Atomic photofragment polarization as a probe of molecular photodissociation dynamics

Mark Brouard

The Department of Chemistry
Oxford University

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Acknowledgements

The Group

Raluca Cireasa	Visiting scientist
Andrew Clark	D.Phil. student
Fabio Quadrini	D.Phil. student
Yuan-Pin Chang	D.Phil. student
Alex Johnsen	D.Phil. student
Chris Eyles	D.Phil. student
Alistair Green	Part II student
Alessandra La Via	Part II student
Weihao Yuen	Part II student

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Collaborations

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Introduction

Angular momentum polarization

Photodissociation

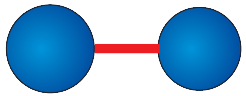
$$\mathrm{ABC} + h\nu \longrightarrow \mathrm{A}(\mathbf{j}) + \mathrm{BC}(\mathrm{v}', \mathbf{j}')$$

Angular momentum can be polarized

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

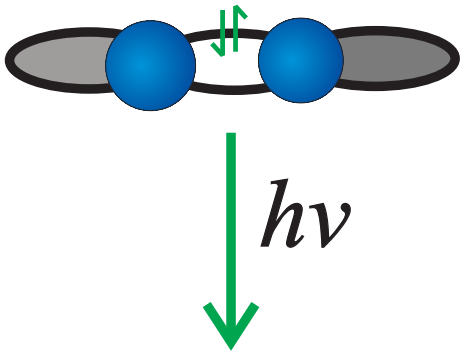
Electronic angular momentum polarization

Molecular photodissociation



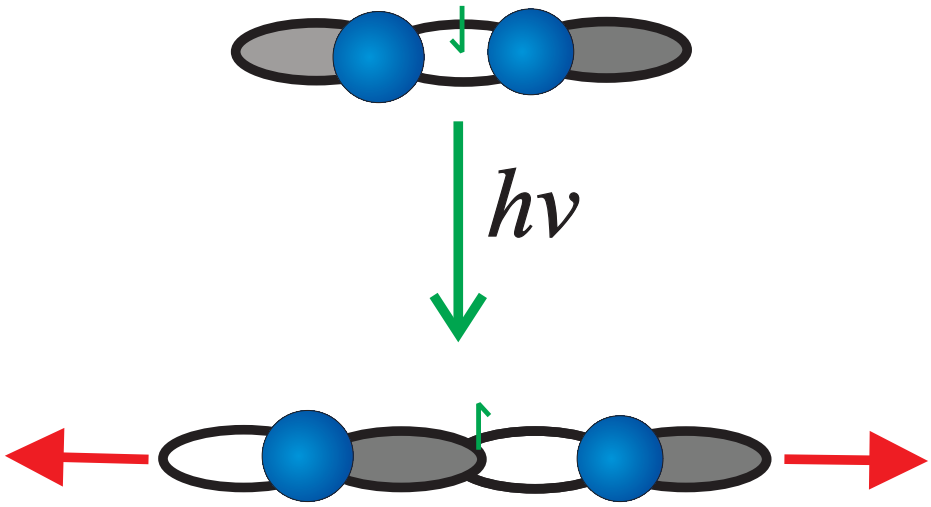
Electronic angular momentum polarization

Molecular photodissociation



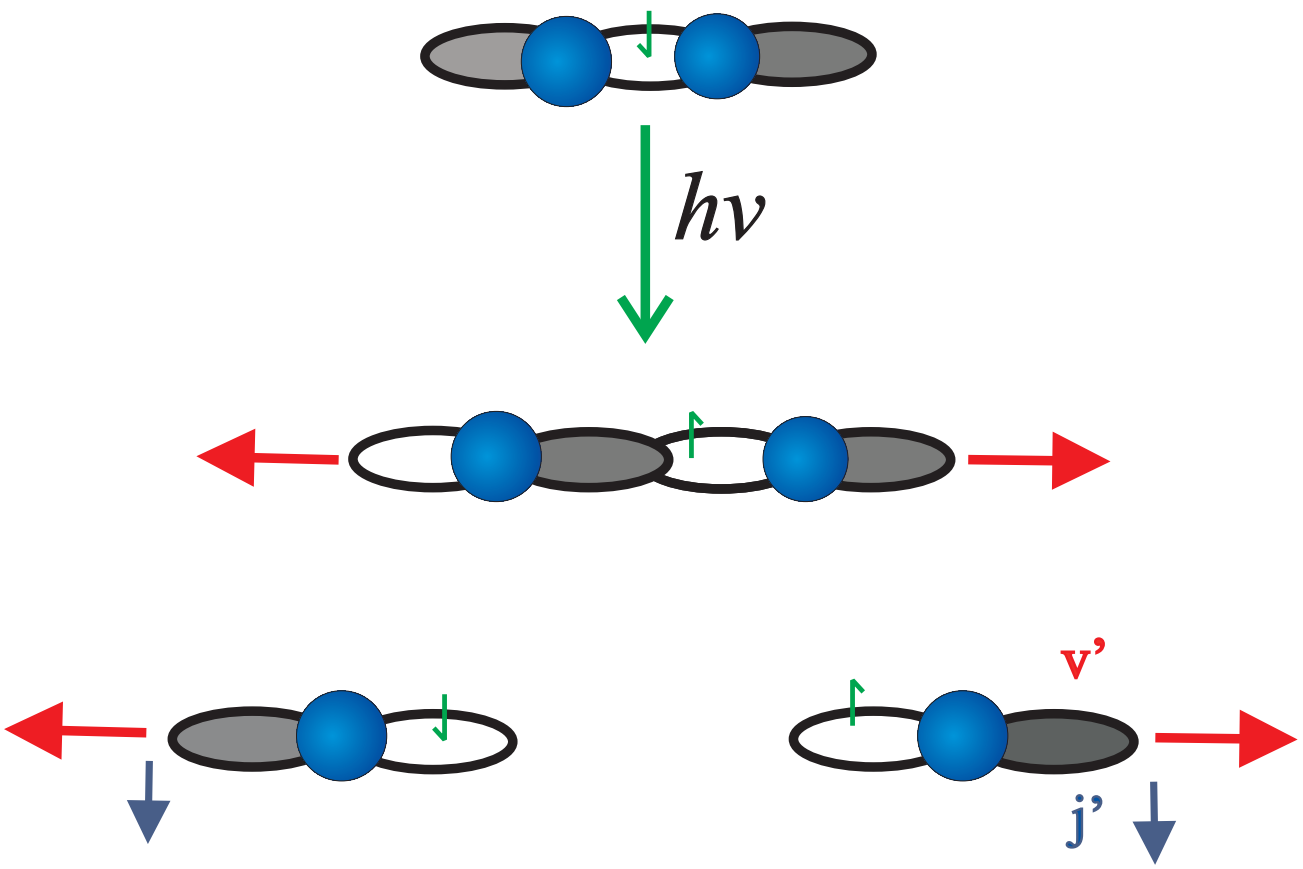
Electronic angular momentum polarization

Molecular photodissociation



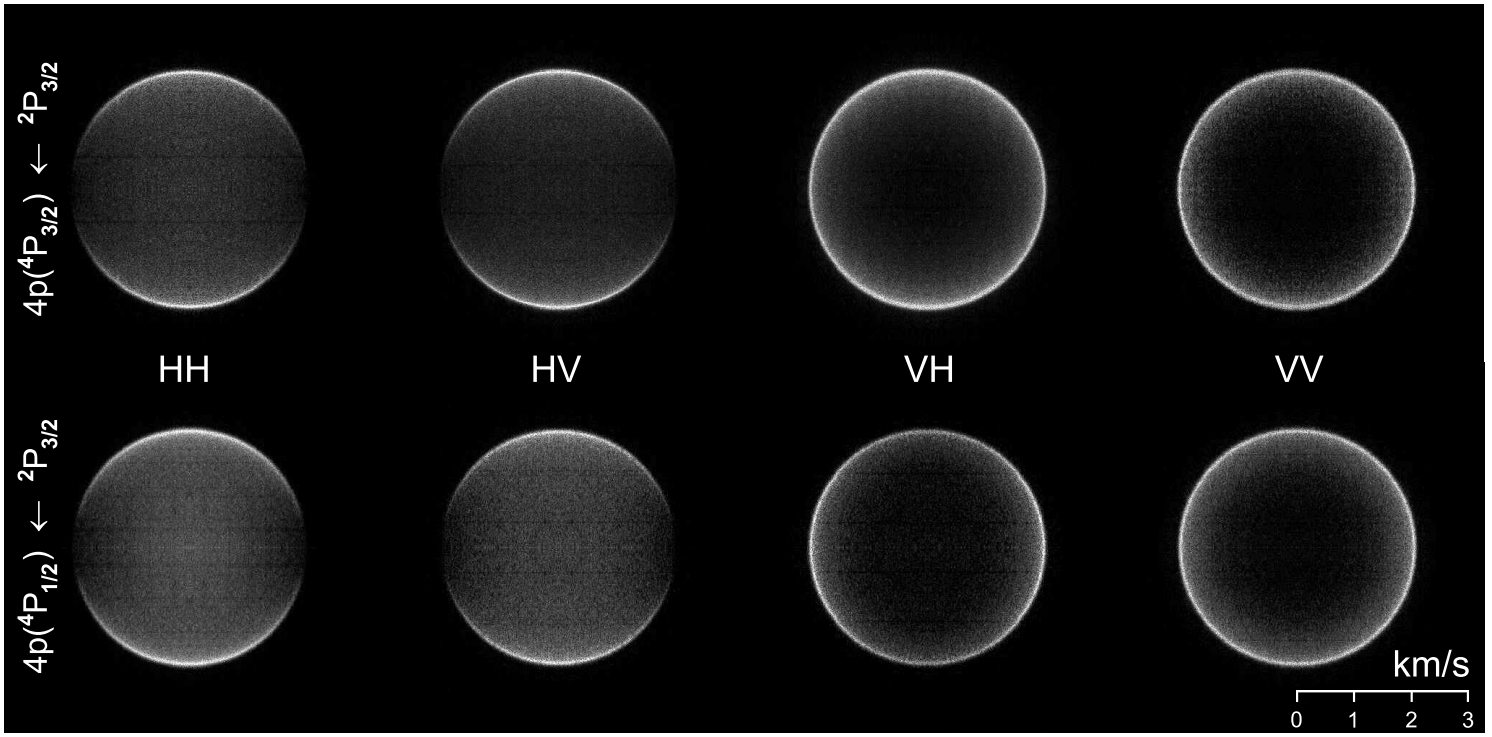
Electronic angular momentum polarization

Molecular photodissociation



How?

