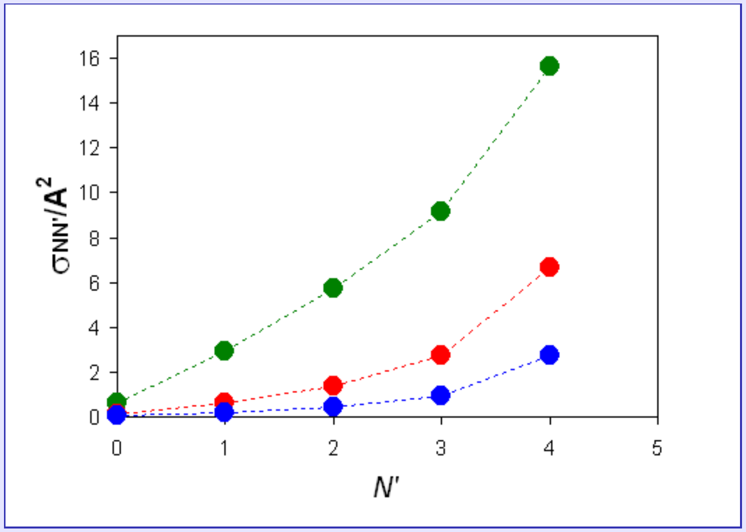
Kinematics or dynamics?

RET cross-sections ($N = 5$)

^{14}NO(A) + Ar ●

^{1}NO(A) + Ar ●

OH(A) + Ar ●



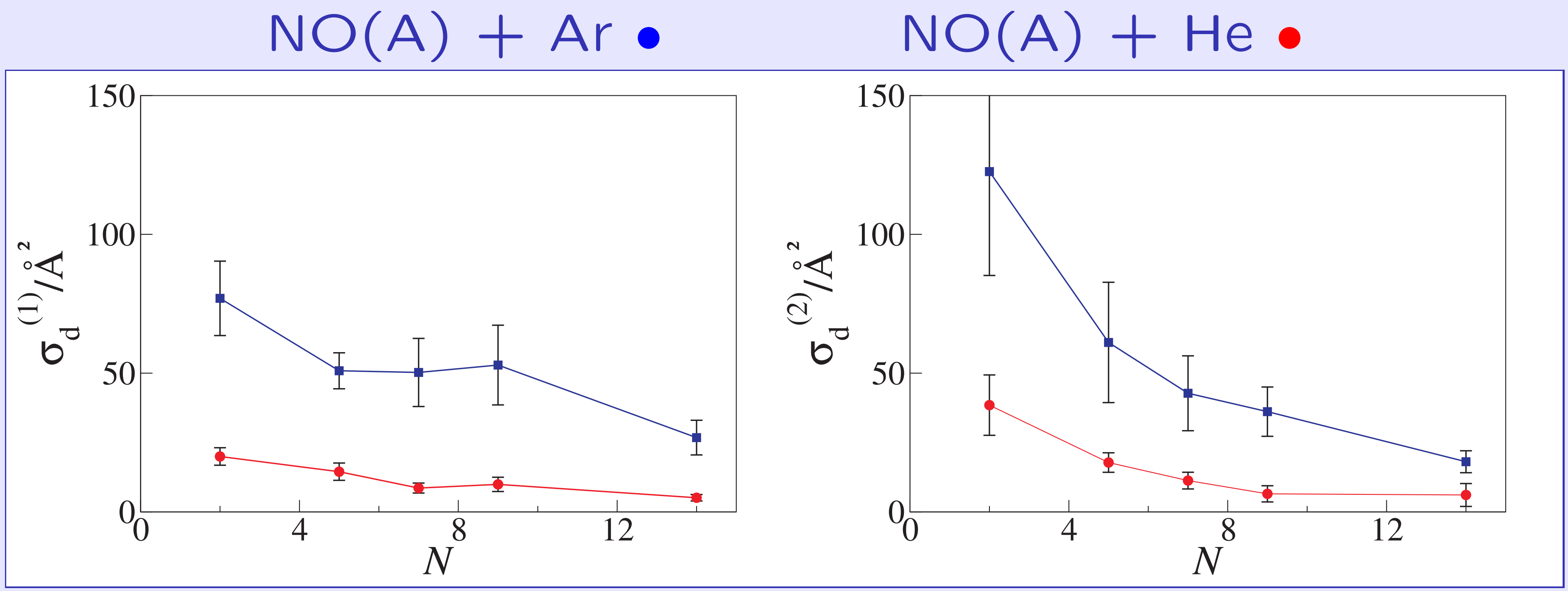
Changing PES makes a factor of ∼2 difference in σ_C

QCT calculations by C.J. Eyles, H. Chadwick and F.J. Aoiz

New PES by J. Kłos and M.H. Alexander

Kinematics or dynamics?

