Atomic photofragment polarization as a probe of molecular photodissociation dynamics

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Acknowledgements

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Introduction
Angular momentum polarization

Photodissociation

\[ \text{ABC} \ + \ h\nu \ \rightarrow \ A(j) \ + \ BC(v', j') \]

Angular momentum can be polarized

Measure angular distribution of \( j \) or \( j' \)
Electronic angular momentum polarization

Molecular photodissociation
Electronic angular momentum polarization

Molecular photodissociation

\[ hv \]
Electronic angular momentum polarization

Molecular photodissociation

\[ h\nu \]
Electronic angular momentum polarization

Molecular photodissociation

hv

v'

j'
How?

\[ \text{Cl}_2 + h\nu \rightarrow \text{Cl}(^2P_j) + \text{Cl}(^2P_j) \]

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
\[
\text{O}_2 + h\nu \rightarrow \text{O}(^{3}P_J) + \text{O}(^{3}P_J)
\]

\[\lambda = 193 \text{ nm}\]

Andrew Clark
Fabio Quadrini
Raluca Cireasa
Gerrit C. Groenenboom
Issues to consider

- Measure polarization of \( J \)
- Polarization of both \( L \) and \( S \) in exit channel is possible
- Theoretically tractable system
- \( \text{O}_2 \) is a well-characterized system
- Extend data to 193 nm
Potential energy curves

Continuum contribution - 95% Herzberg I

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

Photodissociation (20% O$_2$ seeded in He...)

...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

Potential curves‡

Including spin-orbit coupling

Previous semi-classical theory ‡

Includes various couplings between potential curves

Neglects coherence effects during excitation and dissociation

Incoherent alignment

**Semi-classical theory**\(^†\) reproduces trends.

\[ J = 1 \quad J = 2 \]

\[ \lambda \text{ / nm} \]

\[ \lambda \text{ / nm} \]

---


Coherent excitation: a crude estimate

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

Orientation

Alignment


\[ \text{OCS} + h\nu \rightarrow \text{S}(^1D_2) + \text{CO}(^1\Sigma^+) \]

\[ \lambda = 248 \text{ nm} \]

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 $L$
- Coproduct (CO) is closed-shell
- Can polarization of $L$ 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


Source of bimodality

Major fast channel: Dissociation on the $2^1\Sigma^+ (^1\Pi)$ and $1^1\Sigma^\prime\prime (^1\Pi)$ states.

Minor slow channel: Nonadiabatic transition to ground $1^1\Sigma^+$ state.

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

**Major channel:** $f_{\text{rot}}$ changes with dissociation wavelength

**Minor channel:** $f_{\text{rot}}$ constant with dissociation wavelength

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 \( K = 4 \)**

<table>
<thead>
<tr>
<th>Polarization parameter</th>
<th>average</th>
<th>Slow (18%)</th>
<th>Fast (82%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \beta(v) )</td>
<td>0.078</td>
<td>0.734</td>
<td>-0.019</td>
</tr>
<tr>
<td>( \alpha_1(v) )</td>
<td>0.004</td>
<td>-0.003</td>
<td>0.006</td>
</tr>
<tr>
<td>( \gamma_1(v) )</td>
<td>0.085</td>
<td>0.085</td>
<td>0.085</td>
</tr>
<tr>
<td>( \gamma'_1(v) )</td>
<td>0.024</td>
<td>0.012</td>
<td>0.025</td>
</tr>
<tr>
<td>( s_2(v) )</td>
<td>-0.049</td>
<td><strong>0.007</strong></td>
<td><strong>-0.057</strong></td>
</tr>
<tr>
<td>( \alpha_2(v) )</td>
<td>-0.003</td>
<td><strong>0.022</strong></td>
<td><strong>-0.007</strong></td>
</tr>
<tr>
<td>( \gamma_2(v) )</td>
<td>-0.021</td>
<td>-0.040</td>
<td>-0.018</td>
</tr>
<tr>
<td>( \eta_2(v) )</td>
<td>0.024</td>
<td>0.025</td>
<td>0.023</td>
</tr>
<tr>
<td>( \alpha_3(v) )</td>
<td>0.019</td>
<td>-0.010</td>
<td>0.024</td>
</tr>
<tr>
<td>( \gamma_3(v) )</td>
<td>0.090</td>
<td>0.071</td>
<td>0.092</td>
</tr>
<tr>
<td>( \gamma'_3(v) )</td>
<td>0.011</td>
<td>0.141</td>
<td>-0.006</td>
</tr>
<tr>
<td>( s_4(v) )</td>
<td>-0.029</td>
<td>-0.004</td>
<td>-0.033</td>
</tr>
<tr>
<td>( \alpha_4(v) )</td>
<td>-0.008</td>
<td>0.011</td>
<td>-0.011</td>
</tr>
<tr>
<td>( \gamma_4(v) )</td>
<td>0.022</td>
<td>0.000</td>
<td>0.026</td>
</tr>
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<td>( \eta_4(v) )</td>
<td>-0.019</td>
<td>0.003</td>
<td>-0.022</td>
</tr>
</tbody>
</table>

Fast and slow components differently polarized
$J$- and electron-hole distributions

*Fast component*

Note: $z \parallel v$ and $zx$ plane contains $\epsilon$
Potential energy curves

Fast component

Dissociation on state of $\Pi$ symmetry at linearity.

Long range potentials

Angular dependence of electrostatic potentials

Quadrupole-quadrupole interaction

Predicted polarization parameters: fast component

Supports dissociation mainly on $^{2}\text{A}^\prime$ state.

\[ \rho_{20} \quad \cdots \cdots \quad \rho_{21} \quad \cdots \cdots \quad \rho_{22} \]

Calculations neglect coherence effects and averaging over Jacobi angle $\gamma$. 

Predicted polarization parameters: slow component

Dissociation via seam of intersection

Predicted polarization parameters: slow component

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

\[
\begin{align*}
\rho_{20} & \quad \cdots \cdots \quad \rho_{21} \\
\rho_{22} & 
\end{align*}
\]

**Experimental**

**Calculated**

**CO rotation smears out polarization.**

Calculations neglect coherence effects and averaging over Jacobi angle $\gamma$. 
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.
OCS + h\nu \rightarrow S(^3P_J) + CO(^1\Sigma^+) \\

\lambda = 248 \text{ nm} \\

Fabio Quadrini (see Poster) \\
Raluca Cireasa
Issues to consider

- Minor 5% channel
  (Houston and coworkers, *Chem. Phys. Lett.* (1993))

- Both $L$ and $S$ involved.

- Can polarization of $J$ 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 $S(^1D_2)$ channel.
Potential energy curves

Intersystem crossing pathways

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


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

Comparison with the singlet channel

$S(^3P_2)$ may arise from ISC from the ground state (consistent with $\beta(\nu)$)
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)


Molecular frame $J$-polarization

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

Need to consider coupling of $L$ and $S$ during dissociation.
Adiabatic versus diabatic models

Two sources of angular momentum, $L$ and $S$

Only know polarization of $J$

\[ J = 1 \quad J = 2 \]

Sudden recoupling of $S$ and $L$ 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


$S(^3P_2)$ $J$-distribution

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

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

*Note: $z\parallel v$ and $zx$ plane contains $\epsilon$*
Potential surfaces and ISC

Dissociation via ISC between ground singlet and triplet states

Probability of ISC on ground state must be quite high


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