Internal Mixing, Phenyl Ring Torsion and Excitonic Interaction in Diphenylmethane

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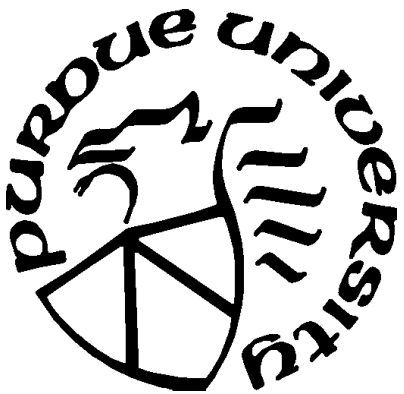
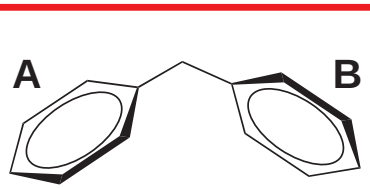
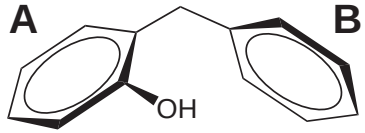


International Symposium on Molecular Spectroscopy: 63rd Meeting – June 16–20, 2008

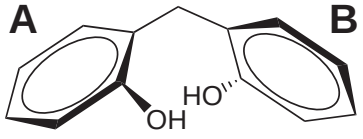
Excitonic Coupling & Flexible Degrees of Freedom in Bichromophores



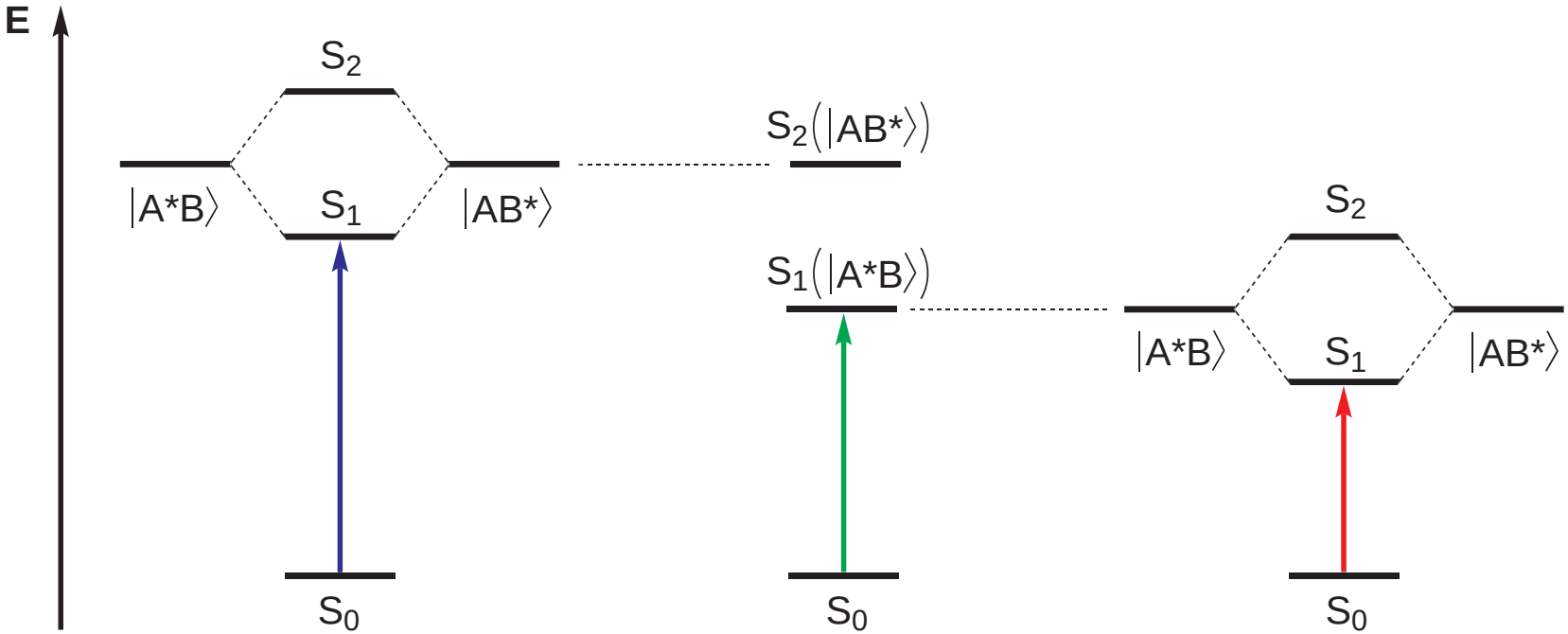
Diphenylmethane



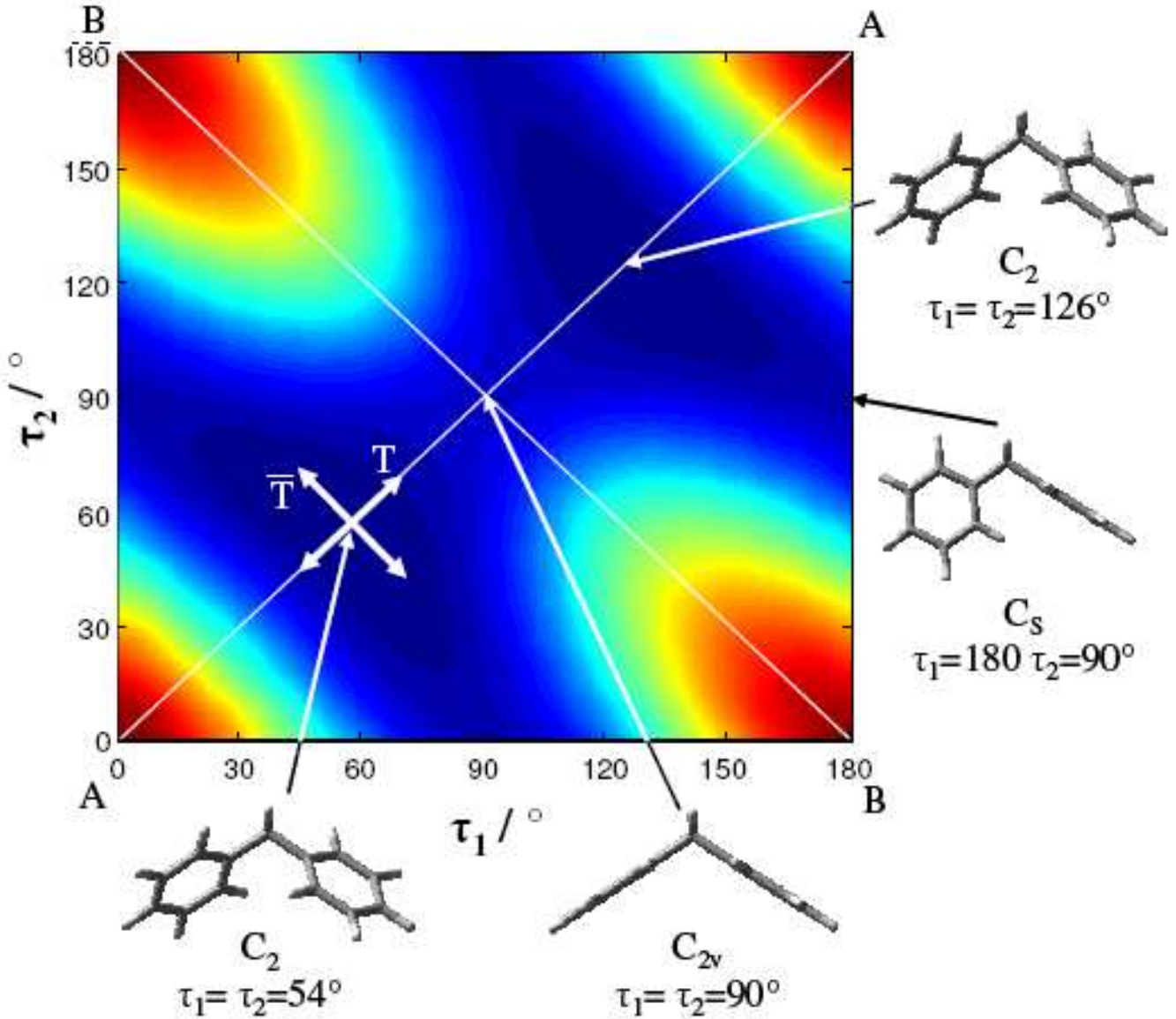
2-Benzylphenol
(Hydroxydiphenylmethane)



bis-(2-Hydroxydiphenyl)-methane



Diphenylmethane: A prototypical flexible bichromophore



MP2/6-311++G(d,p)

S_0: C_2 symmetry

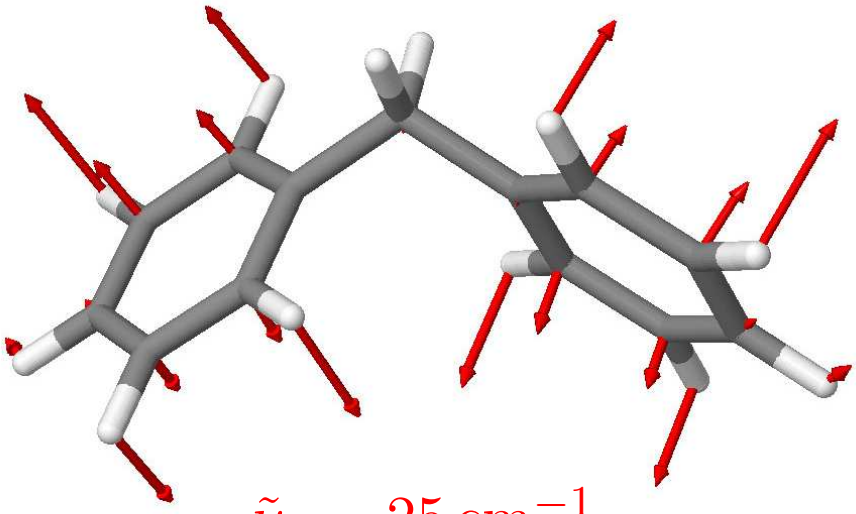
T: totally symmetric torsion (a)

$\overline{T}$: non-totally symmetric torsion (b)