Depolarization cross-sections at 300 K



These differences mainly due to the PES

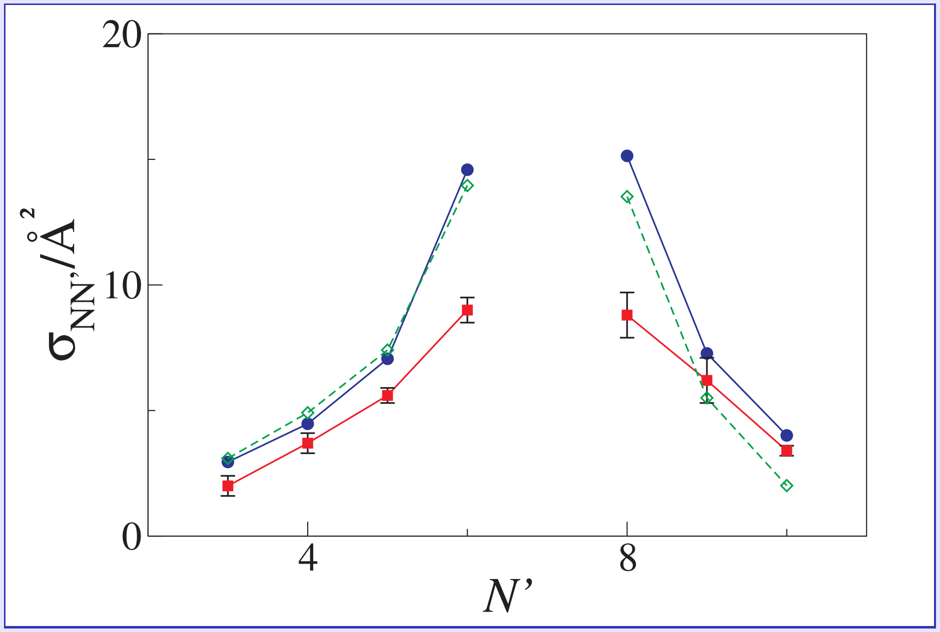
Kinematics or dynamics?

RET cross-sections ($N = 7$)

NO(A) + ^{4}Ar ●

NO(A) + ^{40}Ar ●

NO(A) + He‡ ●



These differences mainly due to the PES and not kinematics

‡ Experiments of Imajo *et al.* Chem. Phys. Lett. (1987).