$$Cl_2 + h\nu \rightarrow Cl(^2P_j) + Cl(^2P_j)$$



Dependence on laser polarization and probe transition

Motivation

Electronic polarization

- Insight into electronic motion
- Helps assignment of dissociation mechanism
- Complementary information to translational anisotropy
- Atmospherically important processes

$$O_2 + h\nu \longrightarrow O(^3P_J) + O(^3P_J)$$

$$\lambda = 193\,\text{nm}$$

Andrew Clark

Fabio Quadrini

Raluca Cireasa

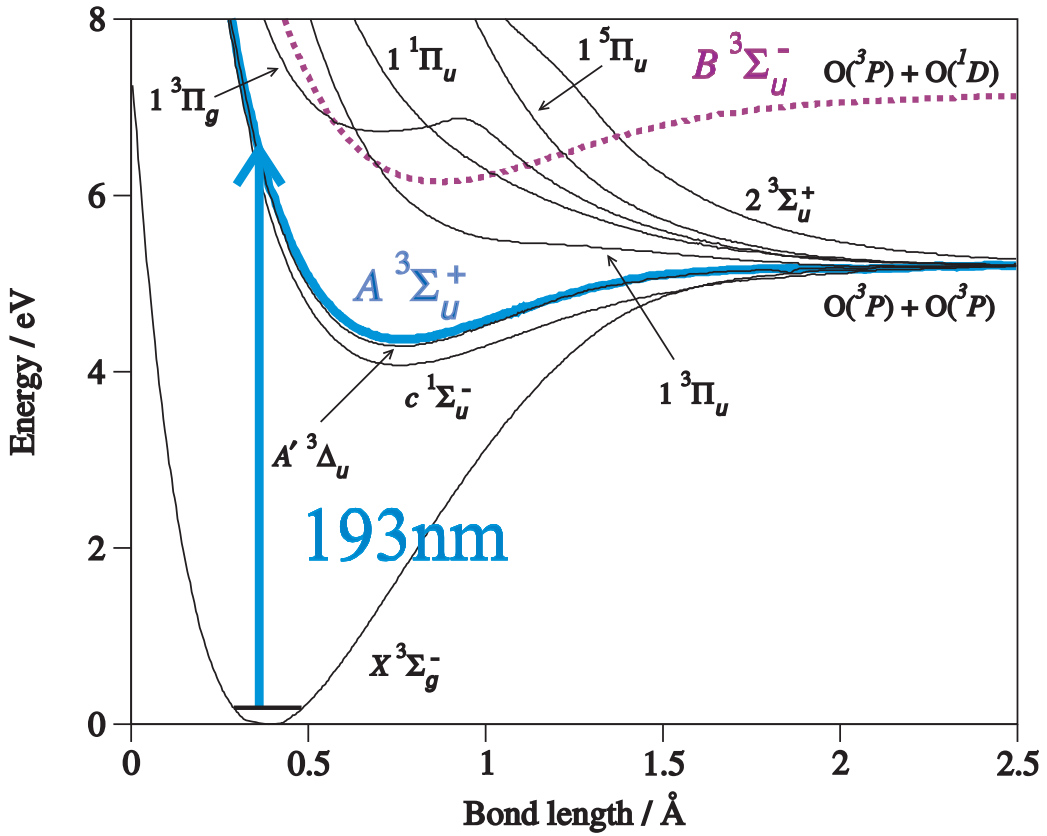
Gerrit C. Groenenboom

Issues to consider

- Measure polarization of $\mathbf{J}$
- Polarization of both $\mathbf{L}$ and $\mathbf{S}$ in exit channel is possible
- Theoretically tractable system
- O_2 is a well-characterized system
- Extend data to 193 nm

Potential energy curves

Continuum contribution - 95% Herzberg I

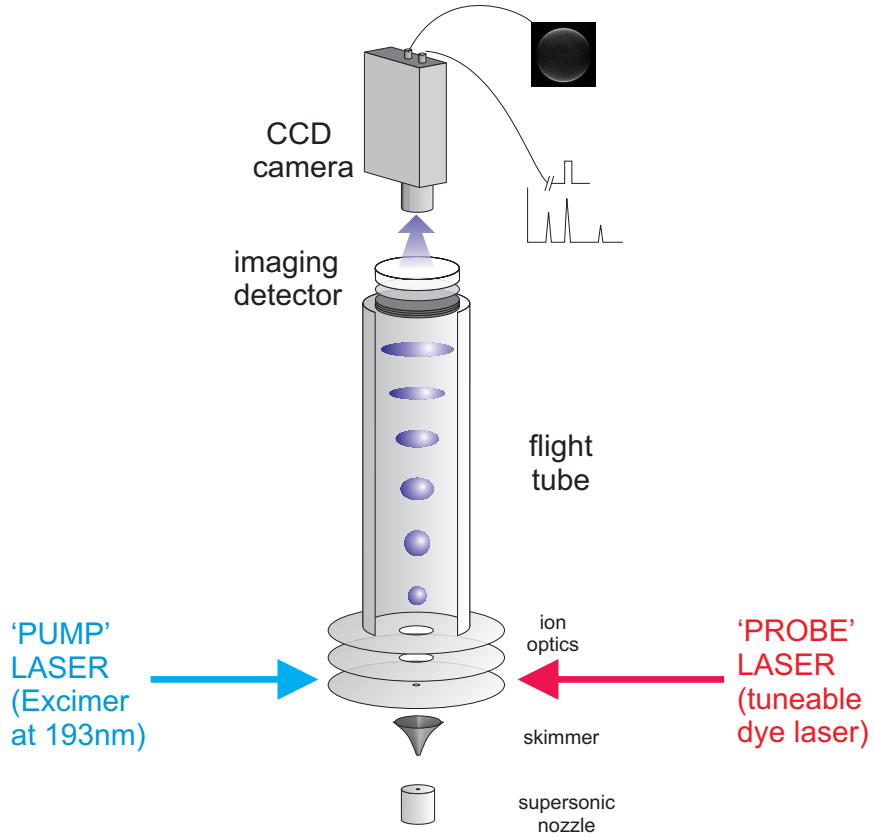


$$A(^3\Sigma_u^+) \leftarrow X(^3\Sigma_g^-)$$

B. Buijsse *et al. J. Chem. Phys.* (1998)

Experiment

Photodissociation (20% O_2 seeded in He...)

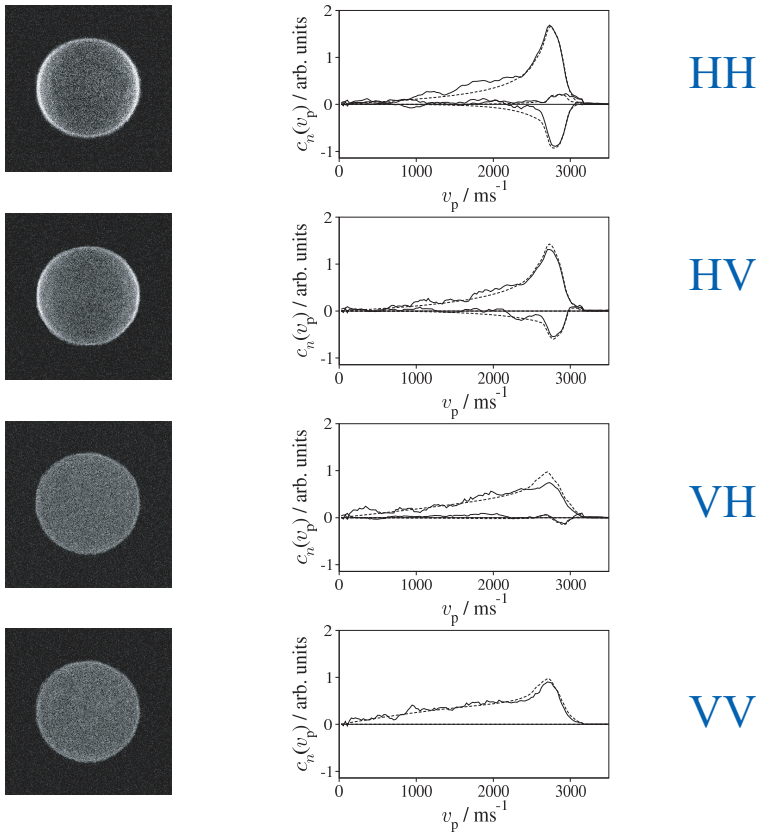


Chandler and Houston, Eppink and Parker

...followed by (2+1) REMPI of $O(^3P_J)$ around 225 nm

O($^3P_2$) ion images and moments

Dependence on pump-probe laser geometry

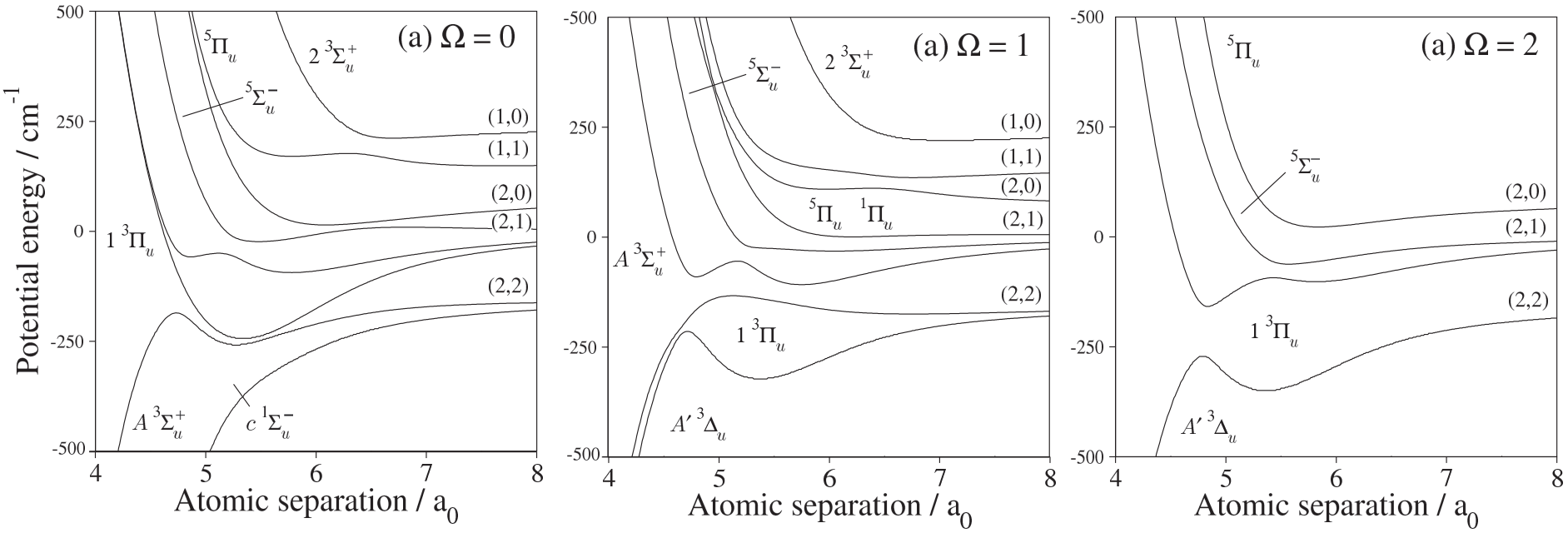


Fit to moments using basis function method

Linestrengths from Vroonhoven and Groenenboom *J. Chem. Phys.* (2002)