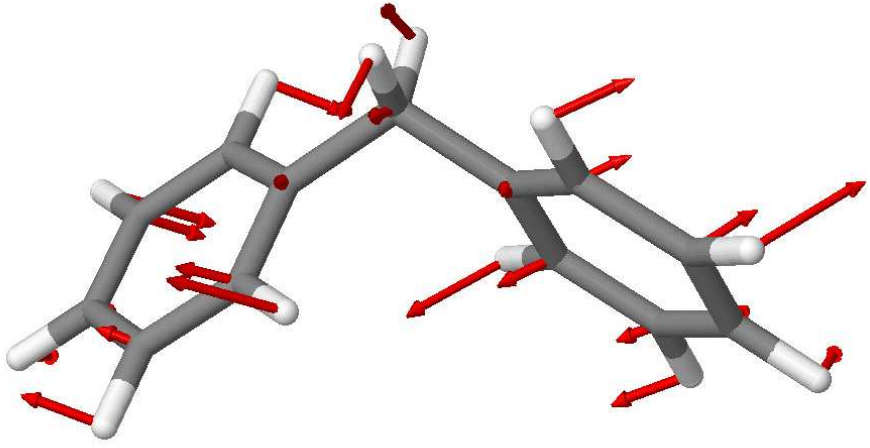
Diphenylmethane: A prototypical flexible bichromophore

Calculated Normal Coordinates of the S_0 State

B3LYP/6-31+G(d)



$\tilde{\nu}_{\mathrm{T}} = 25\,\mathrm{cm}^{-1}$



$\tilde{\nu}_{\overline{\mathrm{T}}} = 19\,\mathrm{cm}^{-1}$

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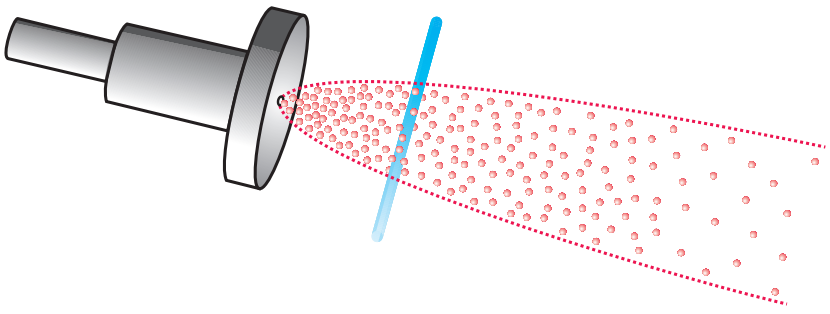
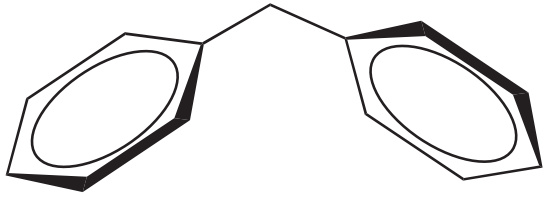
Outline

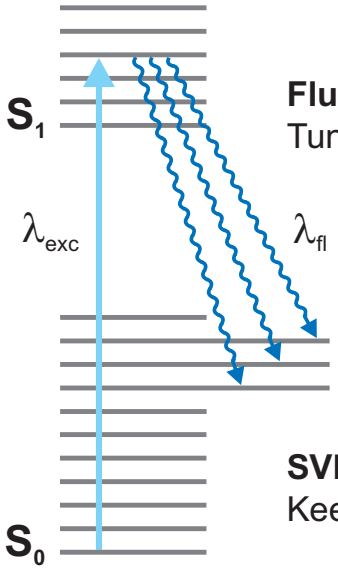
Outline

Fluorescence Excitation and SVLF Spectroscopy

Experimental Conditions







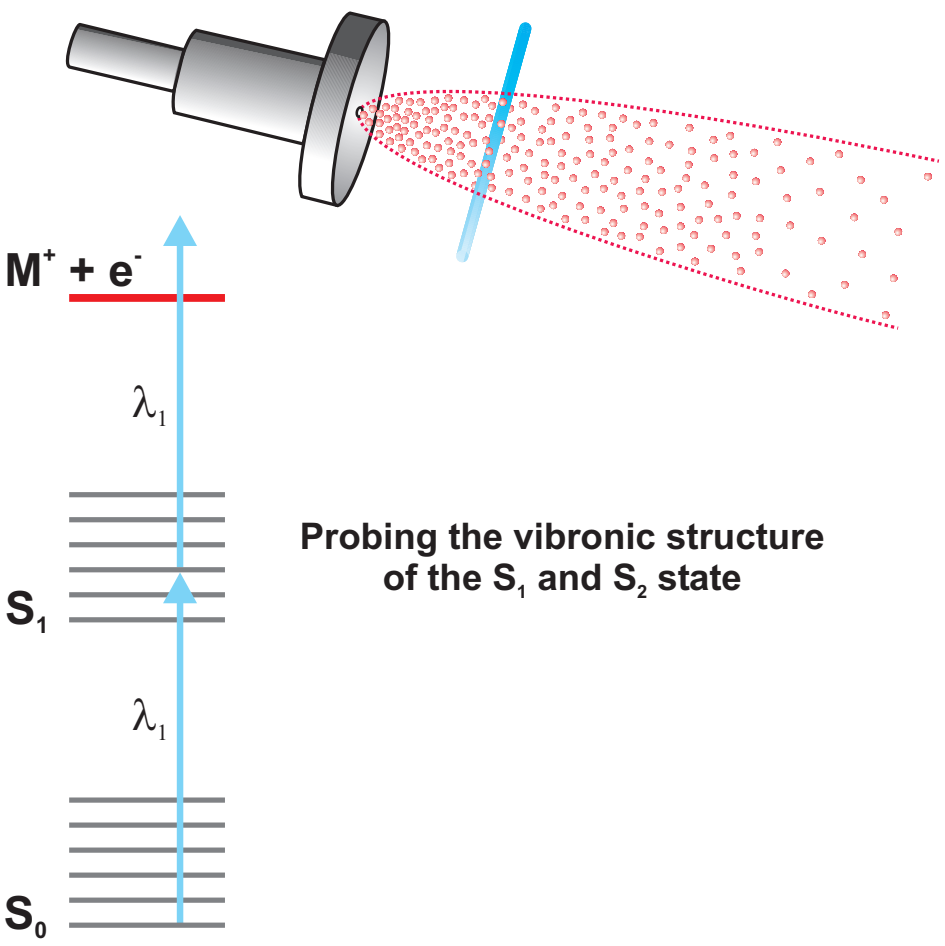
Fluorescence Excitation Spectroscopy
Tuning λ_{exc} and detecting total λ_{fl}

SVLF Spectroscopy
Keeping λ_{exc} constant and tuning through λ_{fl}

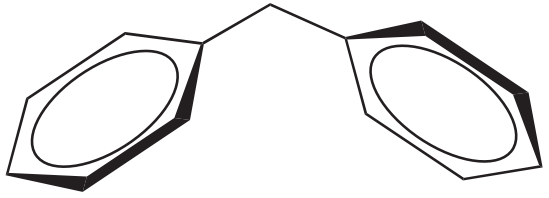
- Diphenylmethane: Sigma-Aldrich
- Stagnation temperature: $\sim 60\,^{\circ}\mathrm{C}$
- Stagnation pressure: $2\,\mathrm{bar}$ of Helium
- Pulsed expansion: 20 Hz
- Nozzle orifice diameter: $d = 800\,\mu\mathrm{m}$
- FES resolution: $\sim 0.2\,\mathrm{cm}^{-1}$
- SVLF resolution: $6-8\,\mathrm{cm}^{-1}$

Resonance Enhanced Two-Photon Ionization

Experimental Conditions



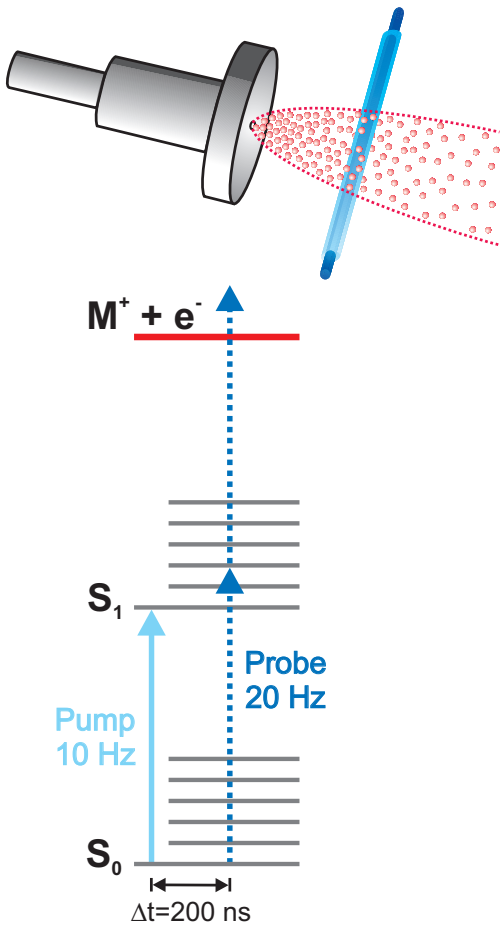
Probing the vibronic structure of the S_1 and S_2 state

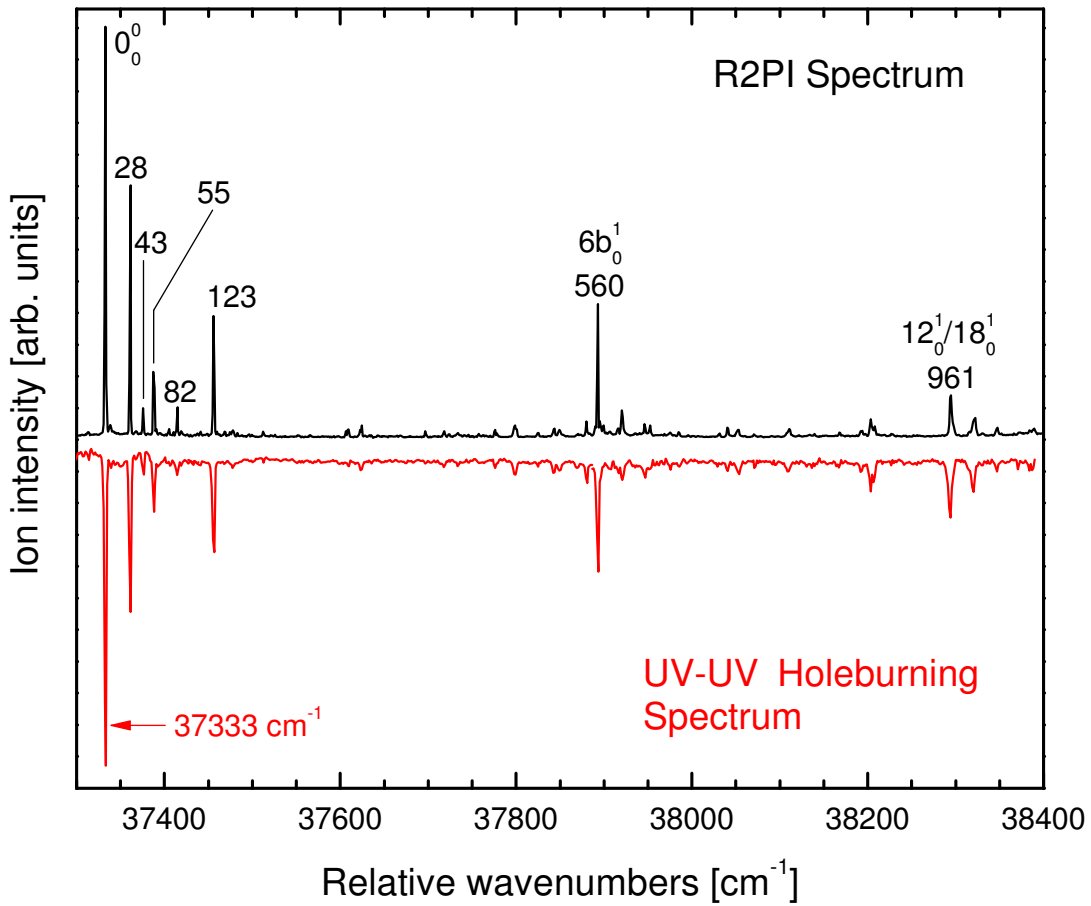


- Diphenylmethane: Sigma-Aldrich
- Stagnation temperature: $\sim 60\,^{\circ}\mathrm{C}$
- Stagnation pressure: $2\,\mathrm{bar}$ of Helium
- Pulsed expansion: 20 Hz
- Nozzle orifice diameter: $d = 400\,\mu\mathrm{m}$
- R2PI resolution: $\sim 0.2\,\mathrm{cm}^{-1}$