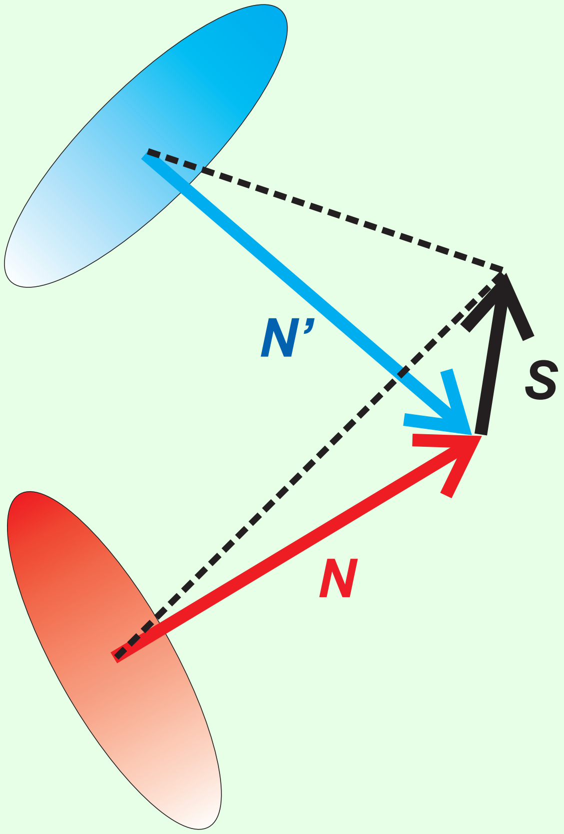
Role of electron and nuclear spin

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

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

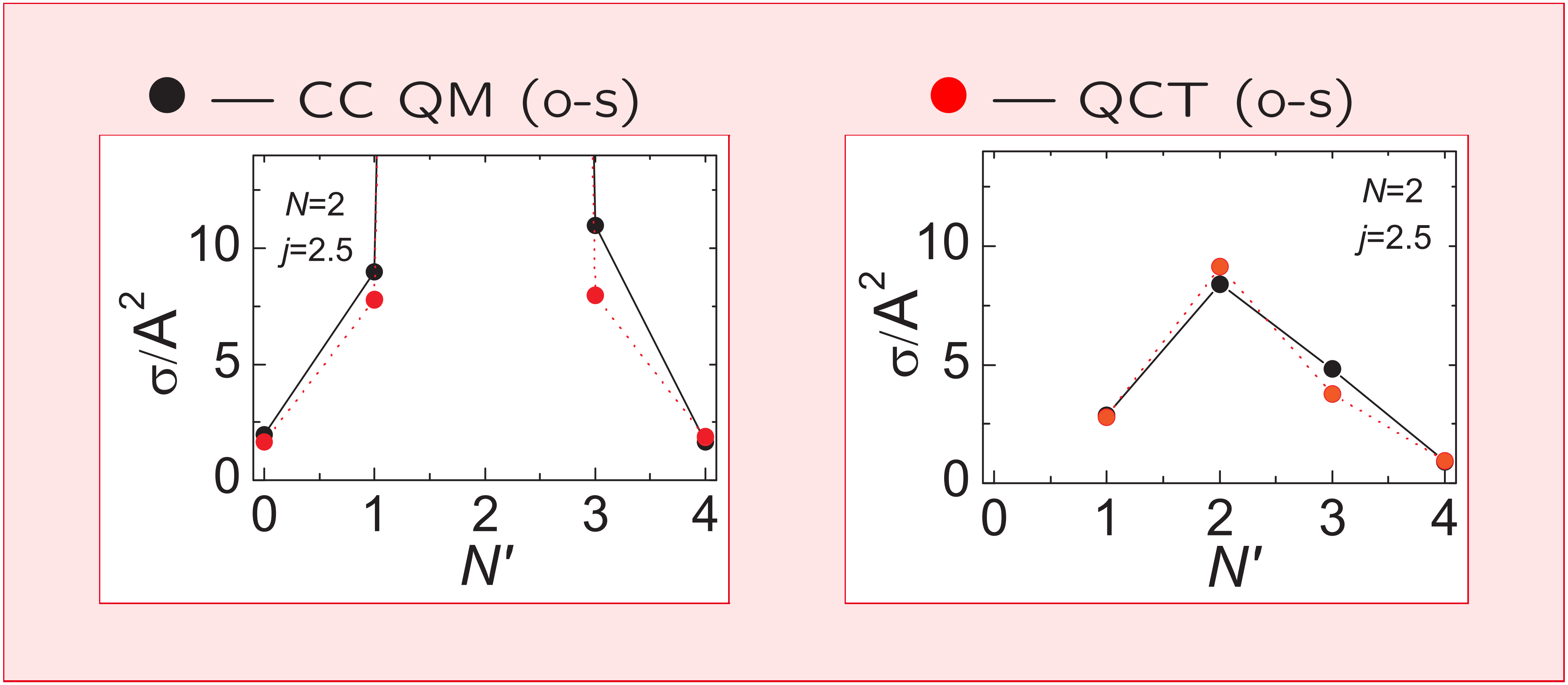
$$\uparrow$$

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



Spin-rotation changing collisions only occur if $\boldsymbol{N}$ is *strongly depolarized*.

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



Spin-rotation changing collisions play an important role for OH(A) + Ar

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

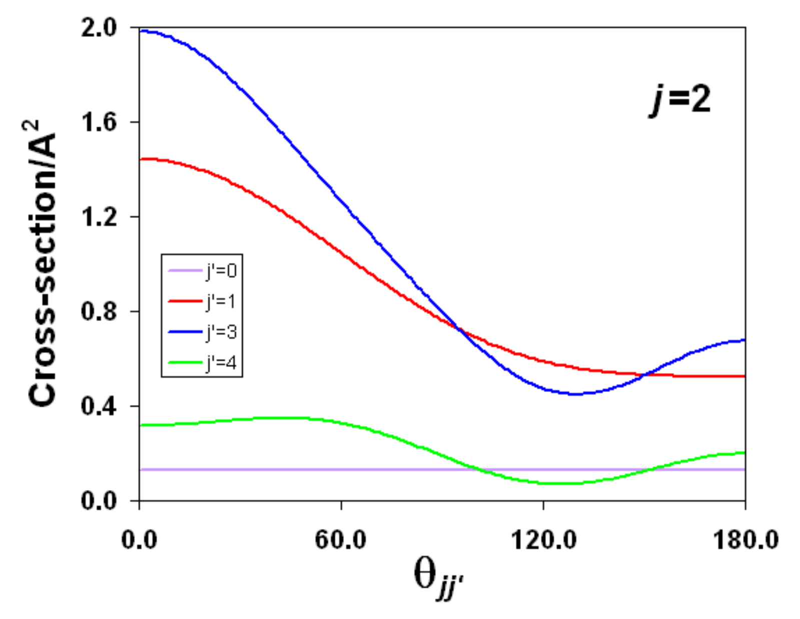
QM and new PES by J. Kłos and M.H. Alexander