Potential curves ‡

Including spin-orbit coupling

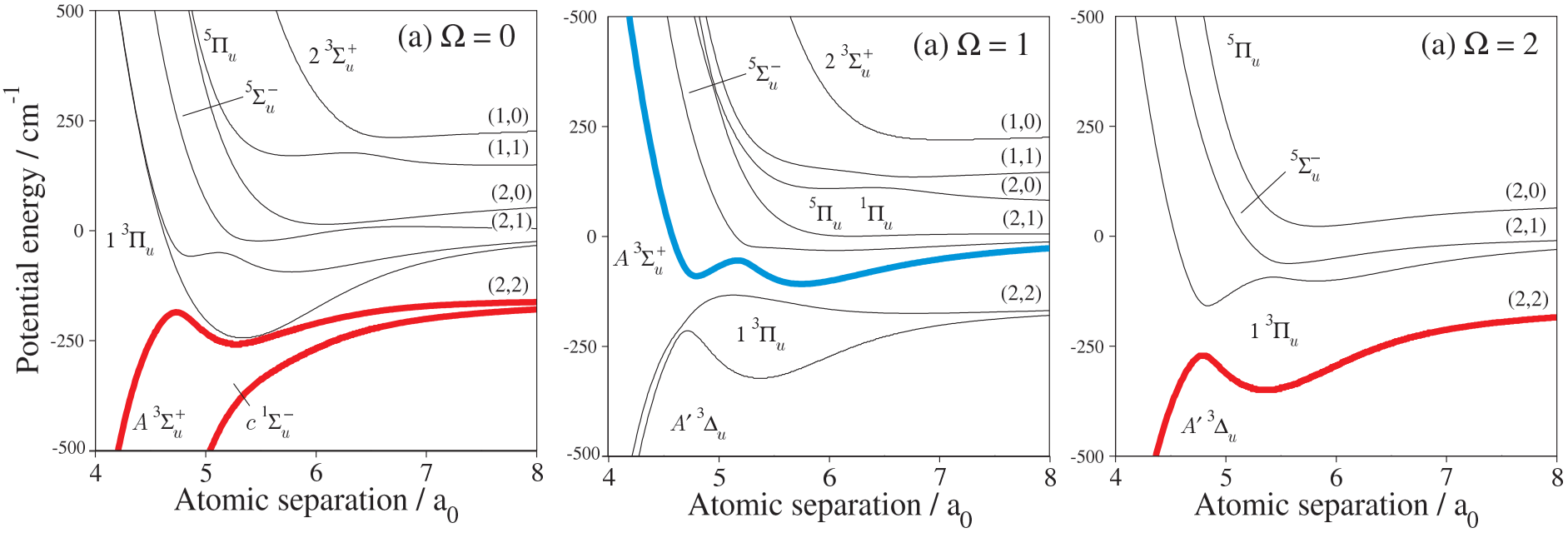


‡ M.C.G.N. van Vroonhoven and G.C. Groenenboom *J. Chem. Phys.* (2002)

Previous semi-classical theory ‡

Includes various couplings between potential curves

Neglects coherence effects during excitation and dissociation

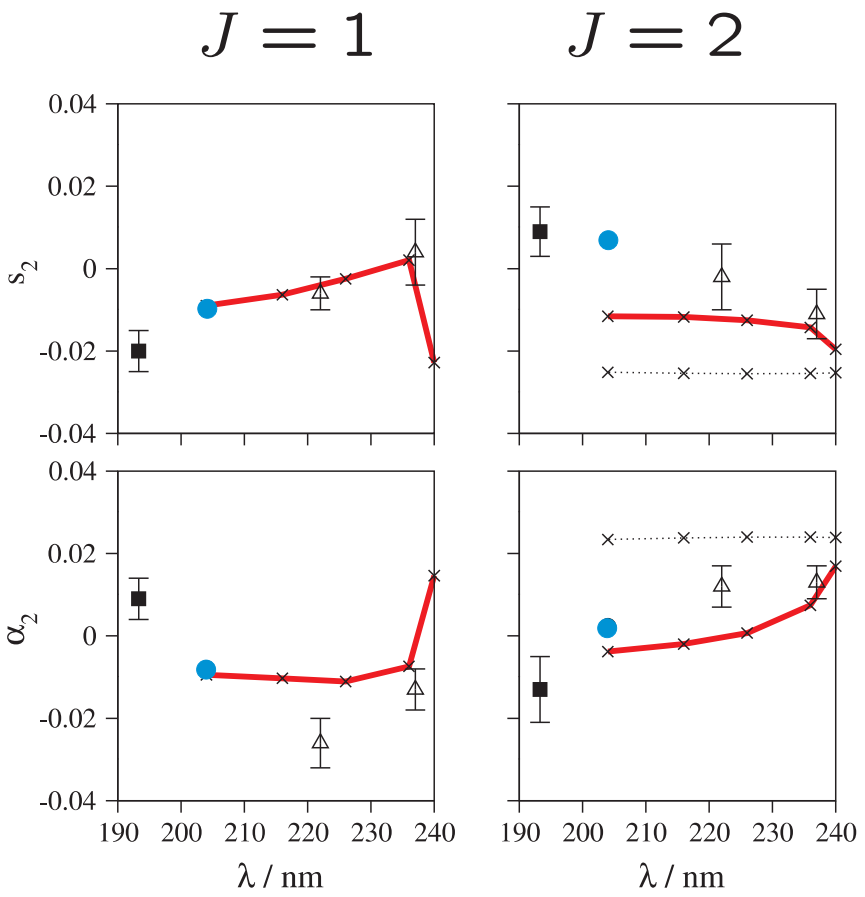


‡ M.C.G.N. van Vroonhoven and G.C. Groenenboom *J. Chem. Phys.* (2002)

Incoherent alignment

Semi-classical theory‡ *reproduces trends.*

- Extended diabatic model‡



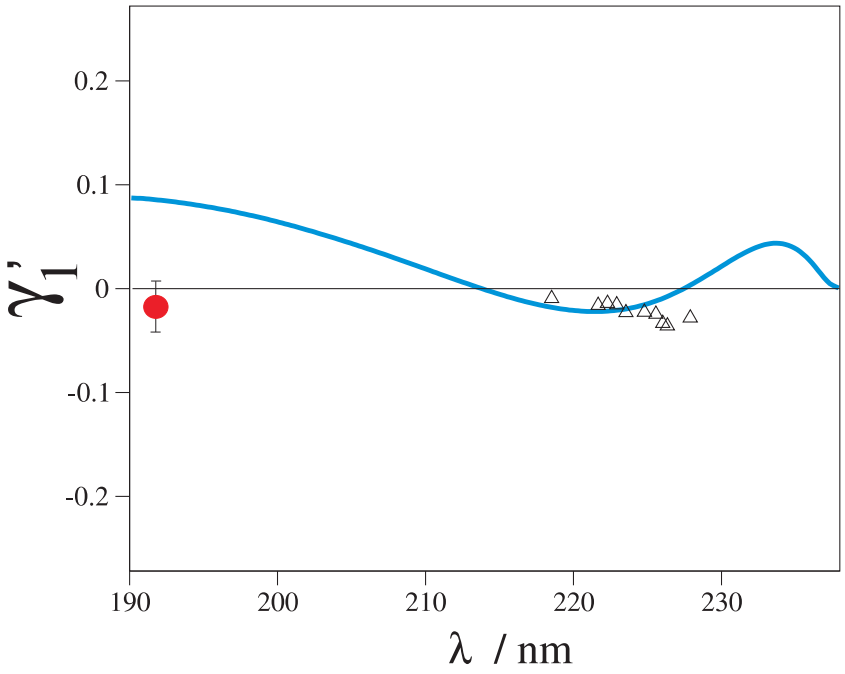
△ A.J. Alexander, Z.H. Kim, and R.N. Zare, *J. Chem. Phys.* (2003)

‡ M.C.G.N. van Vroonhoven and G.C. Groenenboom *J. Chem. Phys.* (2002)

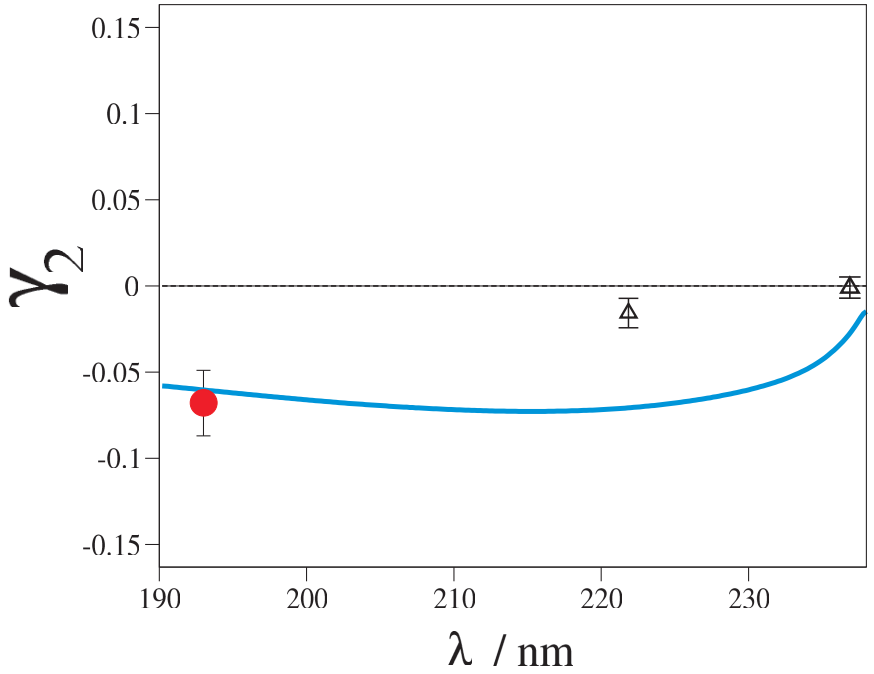
Coherent excitation: a crude estimate

Determine phase difference between $\parallel$ and $\perp$ channels

Orientation



Alignment



△ A.J. Alexander, Z.H. Kim, and R.N. Zare, *J. Chem. Phys.* (2003)

Potentials of van Vroonhoven and Groenenboom *J. Chem. Phys.* (2002)