UV-UV Holeburning Spectroscopy

Conformation-specific Excitation Spectrum





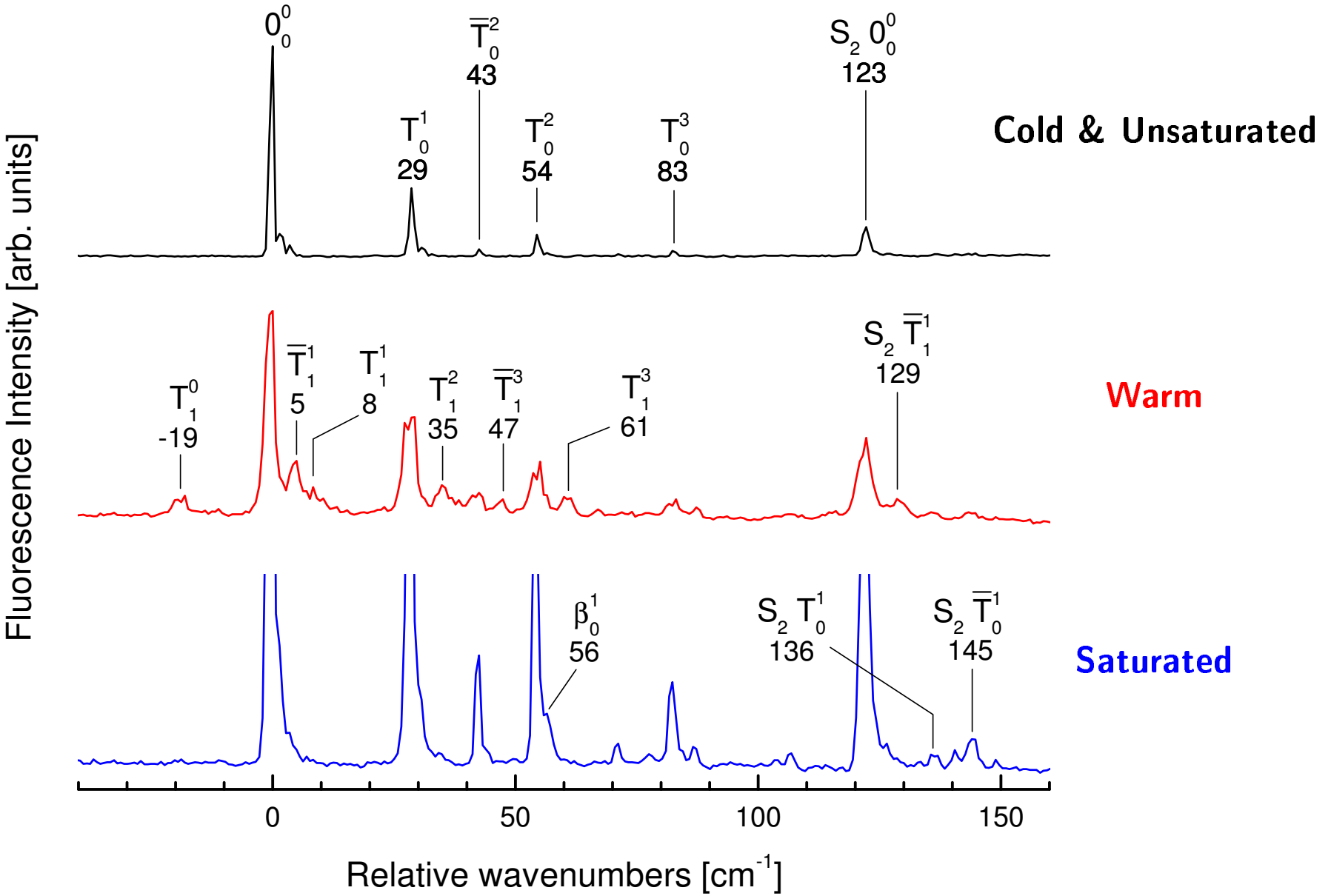
- All transitions are due to one conformer.
- Electronic origin red-shifted by $144\,\mathrm{cm}^{-1}$ from $\mathrm{S}_1 \leftarrow \mathrm{S}_0$ origin of toluene*.

* T. Aota *et al.*, *J. Phys. Chem.*, **1989**, *93*, 3519.

Outline

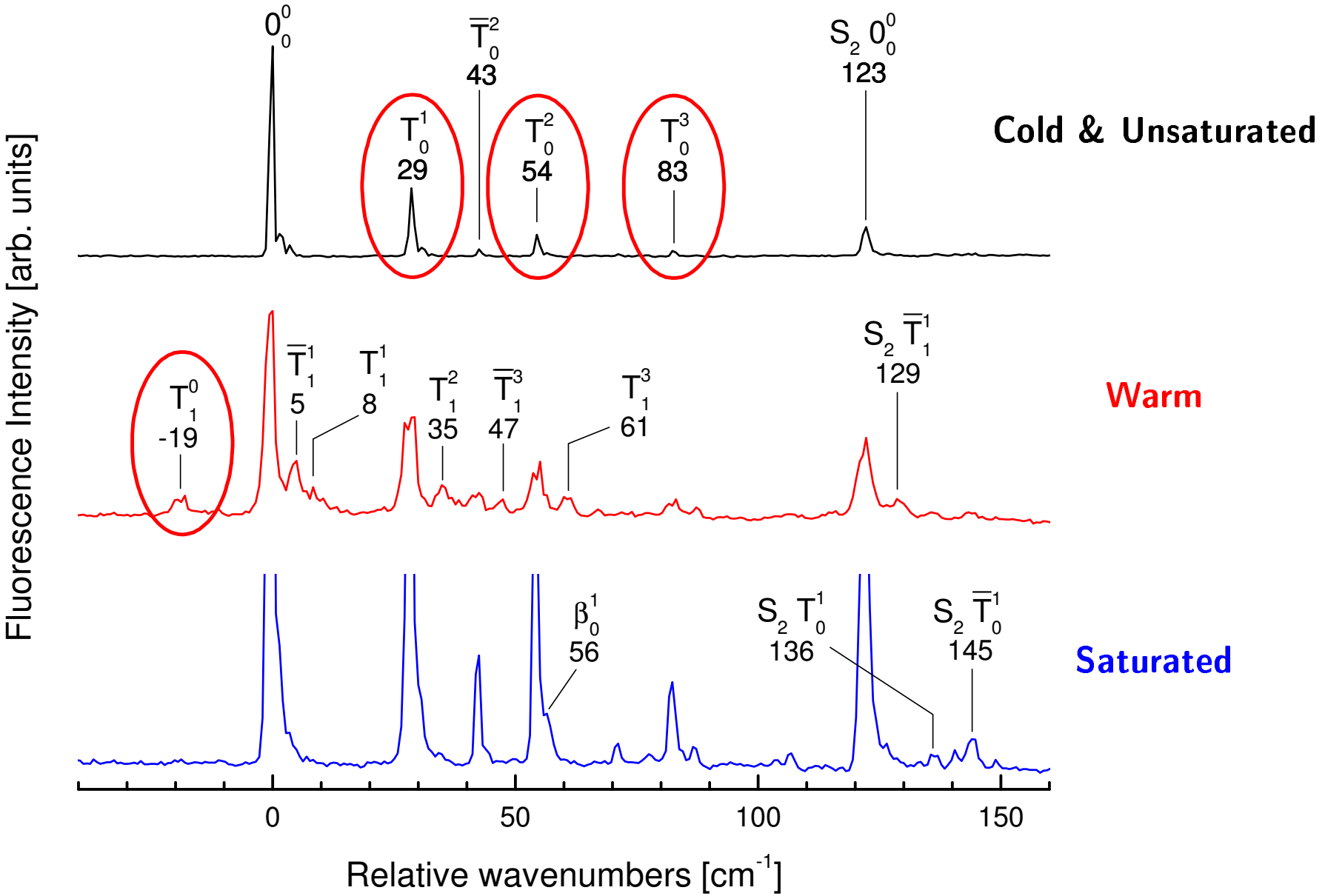
Unraveling the Vibronic Structure of States S_0, S_1 and S_2