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

Increasing K ⟶

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

New PES by J. Kłos and M.H. Alexander

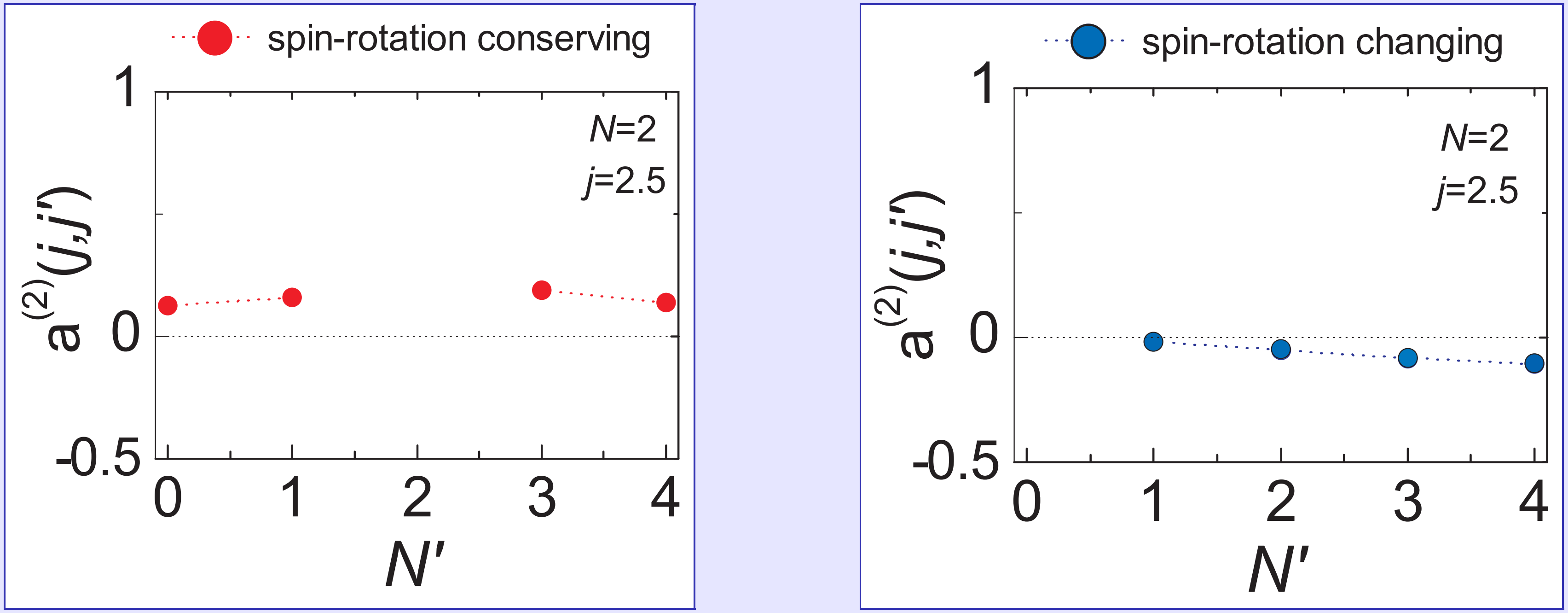


Spin-rotation changing collisions require large K

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

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

‘Disalignment’ coefficients



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

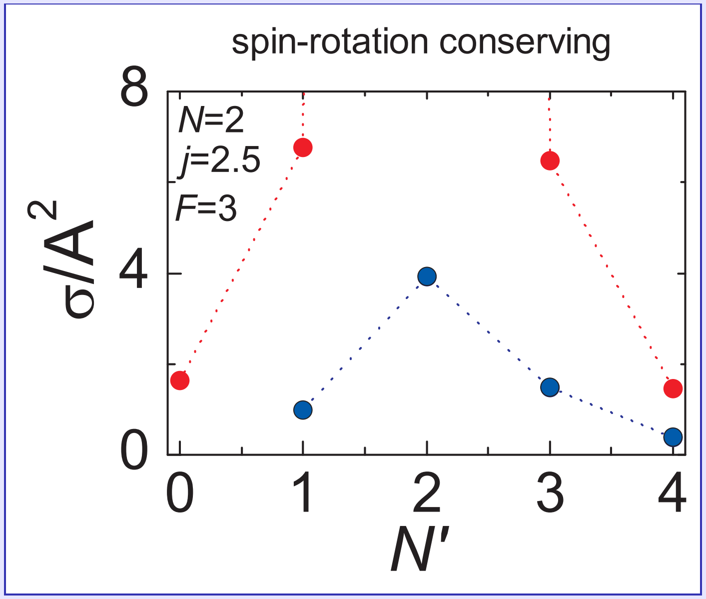