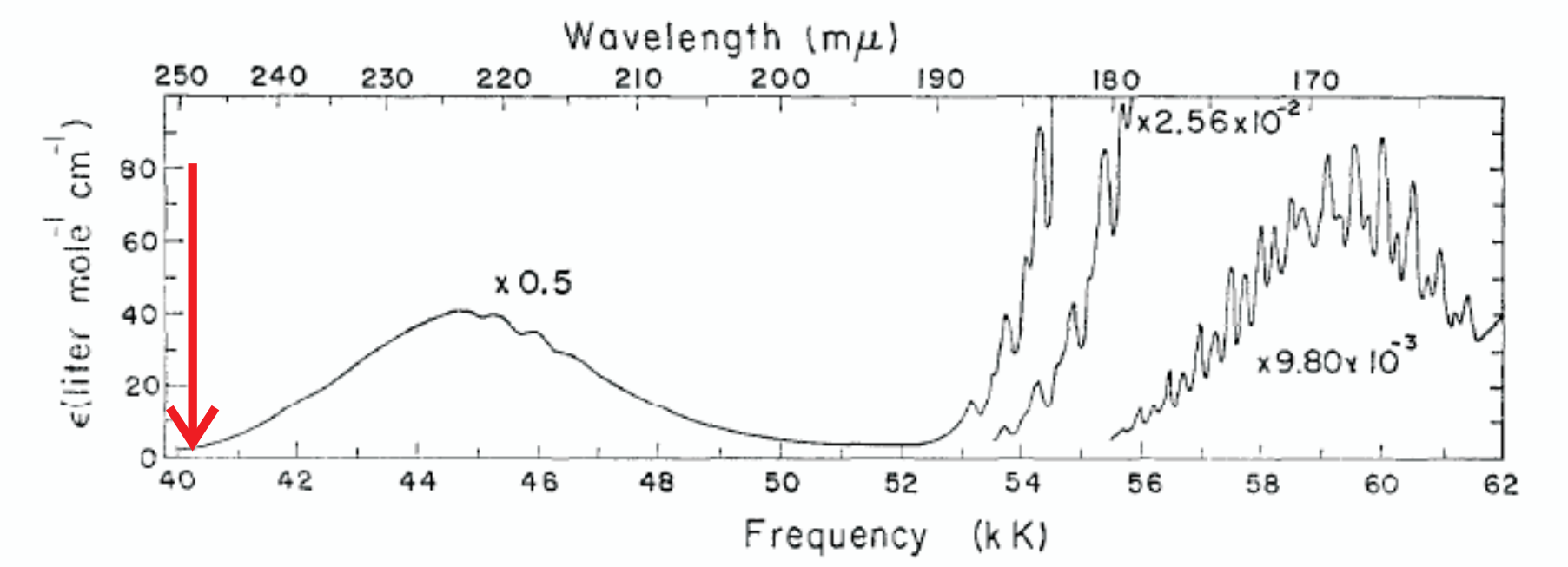
$$\mathrm{OCS} + h\nu \longrightarrow \mathrm{S}(^1D_2) + \mathrm{CO}(^1\Sigma^+)$$

$$\lambda = 248\,\mathrm{nm}$$

Fabio Quadrini (see Poster)

Raluca Cireasa

Absorption Spectrum



Red tail of the first absorption band

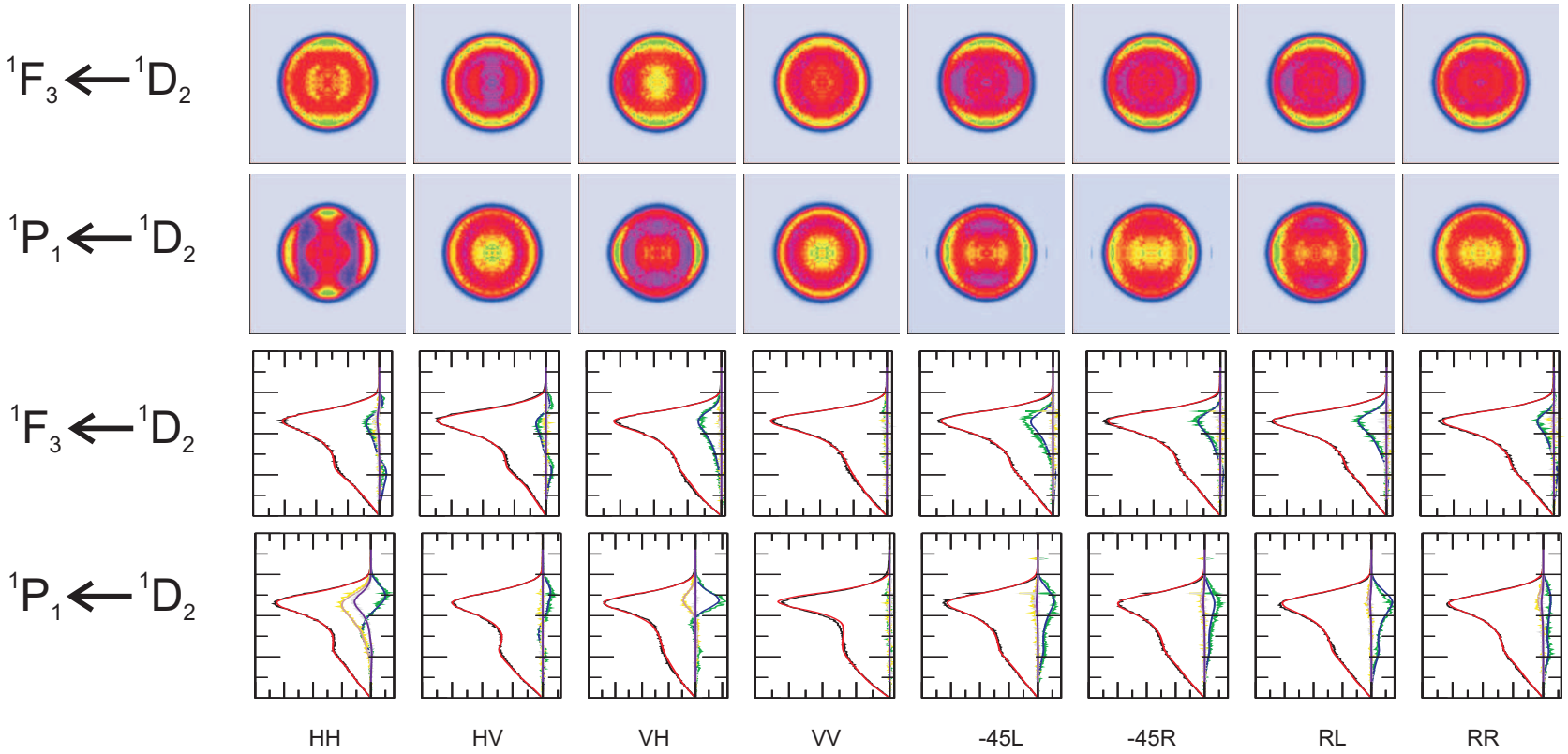
Adapted from J.W. Rabalais *Chem. Rev.* (1971)

Issues to consider

- Atomic angular momentum only arises from $\mathbf{L}$
- Coproduct (CO) is closed-shell
- Can polarization of $\mathbf{L}$ help in assigning mechanism(s)?
- How does polarization vary with dissociation pathway?

S($^1D_2$) Ion images

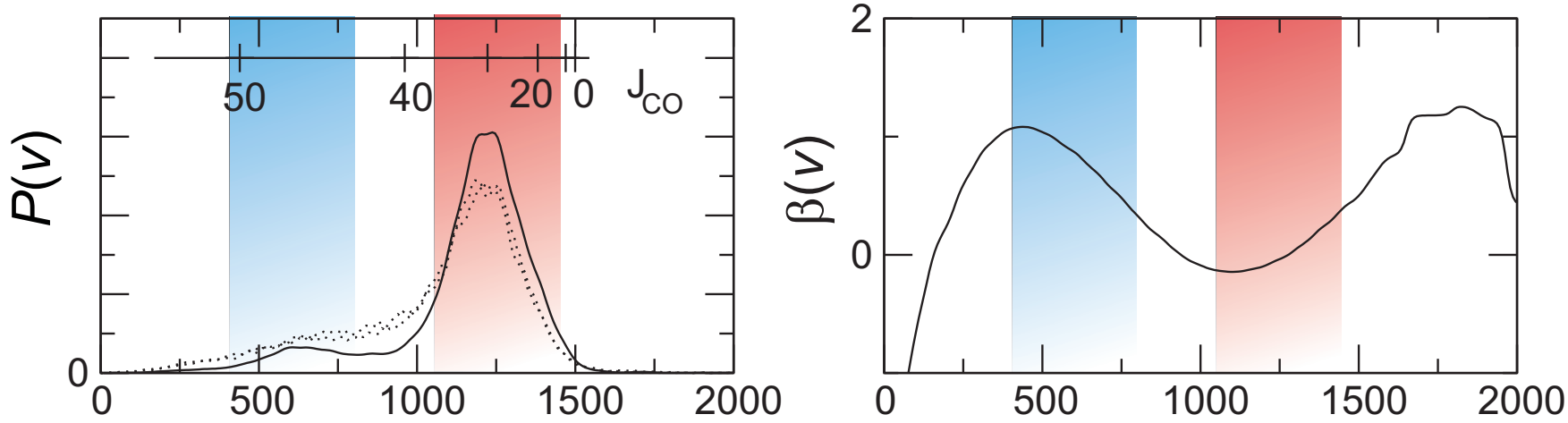
Photodissociation ($\lesssim$1% OCS seeded in He)....



...followed by (2+1) REMPI probing of S($^1D_2$) around 290 nm

S($^1D_2$) speed and anisotropy distributions

Bimodal speed distribution

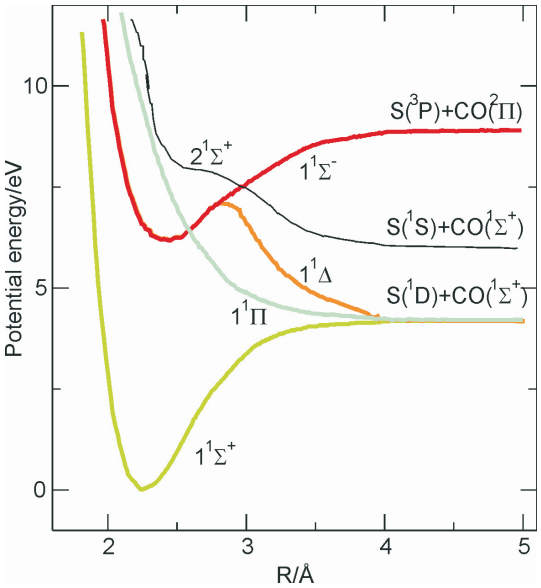


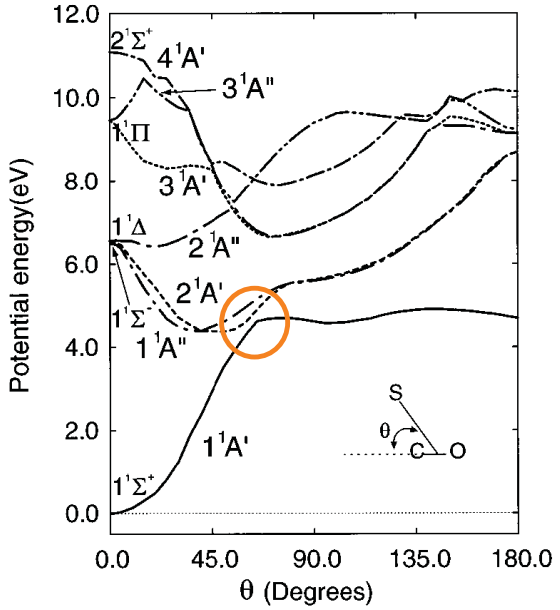
Excellent agreement with Suzuki and coworkers *J. Chem. Phys.* (1998)

CO is rotationally excited: Houston and coworkers *J. Chem. Phys.* (1988)

Source of bimodality

Major fast channel: Dissociation on the $2^1A'(^1\Pi)$ and $1^1A''(^1\Pi)$ states.