Fluorescence Excitation Spectra under Different Conditions



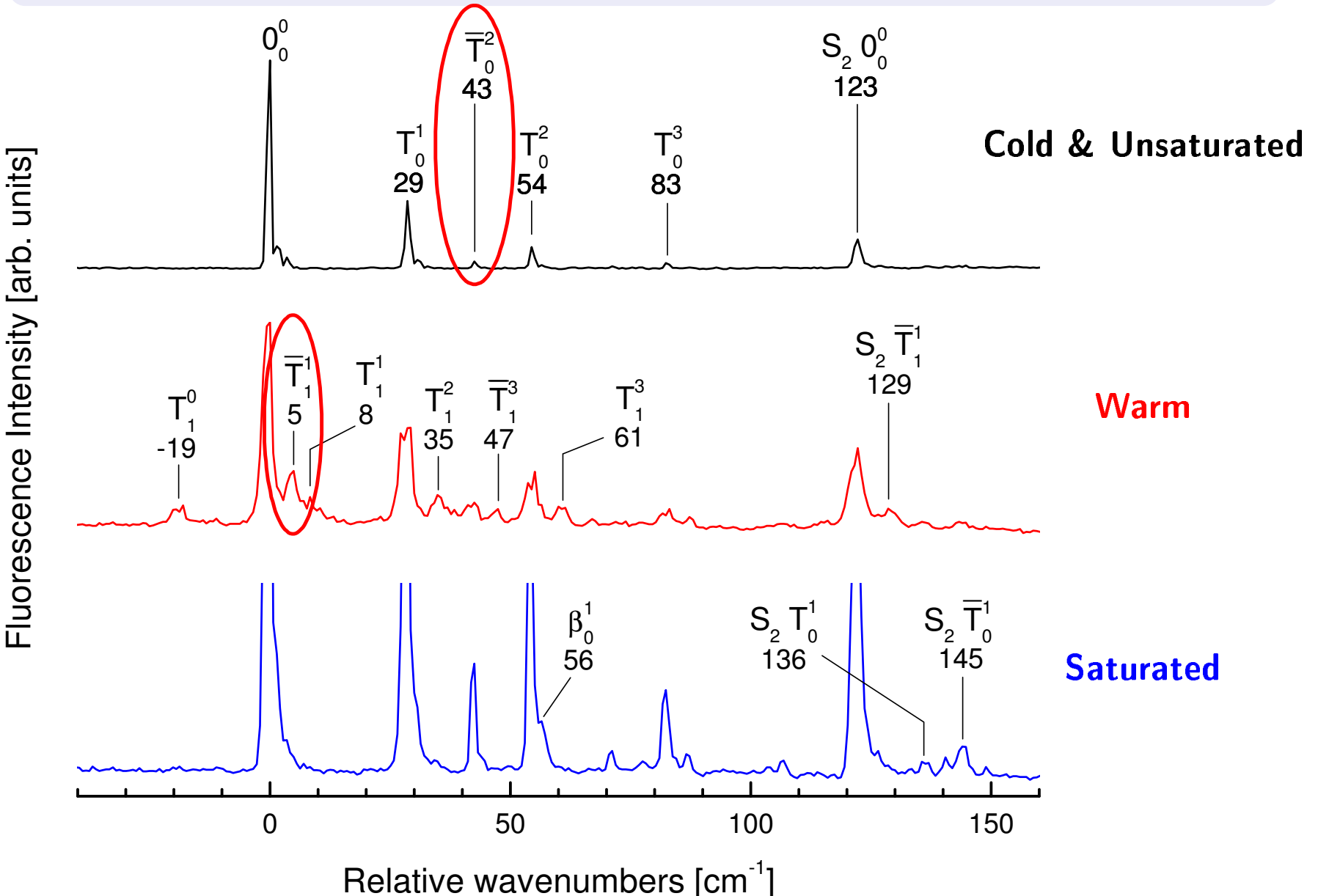
Unraveling the Vibronic Structure of States S_0, S_1 and S_2

Totally Symmetric Torsion T



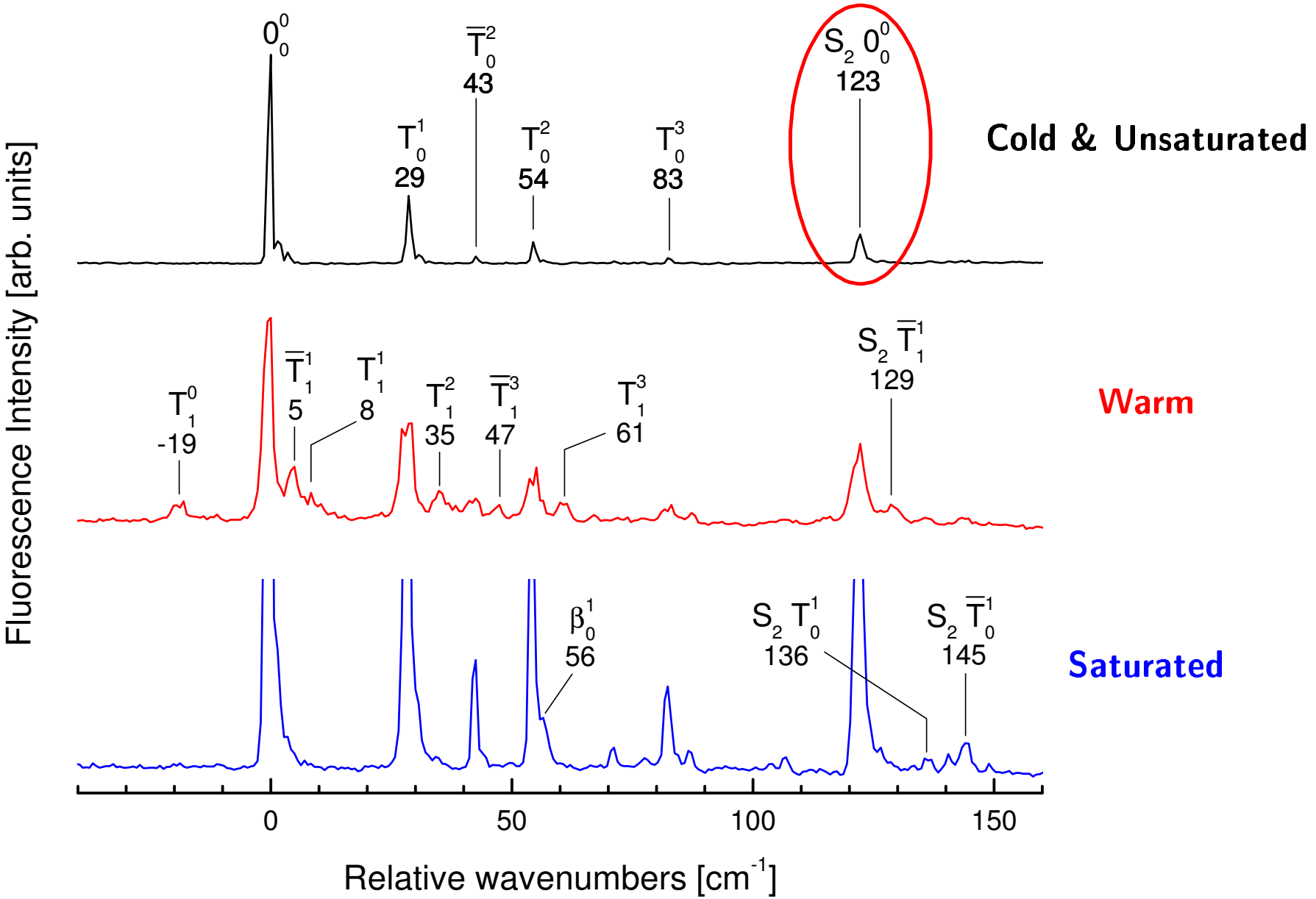
Unraveling the Vibronic Structure of States S_0, S_1 and S_2

Non-totally Symmetric Torsion $\overline{T}$



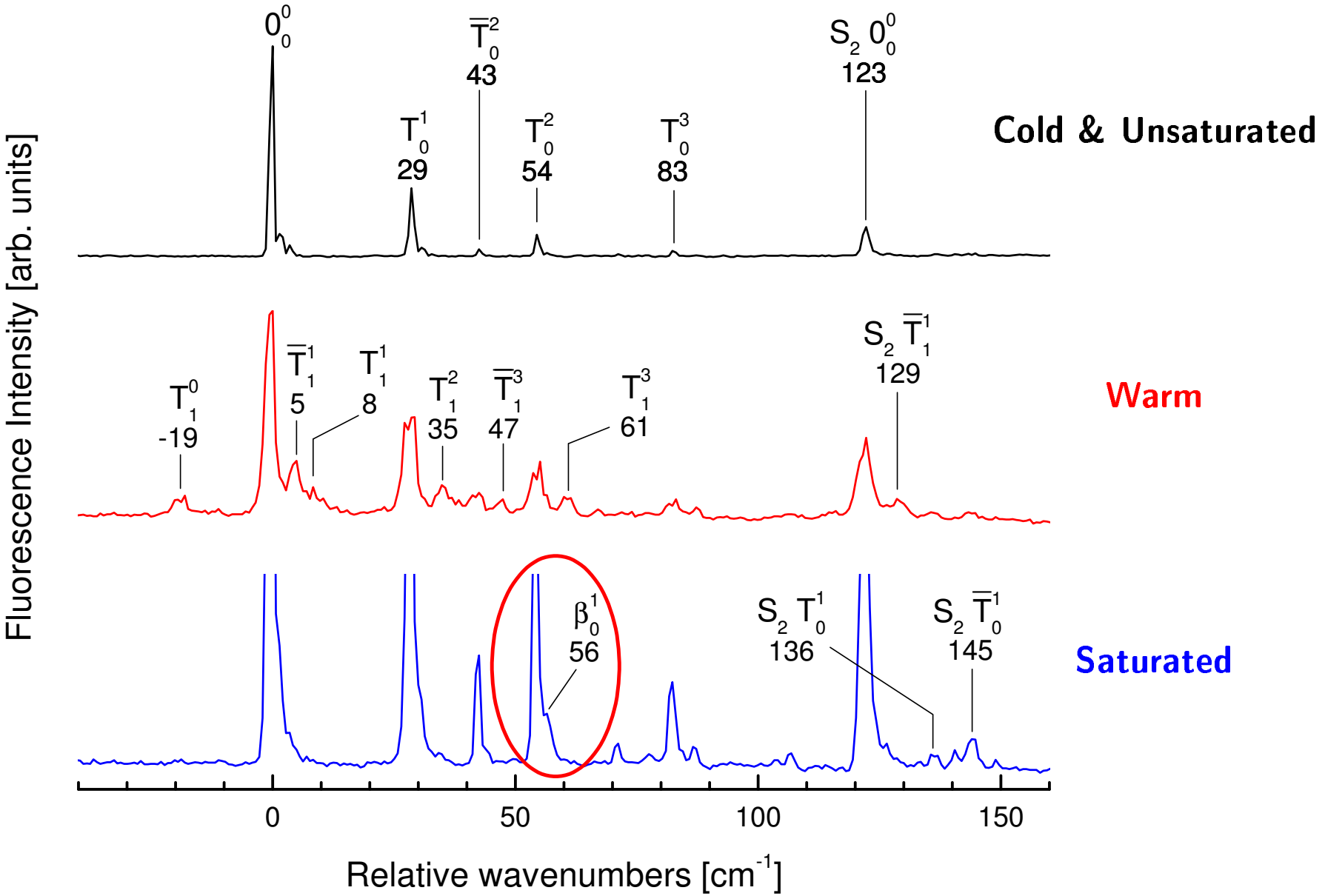
Unraveling the Vibronic Structure of States S_0, S_1 and S_2