New PES by J. Kłos and M.H. Alexander

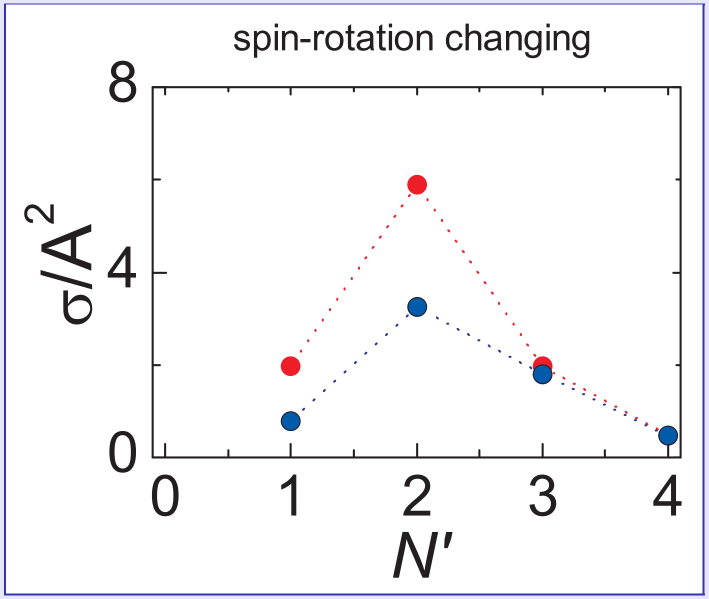
OH(A) + Ar and hyperfine changing collisions

QCT Calculations

● Hyperfine conserving

● Hyperfine changing


spin-rotation conserving


spin-rotation changing

Also play an important role for OH(A) and NO(A) + Ar

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

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

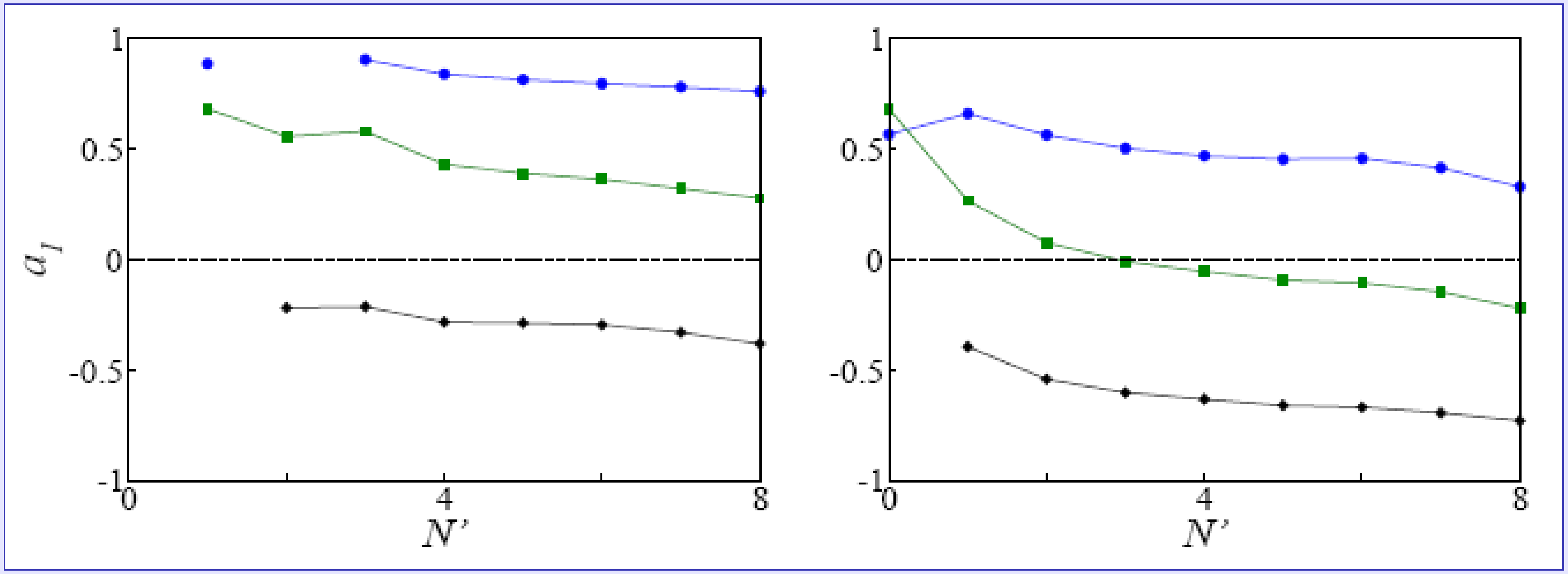
NO(A) + Ar and hyperfine changing collisions