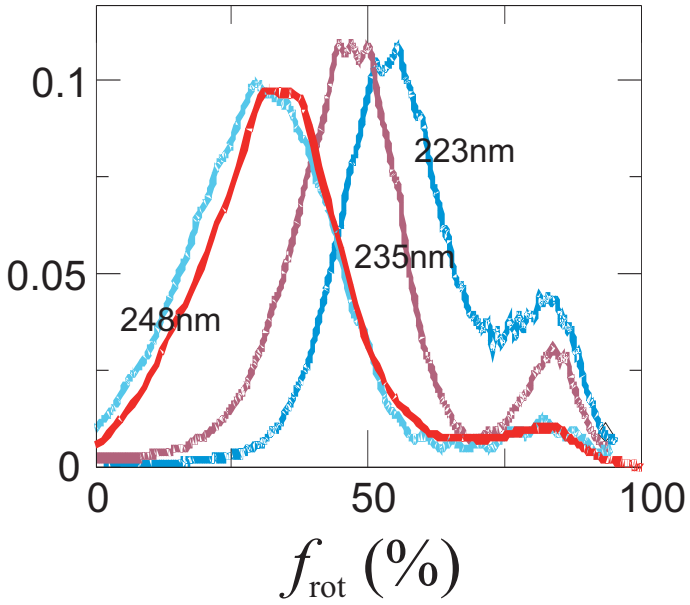


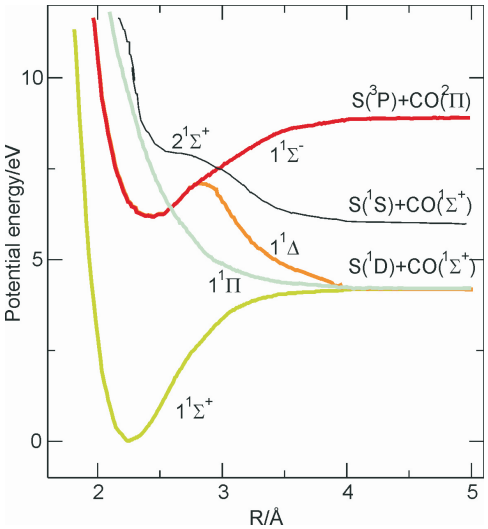
Minor slow channel: Nonadiabatic transition to ground $1^1A'$ state.

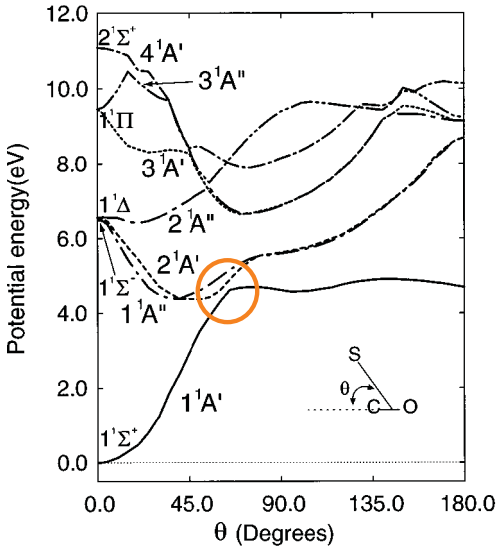
Adapted from Suzuki and coworkers *J. Chem. Phys.* (1998)

Comparison with Suzuki and coworkers

Major channel: f_{rot} changes with dissociation wavelength





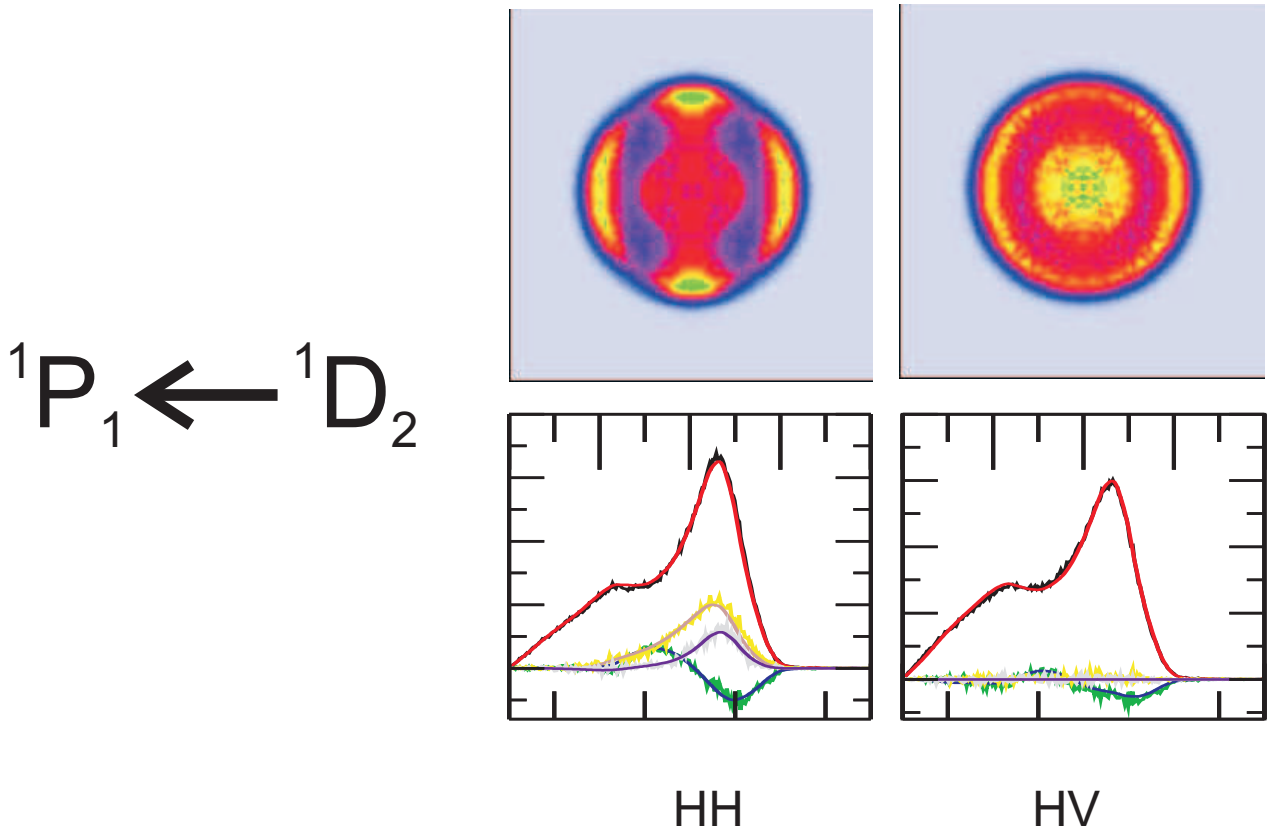


Minor channel: f_{rot} constant with dissociation wavelength

Potential curves from Suzuki and coworkers *J. Chem. Phys.* (1998)

Channel dependent polarization

Major channel: strongly polarized ($K = 4$ component very important).



Minor channel: less strongly and differently polarized.

Speed averaged polarization parameters at 248 nm

Moments with $K = 1$ through to $K = 4$

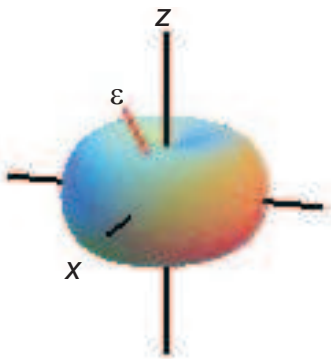
Polarization parameter	average	Slow (18%)	Fast (82%)
$\beta(v)$	0.078	0.734	-0.019
$\alpha_1(v)$	0.004	-0.003	0.006
$\gamma_1(v)$	0.085	0.085	0.085
$\gamma_1'(v)$	0.024	0.012	0.025
$s_2(v)$	-0.049	**0.007**	**-0.057**
$\alpha_2(v)$	-0.003	**0.022**	**-0.007**
$\gamma_2(v)$	-0.021	-0.040	-0.018
$\eta_2(v)$	0.024	0.025	0.023
$\alpha_3(v)$	0.019	-0.010	0.024
$\gamma_3(v)$	0.090	0.071	0.092
$\gamma_3'(v)$	0.011	0.141	-0.006
$s_4(v)$	-0.029	-0.004	-0.033
$\alpha_4(v)$	-0.008	0.011	-0.011
$\gamma_4(v)$	0.022	0.000	0.026
$\eta_4(v)$	-0.019	0.003	-0.022

Fast and slow components differently polarized

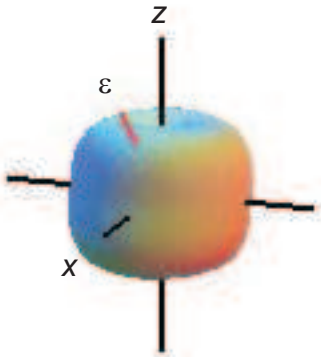
J- and electron-hole distributions

Fast component

J-dist



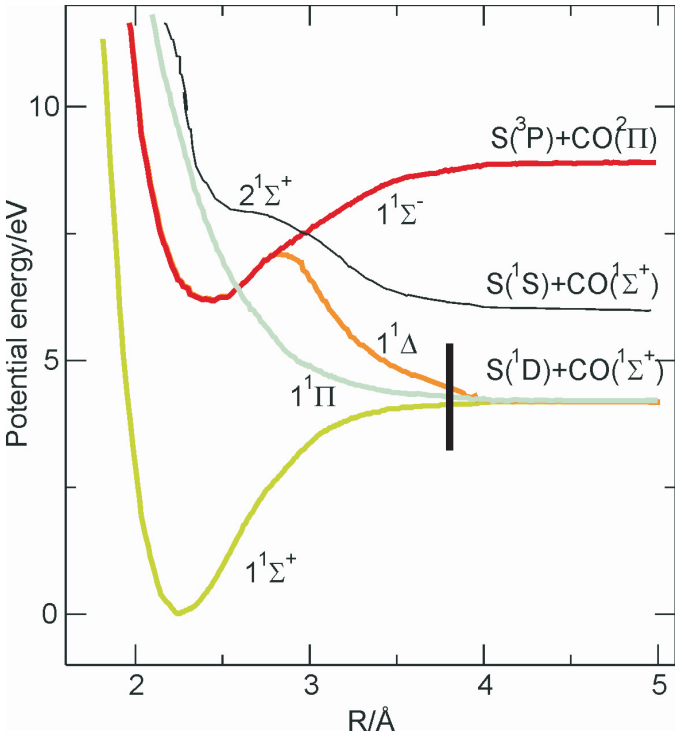
e-dist



Note: $z||v$ and zx plane contains ϵ

Potential energy curves

Fast component

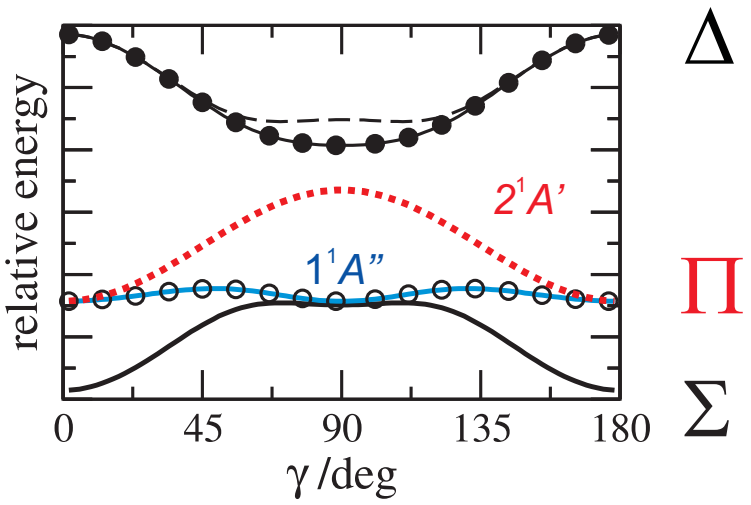


Dissociation on state of Π symmetry at linearity.