Assignment of the S_2 Electronic Origin



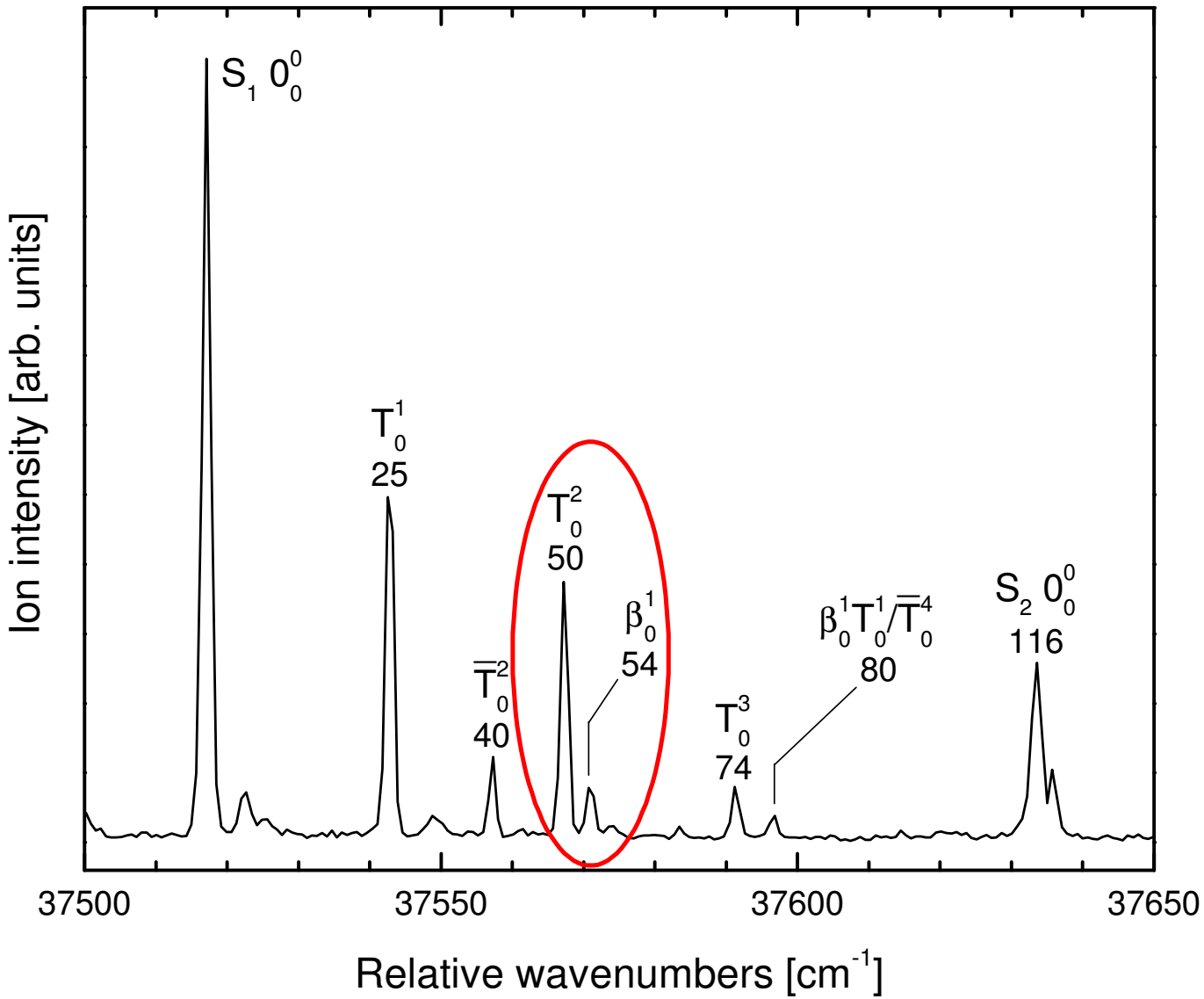
Unraveling the Vibronic Structure of States S_0, S_1 and S_2

Assignment of the Butterfly Motion β



Unraveling the Vibronic Structure of States S_0, S_1 and S_2

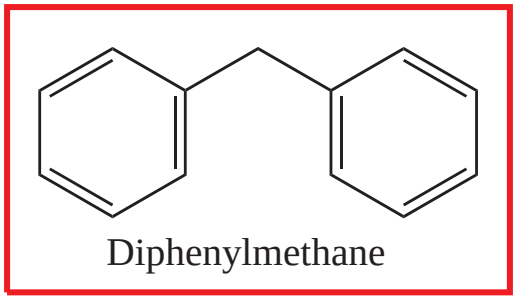
Excitation Spectrum of DPM-d_{12}: Butterfly Motion β



Unraveling the Vibronic Structure of States S_0, S_1 and S_2

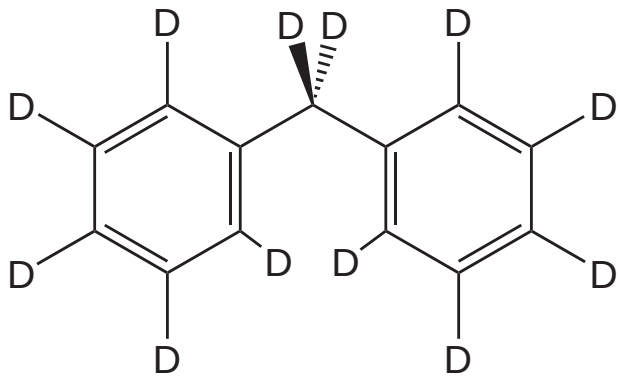
Forthcoming...

The detailed analysis of the vibronic structure of the electronic ground state and the first two excited singlet states of Diphenylmethane is currently peer reviewed at *J. Chem. Phys.*

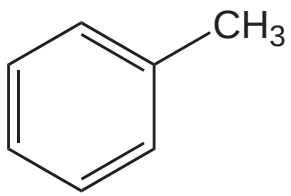


Diphenylmethane

- The electronic origin of the S_2 state lies only $123\,\mathrm{cm}^{-1}$ above that of the S_1 state.
- DPM possesses C_2 symmetry in all three electronic states.
- The orbital symmetries are A for S_0, B for S_1, and A for S_2.
- All totally symmetric (a) fundamentals are allowed, whereas only even-quanta overtones and combination bands of the non-totally symmetric (b) fundamentals possess non-vanishing intensity.



Diphenylmethane-d_{12}



Toluene

Unraveling the Vibronic Structure of States S_0, S_1 and S_2

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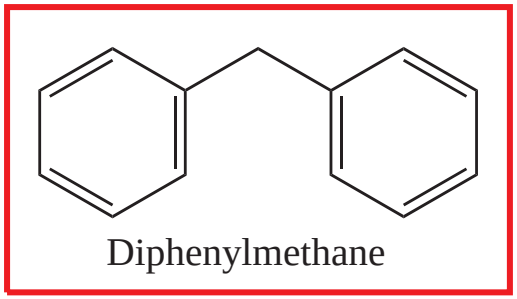
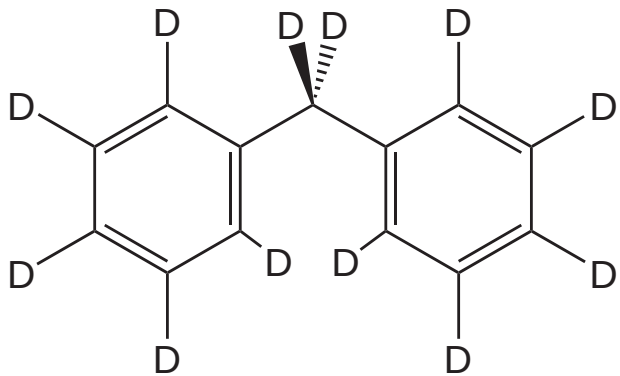
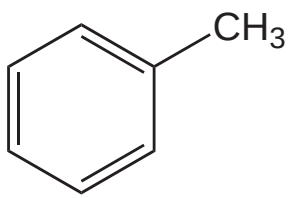

Diphenylmethane

- The vibronic structure at *high frequencies* was assigned by comparison with the ring modes of toluene.
- The vibronic structure at *low frequencies* was assigned by combining information from four sources:

(1) Cold excitation and SVLF spectra
(2) Hot excitation and SVLF spectra
(3) The saturated excitation spectrum
(4) The excitation spectrum of DPM-d_{12}



Diphenylmethane-d_{12}



Toluene

Unraveling the Vibronic Structure of States S_0, S_1 and S_2

Low-frequency normal modes: Torsions and Butterfly Motion

Isotopomer	State	$T\,[\mathrm{cm}^{-1}]$	$\overline{T}\,[\mathrm{cm}^{-1}]$	$\beta\,[\mathrm{cm}^{-1}]$
DPM-d_0	S_0	19	16.5	64
	S_1	29	21.5	~ 56
	S_2	13	22	—
B3LYP/6-31+G(d)	S_0	25	19	64
MP2/6-311++G(d,p)	S_0	28	7	54
DPM-d_{12}	S_0	18	15	60
	S_1	25	20	54

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Yet, we have not understood all available vibronic structure so far!