‘Disorientation’ coefficients

$N = 2,\ j = 1.5,\ F = 2.5$

Spin-rotation conserving

Spin-rotation changing

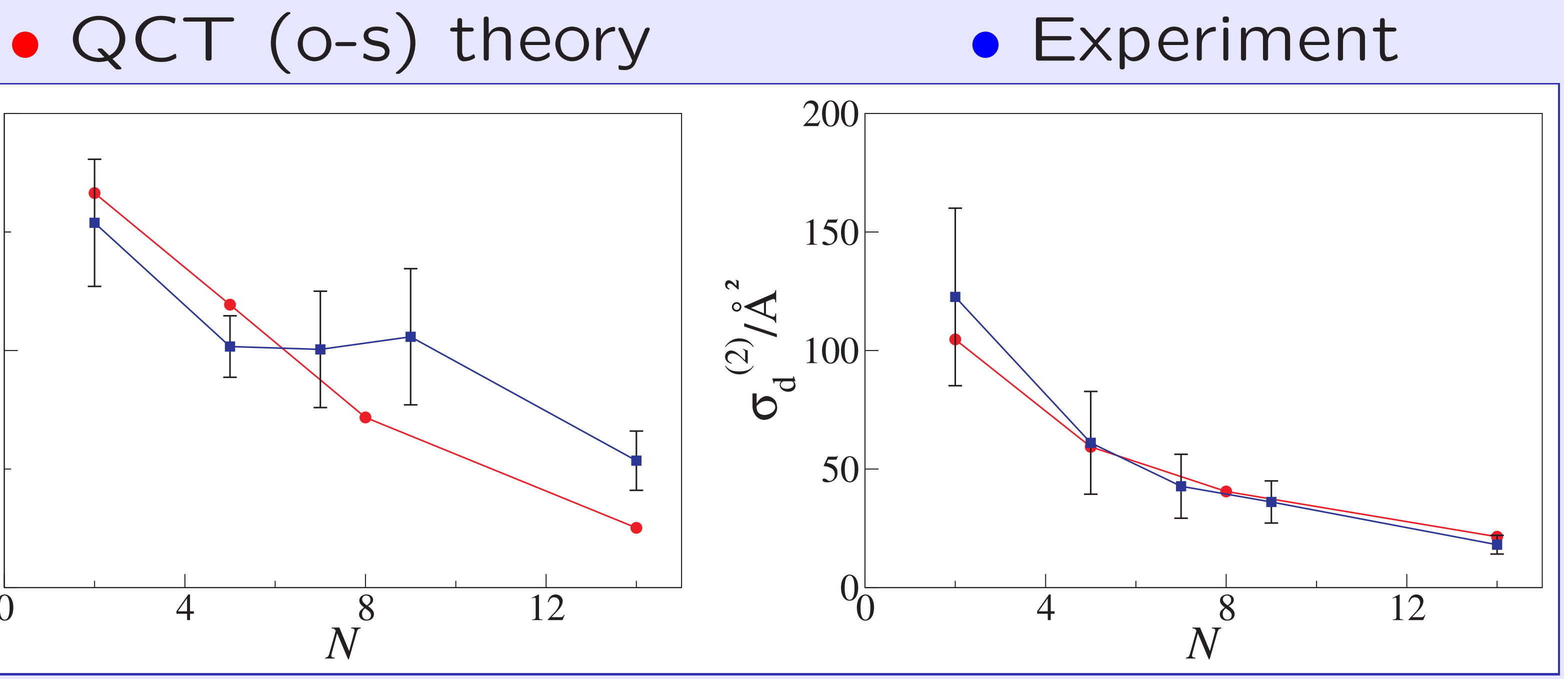


QCT calculations by C.J. Eyles, H. Chadwick and F.J. Aoiz

New PES by J. Kłos and M.H. Alexander

Full simulation of experiment

NO(A) + Ar



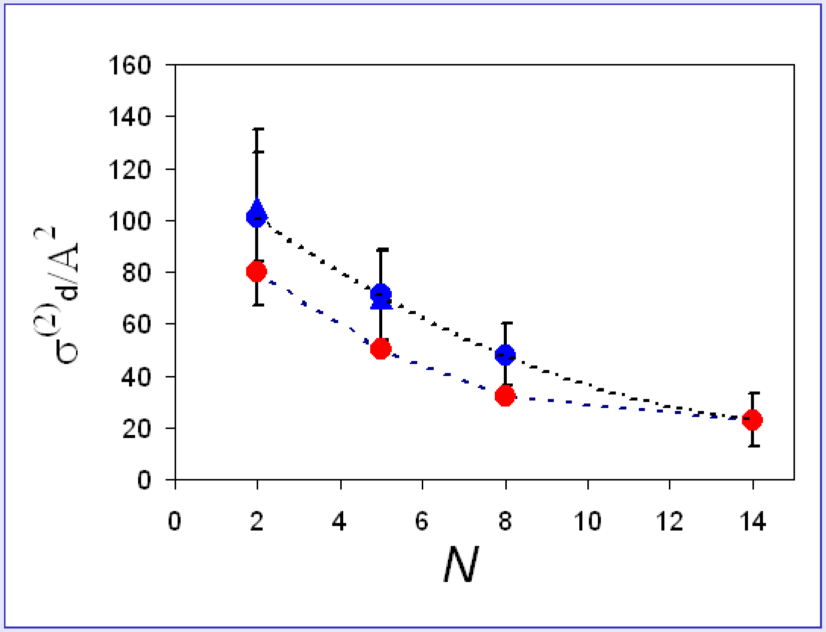
QCT calculations by C.J. Eyles, H. Chadwick, and F.J. Aoiz