Potential curves from Suzuki and coworkers, *J. Chem. Phys.* (1998)

Long range potentials

Angular dependence of electrostatic potentials



Quadrupole-quadrupole interaction

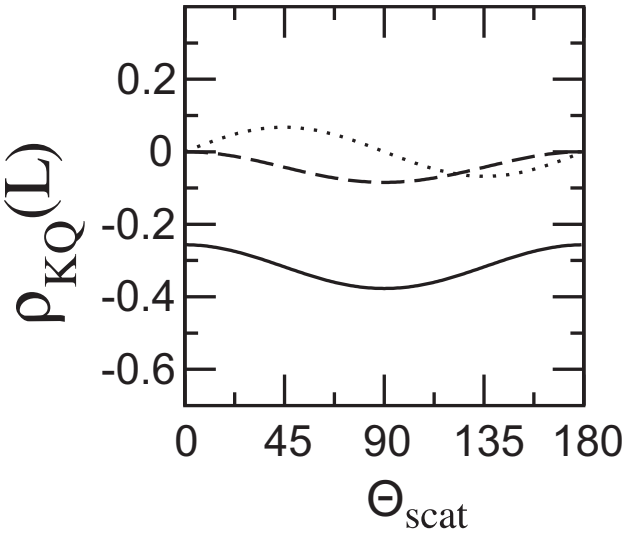
G.C. Groenenboom and coworkers, *J. Phys. Chem. A* (2004)

Predicted polarization parameters: fast component

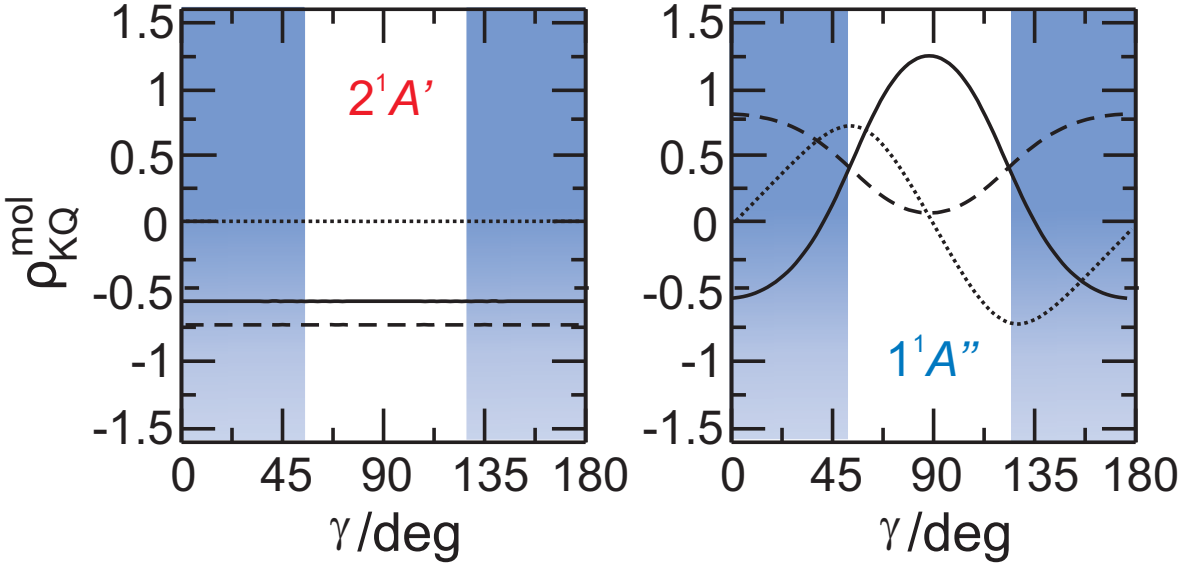
Supports dissociation mainly on $2^1A'$ state.

—— ρ_{20} ····· ρ_{21} – – –– ρ_{22}

Experimental



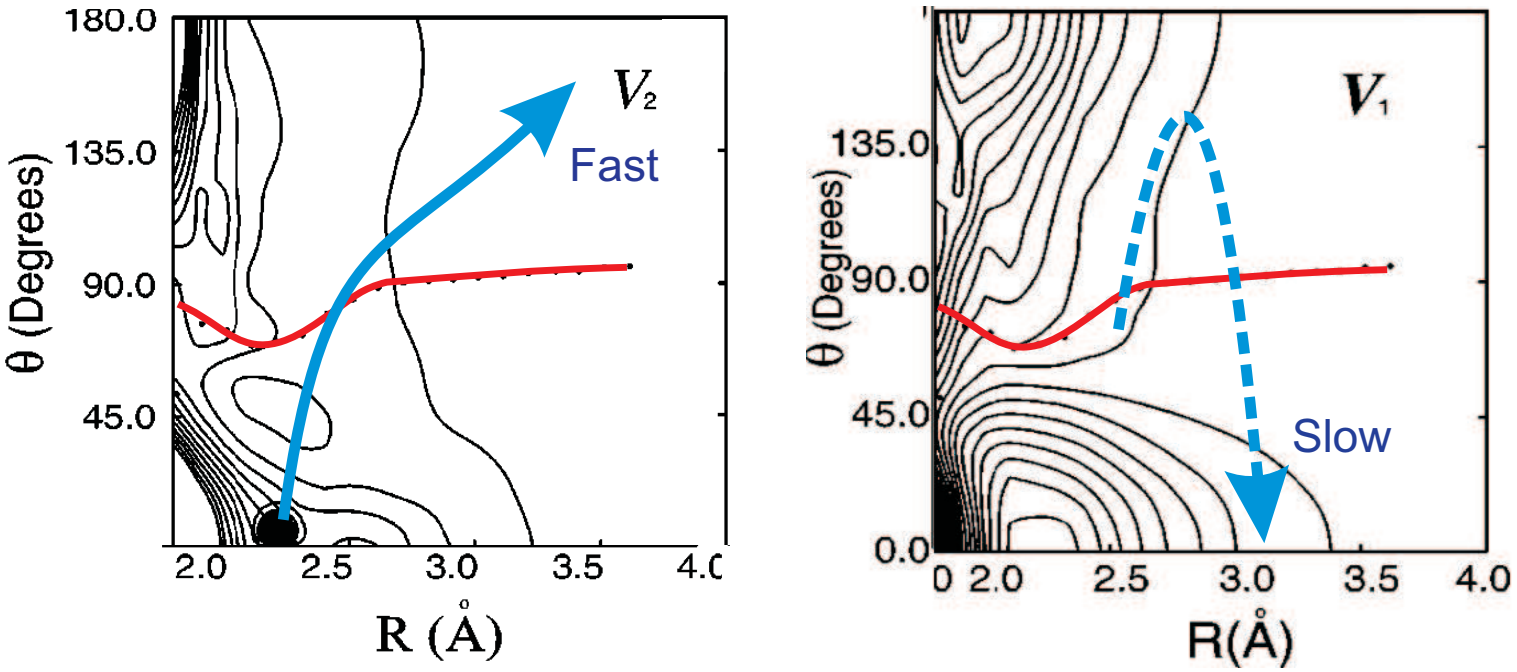
Calculated



Calculations neglect coherence effects and averaging over Jacobi angle γ.

Predicted polarization parameters: slow component

Dissociation via seam of intersection



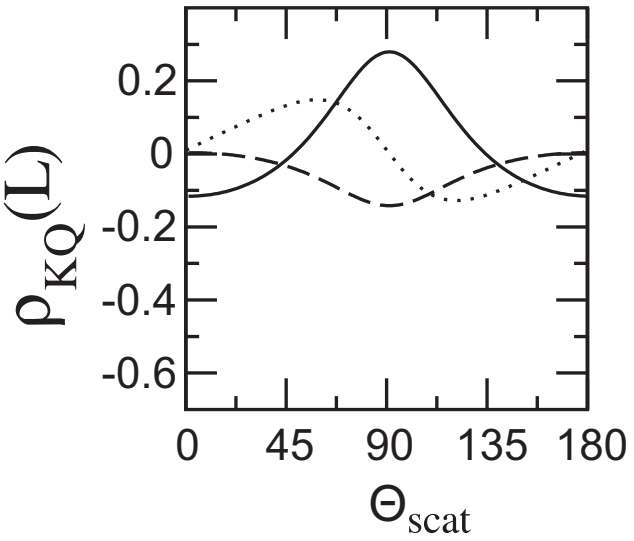
Diabatic potentials from Suzuki and coworkers, *J. Chem. Phys.* (1998)

Predicted polarization parameters: slow component

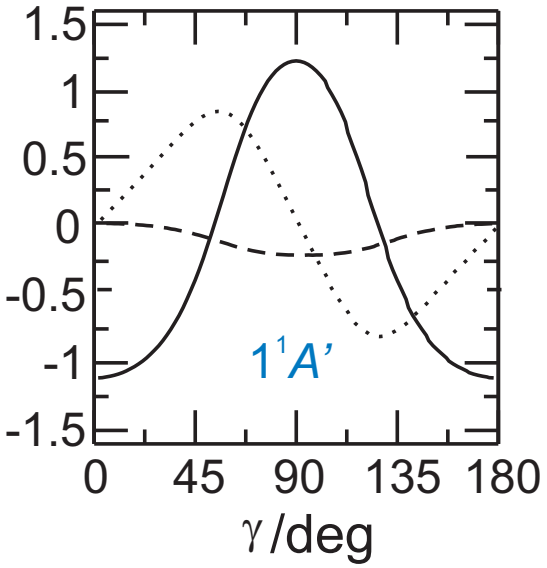
Supports dissociation via ground $1^1A'$ state.

—— ρ_{20} ····· ρ_{21} – – –– ρ_{22}

Experimental



Calculated



CO rotation smears out polarization.

Calculations neglect coherence effects and averaging over Jacobi angle γ.

Summary

- Large orbital polarization observed at 248 nm.
- All polarization moments determined, including up to $K = 4$.
- Contributions from $K = 4$ moments are significant.
- Polarization is different for fast and slow $S(^1D_2)$.
- Polarization reflects different dissociative pathway.
- Further theoretical work is needed interpret polarization.

$$\mathrm{OCS} + h\nu \longrightarrow \mathrm{S}(^3P_J) + \mathrm{CO}(^1\Sigma^+)$$

$$\lambda = 248\,\mathrm{nm}$$

Fabio Quadrini (see Poster)

Raluca Cireasa

Issues to consider

- Minor 5% channel

  (Houston and coworkers, *Chem. Phys. Lett.* (1993))

- Both $\mathbf{L}$ and $\mathbf{S}$ involved.