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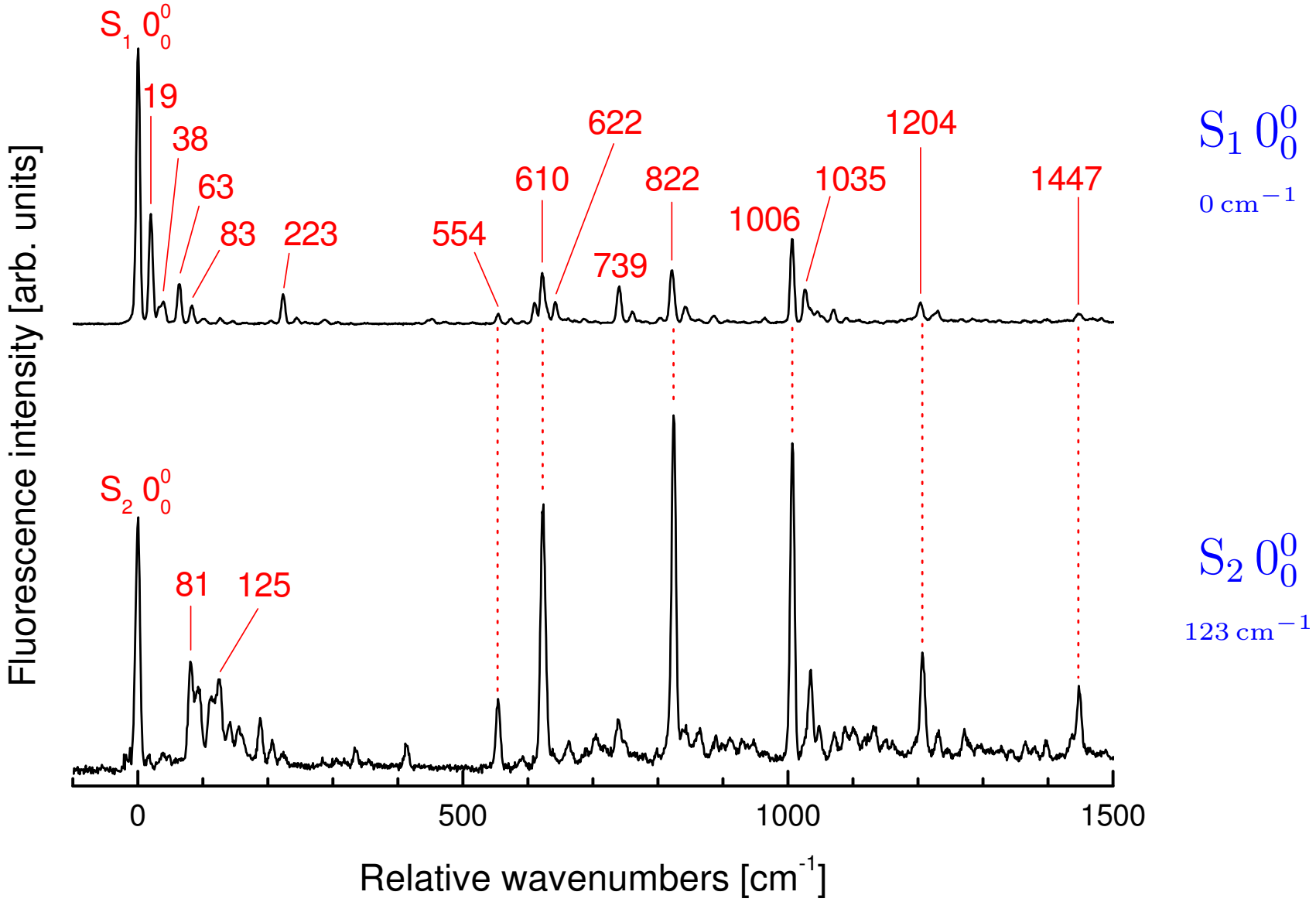
Particularly intriguing are the $S_2\,0_0^0$, $S_2\,\overline{T}_1^1$, $S_2\,T_0^1$ and $S_2\,\overline{T}_0^1$ SVLF spectra at $123\,\mathrm{cm}^{-1}$, $129\,\mathrm{cm}^{-1}$, $136\,\mathrm{cm}^{-1}$ and $145\,\mathrm{cm}^{-1}$.