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

Full simulation of experiment

OH(A) + Ar

● QCT (o-s) theory ● Experiment

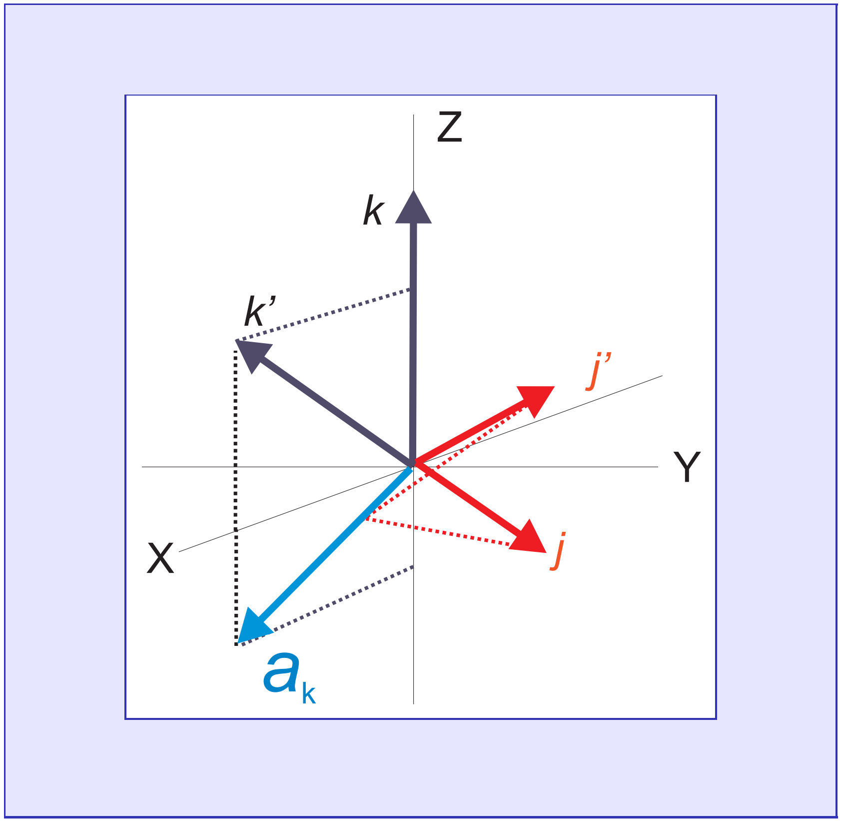


QCT calculations by C.J. Eyles, H. Chadwick and F.J. Aoiz

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

Mechanisms of depolarization

Impulsive collision conserve projection of $\boldsymbol{j}$ (M_{a}) along kinematic apse

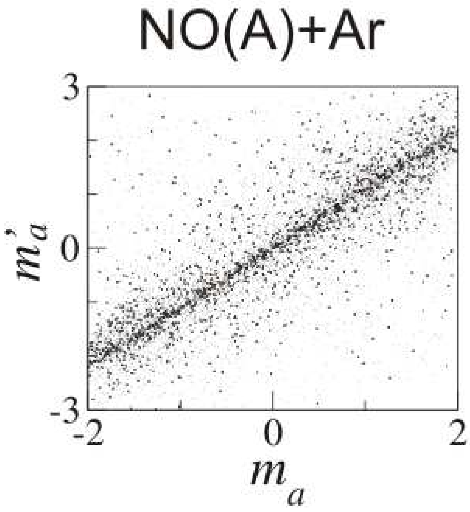


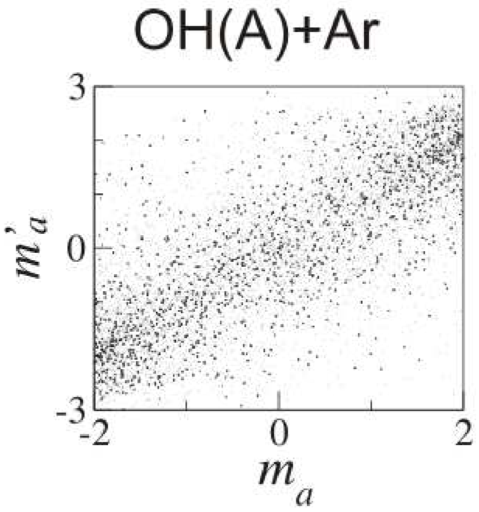
$$\boxed{\hat{a}_{\mathrm{K}} = \frac{\boldsymbol{k}' - \boldsymbol{k}}{|\boldsymbol{k}' - \boldsymbol{k}|}}$$

Mechanisms of depolarization

NO(A) + Ar tends to be impulsive.