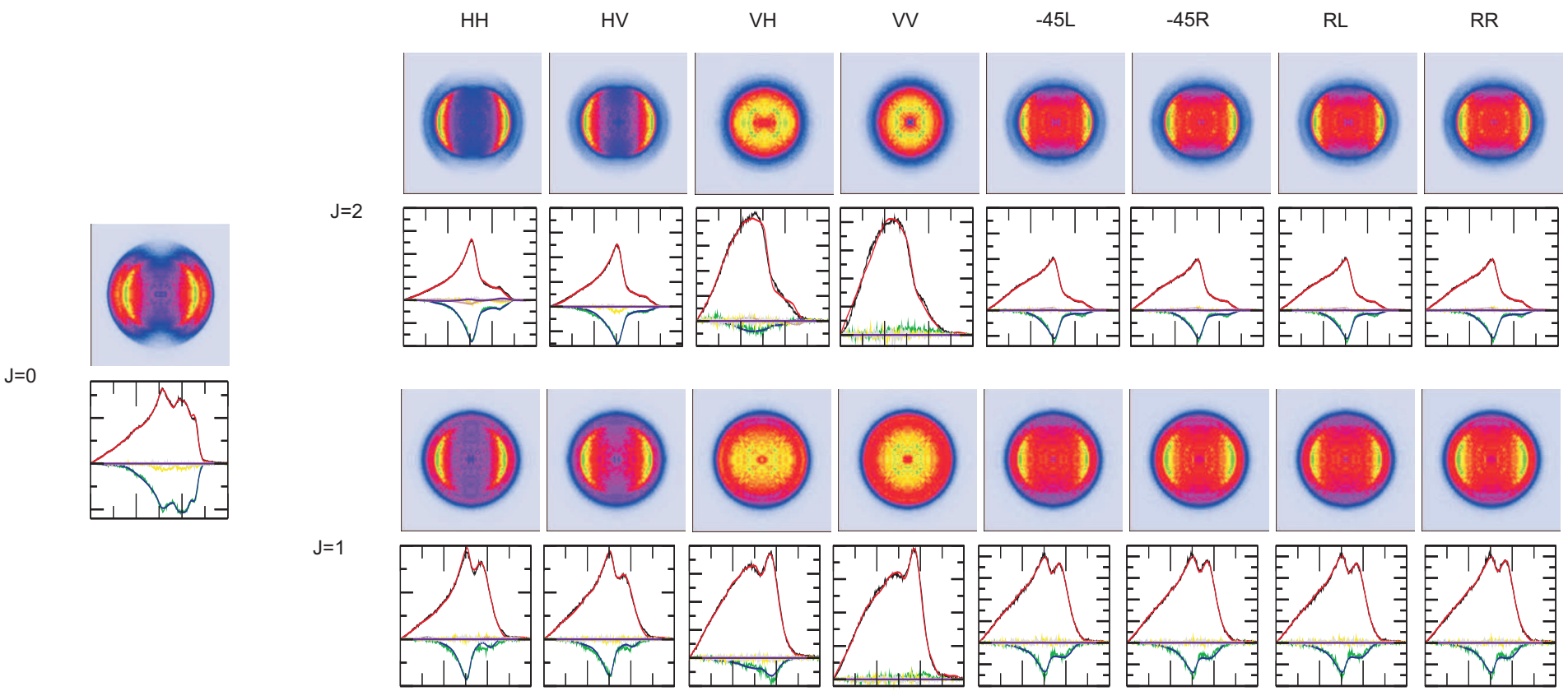
- Can polarization of $\mathbf{J}$ still provide helpful information?

- Test out using OCS at 248 nm.

- Help assign dissociation mechanism for $S(^3P_J)$ formation.

S(^3P_J) images and moments

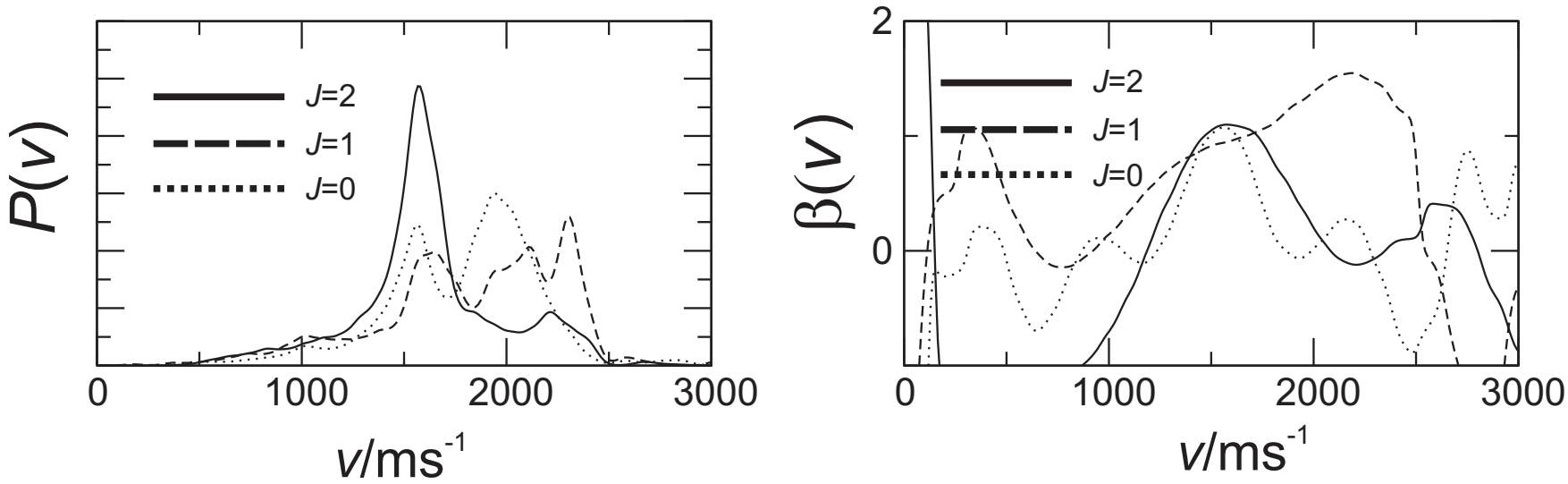
Moment analysis



Fit using basis function method

S(^3P_J) speed and anisotropy distributions

J-dependent speed and anisotropy distributions

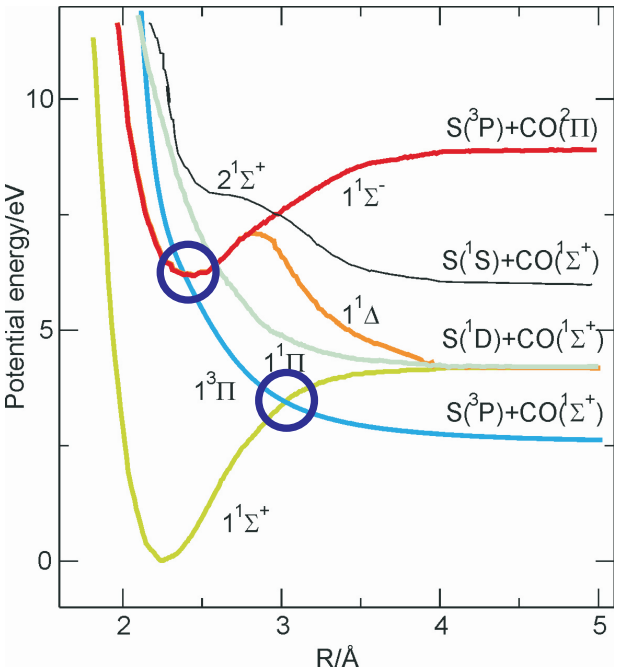


Spin-orbit populations $P(J = 2 : 1 : 0) = 8 : 3 : 1$

At 1500 m s^{-1} $\beta(v)$ for each J close to that for slow S(^{1}D$_2$) channel.

Potential energy curves

Intersystem crossing pathways



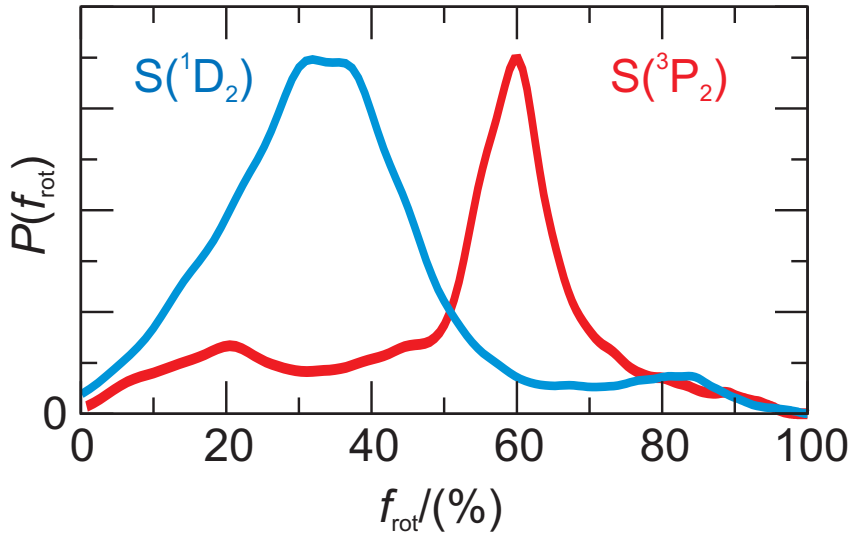
ISC from ground state involves $1^3A'(^3\Pi)$ state (c.f. collisional quenching)

Singlet curves from Suzuki and coworkers, *J. Chem. Phys.* (1998)

Triplet curve from Y. Inagaki *et al.*, *J. Chem. Phys.* (1995)

S($^3P_2$) speed and anisotropy distributions

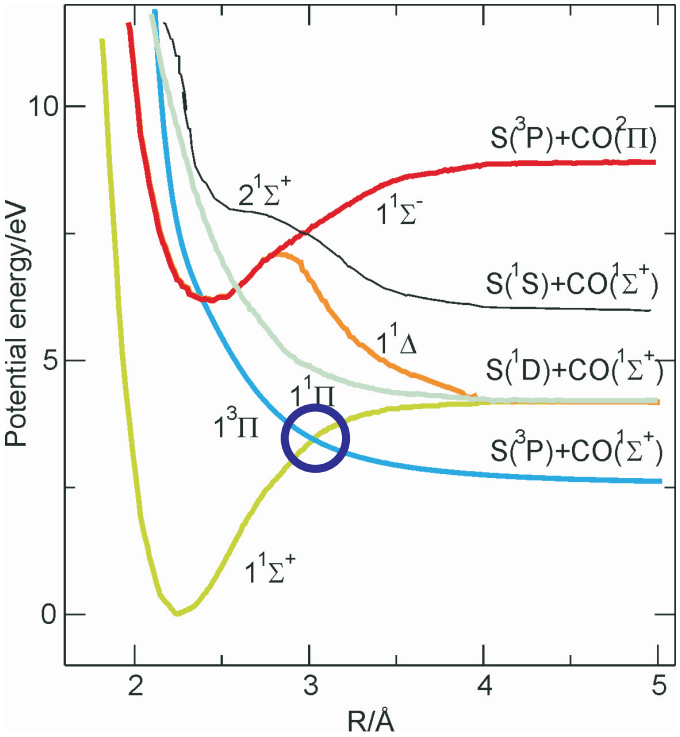
Comparison with the singlet channel



S(^{3}P$_2$) may arise from ISC from the ground state (consistent with $\beta(v)$)