Outline

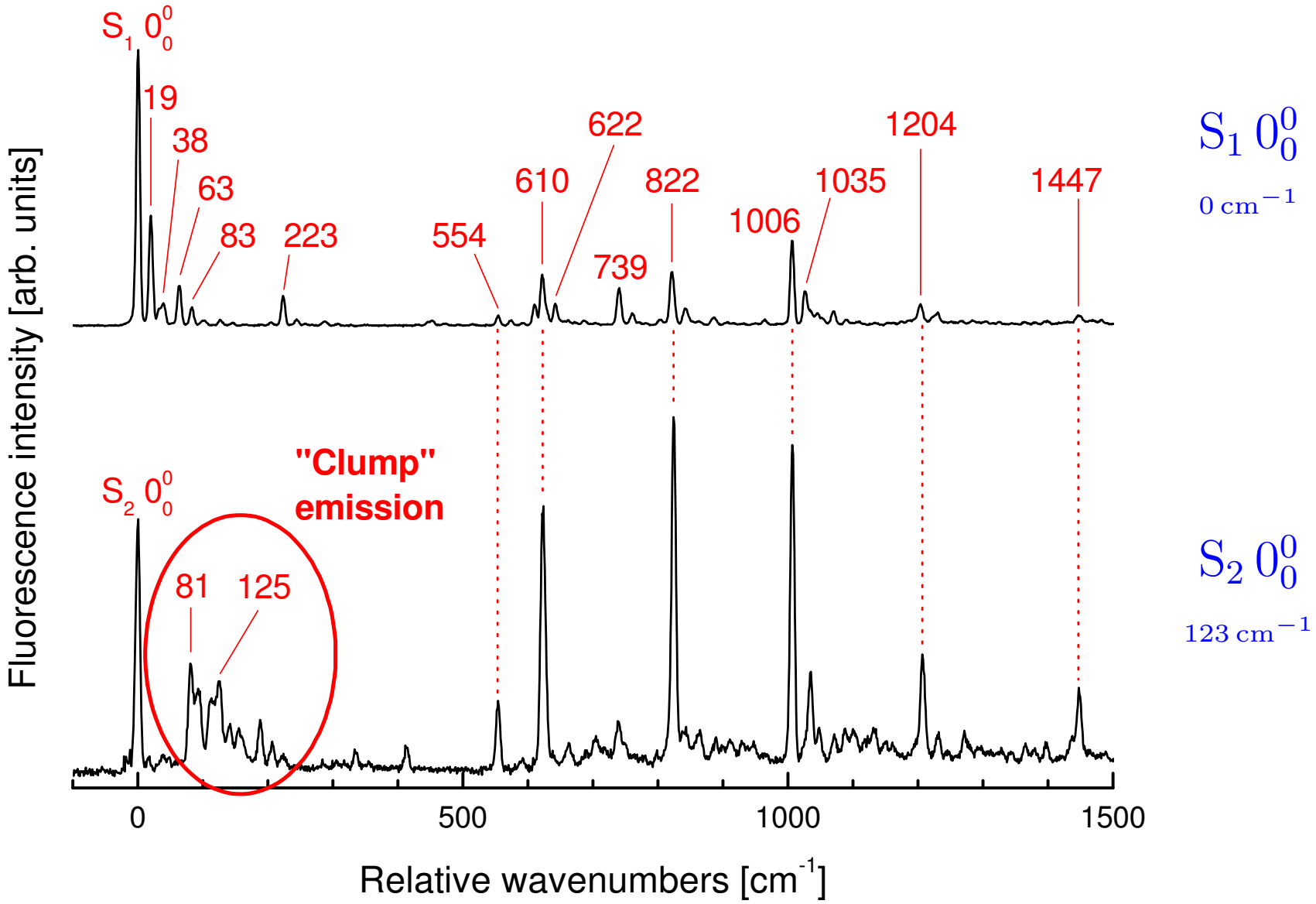
Evidence for Internal Mixing

Comparison between the $S_1\,0_0^0$ and $S_2\,0_0^0$ SVLF Spectra



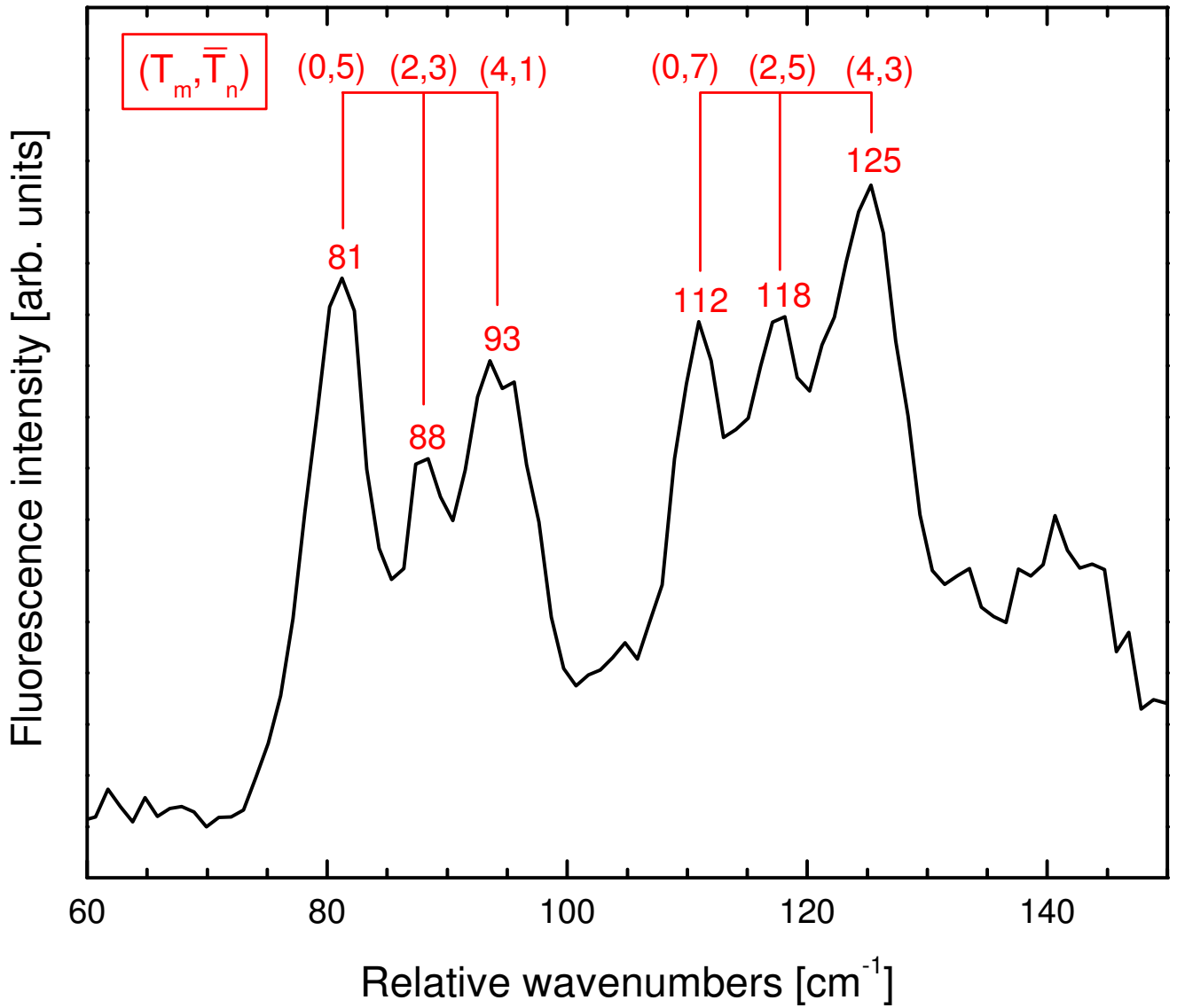
Evidence for Internal Mixing

Comparison between the $S_1\,0_0^0$ and $S_2\,0_0^0$ SVLF Spectra



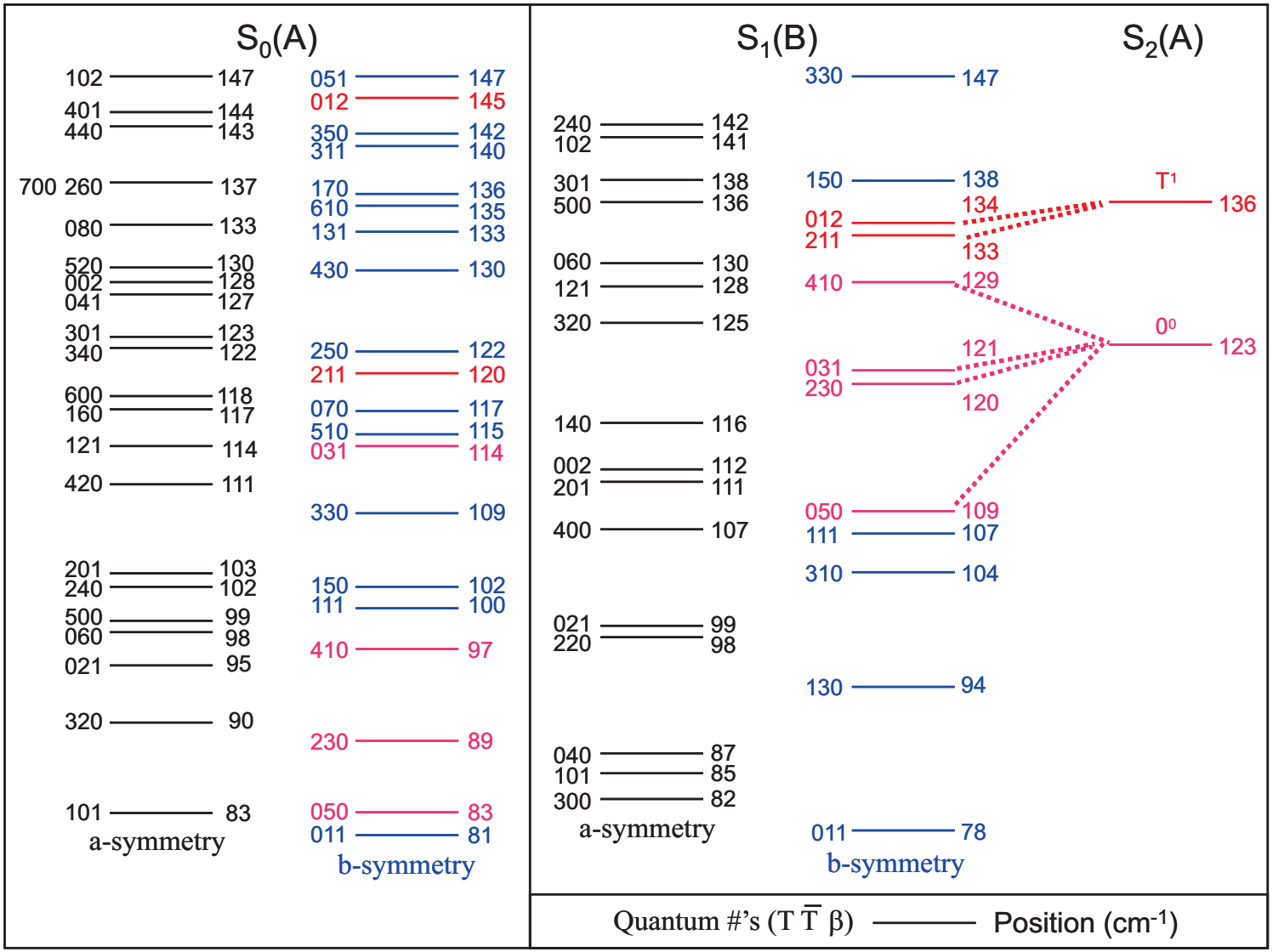
Evidence for Internal Mixing

$S_2\, 0_0^0$ SVLF Spectrum in the "Clump" Region



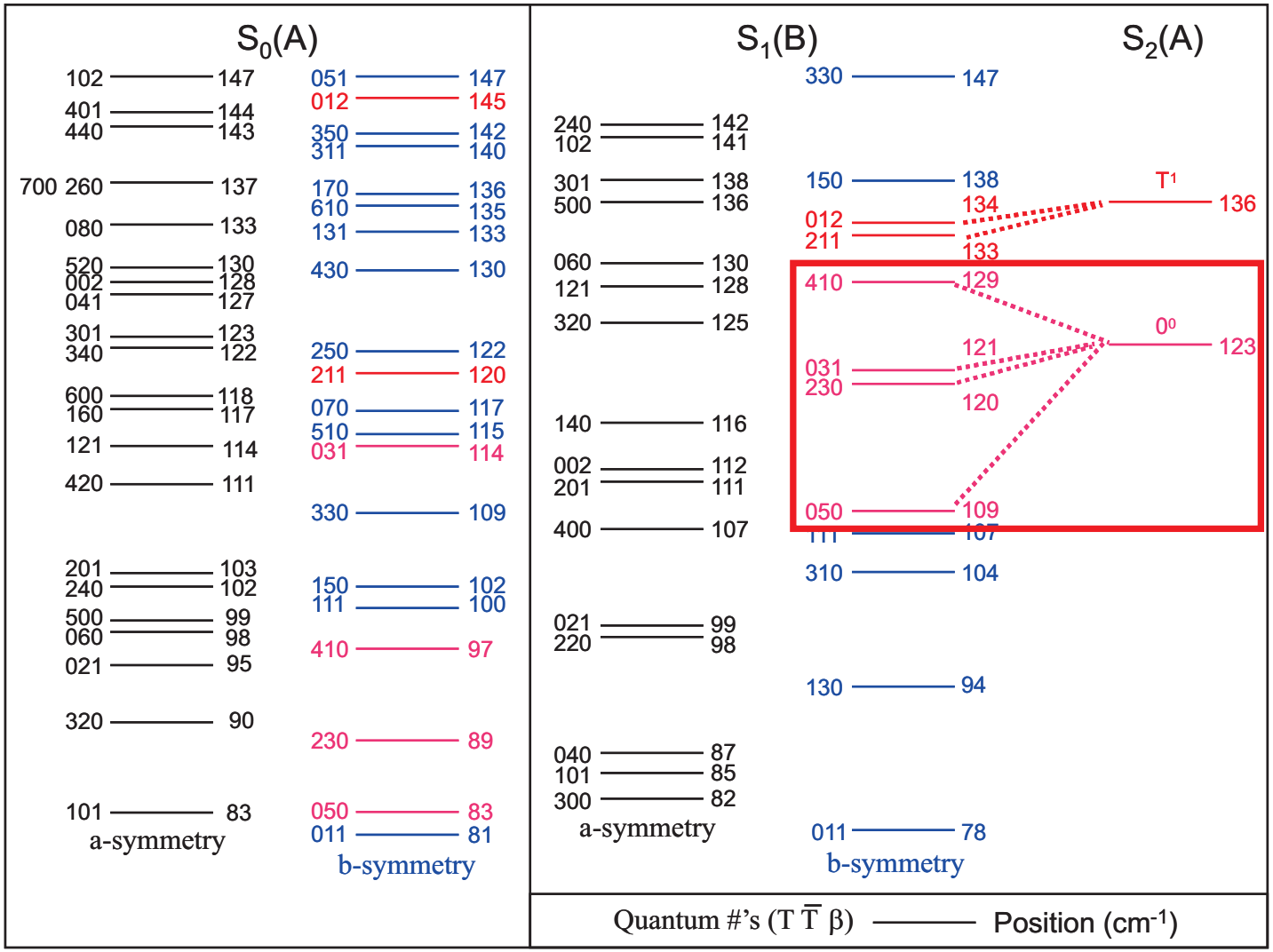
Evidence for Internal Mixing

Experimental and Interpolated Vibronic Levels at Low Energies



Evidence for Internal Mixing

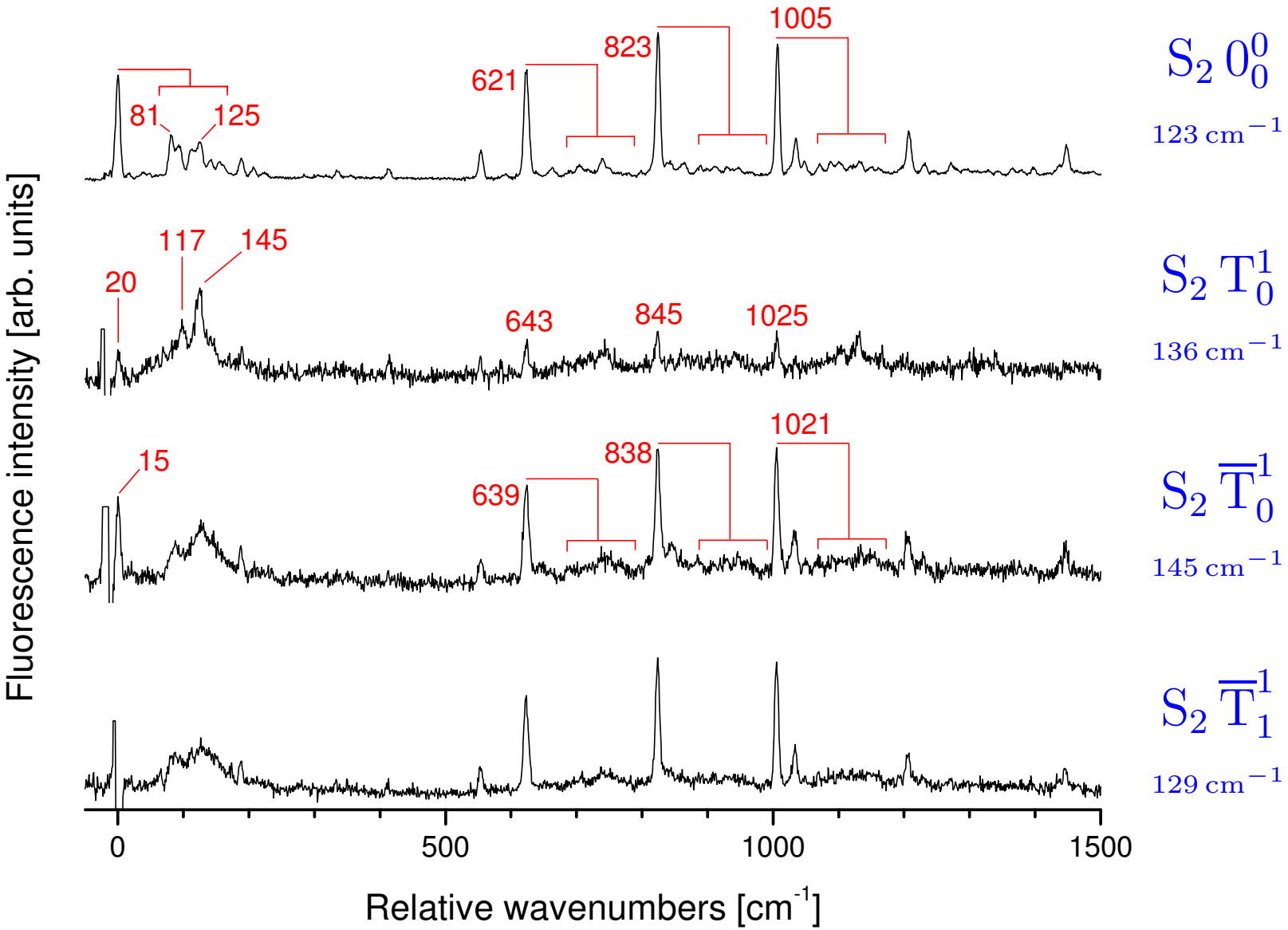
S_1 Vibronic Levels Near the S_2 Electronic Origin



$$|\Psi(123\,\mathrm{cm}^{-1})\rangle = c_{S_2,000}|S_2,000\rangle + c_{S_1,050}|S_1,050\rangle + c_{S_1,230}|S_1,230\rangle + c_{S_1,410}|S_1,410\rangle + c_{S_1,031}|S_1,031\rangle$$