QCT $N = 2 \rightarrow N' = 3$





OH(A) + Ar is impulsive only for larger Δj.

QCT calculations by C.J. Eyles, H. Chadwick and F.J. Aoiz

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

Mechanisms of depolarization

NO(A) + Ar tends to be impulsive ($a_k \gtrsim 0$).

QCT $N = 2 \rightarrow N' = 4$

NOAr.mpg

QCT calculations by C.J. Eyles, H. Chadwick and F.J. Aoiz

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

Mechanisms of depolarization

OH(A) + Ar is not impulsive at low Δj ($a_k \lesssim 0$).

QCT $N = 2 \rightarrow N' = 4$

OHArimp.mpg

QCT calculations by C.J. Eyles, H. Chadwick and F.J. Aoiz

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

Mechanisms of depolarization

‘Roaming’ trajectories seen at low Δj for OH(A) + Ar

QCT $N = 2 \rightarrow N' = 4$

OHArorb.mpg

QCT calculations by C.J. Eyles, H. Chadwick and F.J. Aoiz

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

Mechanisms of depolarization

Complex trajectories seen at low Δj for OH(A) + Ar

QCT $N = 2 \rightarrow N' = 4$

Cricket.mpg

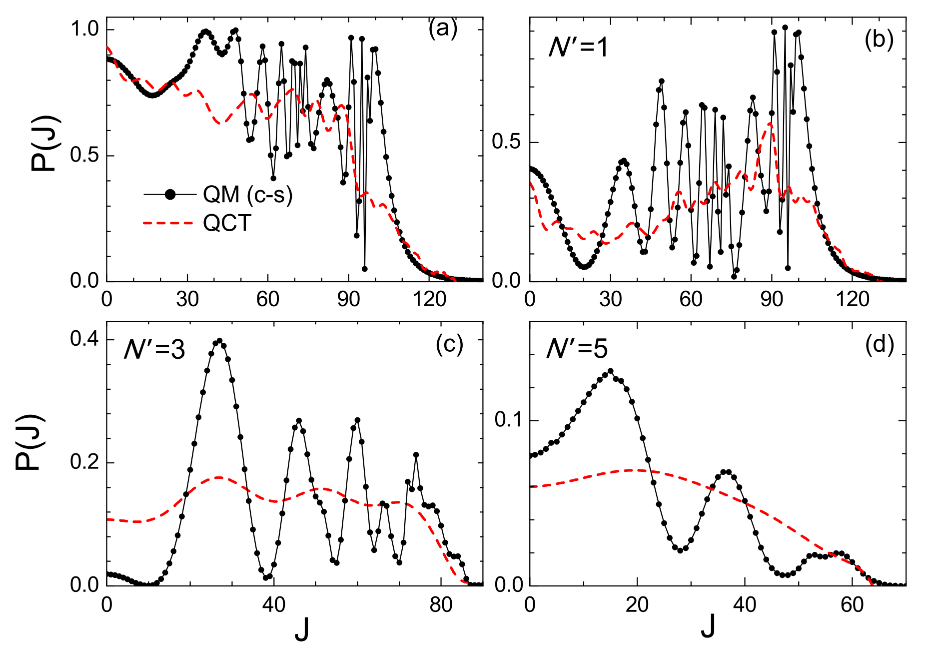
QCT calculations by C.J. Eyles, H. Chadwick and F.J. Aoiz

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

Mechanisms of depolarization: opacity functions

OH(A) + Ar and the role of OH(A)—Ar complexes.

QCT versus CC QM (c-s) ($N = 2$)



QM calculations by J. Kløs and C.J. Eyles

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

Zeeman quantum beats

Collisional depolarization: Some conclusions.

- Less efficient at high N - *angular momentum conservation*.
- Attractive long-range interaction plays crucial role for OH(A)+Ar.
- Both elastic and inelastic depolarization are important.
- Depolarization efficiency relative to RET is very system dependent.
- For $^2\Sigma^+$ radicals $\boldsymbol{S}$ and $\boldsymbol{I}$ are spectators in the collision.
- The effects of $\boldsymbol{S}$ and $\boldsymbol{I}$ can be accommodated in QCT calculations.
- $\sigma_{\mathrm{d}}^{(k)}$ are large for spin-rotation and hyperfine state-changing collisions.

The End