Potential energy curves

Implies intersystem crossing from the ground $1^1A'(^1\Sigma)$ *state*



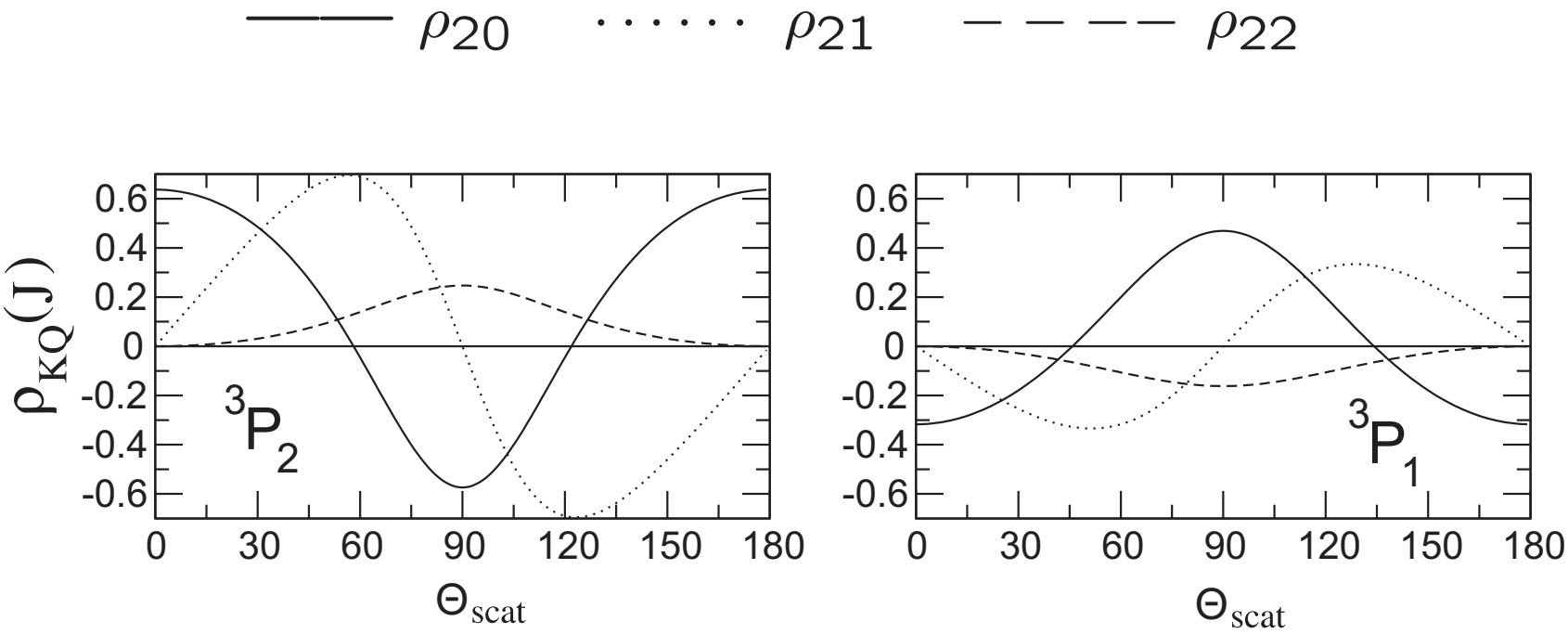
Higher kinetic energy release (c.f. dissociation on ground singlet state)

Singlet curves from Suzuki and coworkers, *J. Chem. Phys.* (1998)

Triplet curve from Y. Inagaki *et al.*, *J. Chem. Phys.* (1995)

Molecular frame J-polarization

$J = 2$ and $J = 1$ are differently polarized

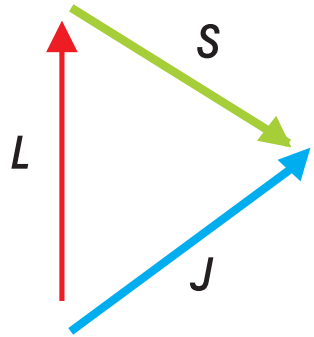


Need to consider coupling of $\mathbf{L}$ and $\mathbf{S}$ during dissociation.

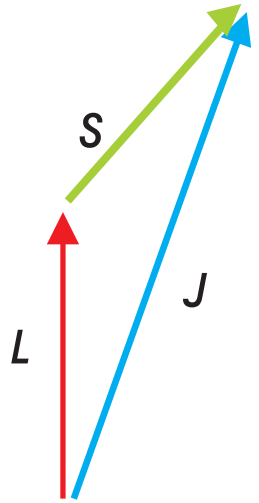
Adiabatic versus diabatic models

Two sources of angular momentum, $\mathbf{L}$ *and* $\mathbf{S}$

Only know polarization of $\mathbf{J}$



$J = 1$

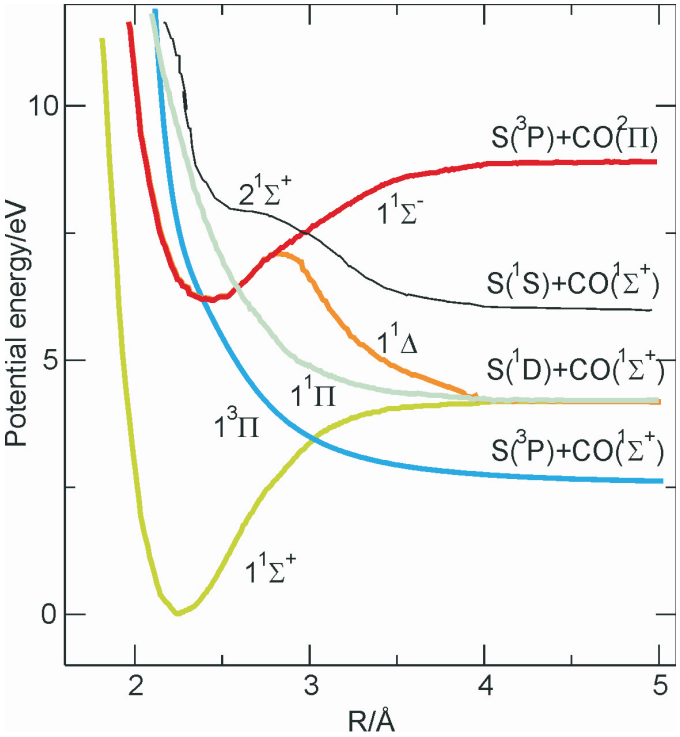


$J = 2$

Sudden recoupling of $\mathbf{S}$ and $\mathbf{L}$ is inappropriate in this case.

Potential energy curves

$S(^3P_J)$ motion is relatively slow through the recoupling zone



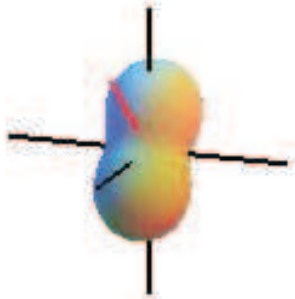
Spin-orbit populations and speed distributions are non-statistical

Singlet curves from Suzuki and coworkers, *J. Chem. Phys.* (1998)

Triplet curve from Y. Inagaki *et al.*, *J. Chem. Phys.* (1995)

S(^{3}P$_2$) J-distribution

Preferential population of $M_J = \pm 1, \pm 2$

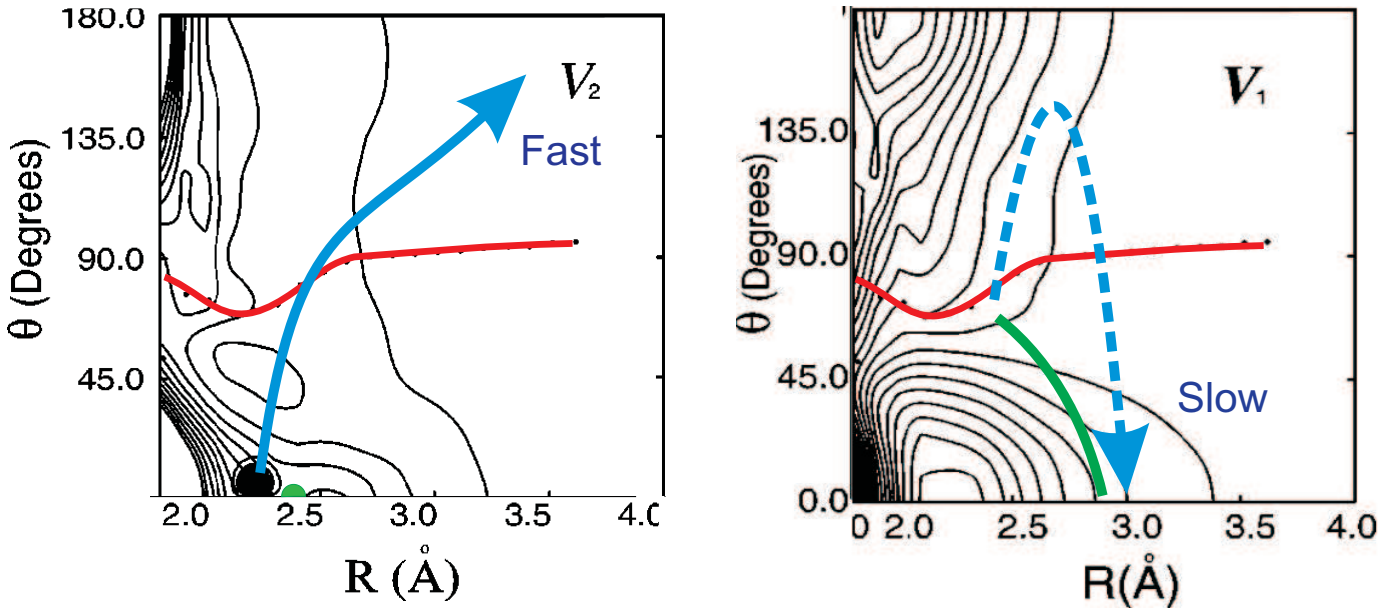


Consistent with adiabatic dissociation *via* lowest $^3A'$ state.

Note: $z||v$ and zx plane contains ϵ

Potential surfaces and ISC

Dissociation via ISC between ground singlet and triplet states



Probability of ISC on ground state must be quite high

Diabatic potentials from Suzuki and coworkers, *J. Chem. Phys.* (1998)

Triplet surface from Y. Inagaki *et al.*, *J. Chem. Phys.* (1995)

Summary

- S^3P_J channel extremely complex.
- Speed and anisotropy data are J-dependent.
- S^3P_2 data suggests an ISC pathway *via* ground state.
- Polarization data seems to support this interpretation.
- Further theoretical work required particularly for triatomics.

The end