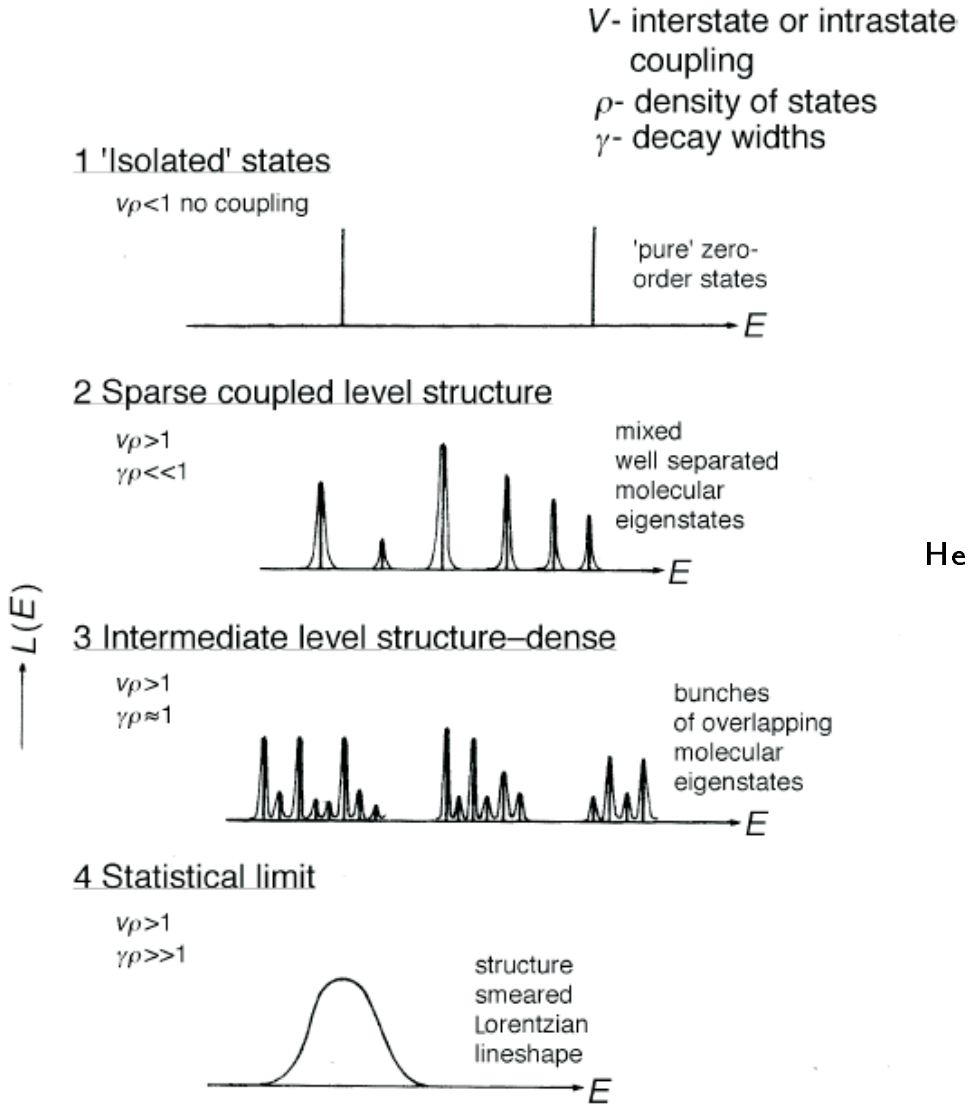
Evidence for Internal Mixing

SVLF Spectra Originating in Different S_2 Vibronic Levels



Internal Mixing & Internal Conversion

Classification of Intramolecular Level Structure



Internal Mixing

stationary-state picture

Jortner, *Faraday Discuss.*, **1997**, *108*, 1.

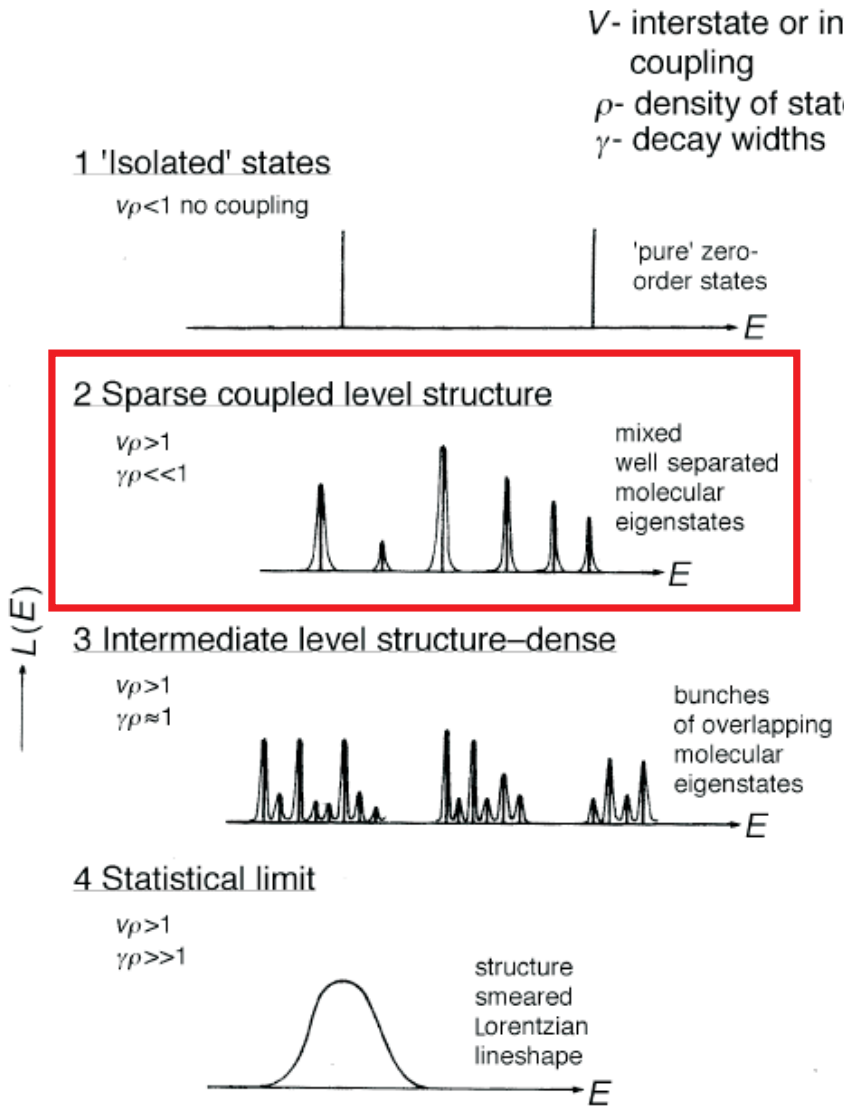
Henry & Kasha, *Annu. Rev. Phys. Chem.*, **1968**, *19*, 161.

Internal Conversion

time-dependent picture

Internal Mixing & Internal Conversion

DPM: Internal Mixing in the Sparse Coupled Level Structure Limit



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Jortner, *Faraday Discuss.*, **1997**, *108*, 1.

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Internal Conversion

time-dependent picture

Internal Mixing in the Sparse Coupled Level Structure Limit

A Little Mathematical Background: The Vibronic Coupling Matrix Element V

S_1 level	$\Delta\mathcal{E}$	Δv_{T}	$\Delta v_{\overline{\mathrm{T}}}$	Δv_{β}
$\lvert 050\rangle$	-14	0	5	0
$\lvert 230\rangle$	-3	2	3	0
$\lvert 410\rangle$	$+9$	4	1	0
$\lvert 031\rangle$	-2	0	3	1

$$V \approx \gamma \left[1 - \frac{\mathcal{E}_{v'}^{\mathrm{S}_2} - \mathcal{E}_{v''}^{\mathrm{S}_1}}{E_{\mathrm{S}_2}(Q_0) - E_{\mathrm{S}_1}(Q_0)}\right] \left\langle \chi_{v'_{\mathrm{T}}}^{\mathrm{S}_2} \middle| \chi_{v''_{\mathrm{T}}}^{\mathrm{S}_1} \right\rangle_{Q_{\mathrm{T}}} \left\langle \chi_{v'_{\overline{\mathrm{T}}}}^{\mathrm{S}_2} \middle| Q_{\overline{\mathrm{T}}} \middle| \chi_{v''_{\overline{\mathrm{T}}}}^{\mathrm{S}_1} \right\rangle_{Q_{\overline{\mathrm{T}}}} \prod_{j \neq \overline{\mathrm{T}} \neq \mathrm{T}}^{3N-6} \left\langle \chi_{v'_j}^{\mathrm{S}_2} \middle| \chi_{v''_j}^{\mathrm{S}_1} \right\rangle_{Q_j}$$

$$\gamma = \left\langle \psi_{\mathrm{S}_2}(q; Q_0) \middle| \left(\frac{\partial U(q,Q)}{\partial Q_{\overline{\mathrm{T}}}}\right)_{Q_0} \middle| \psi_{\mathrm{S}_1}(q; Q_0) \right\rangle_q$$

Jortner & Berry, *J. Chem. Phys.*, **1968**, *48*, 2757. Sharf & Silbey, *Chem. Phys. Lett.*, **1971**, *9*, 125.
Scharf, *Chem. Phys.*, **1975**, *7*, 478.

Internal Mixing in the Sparse Coupled Level Structure Limit

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$\|230\rangle$	-3	2	3	0
$\|410\rangle$	$+9$	4	1	0
$\|031\rangle$	-2	0	3	1

$$V \approx \gamma \left[1 - \frac{\mathcal{E}^{S_2}_{v'} - \mathcal{E}^{S_1}_{v''}}{E_{S_2}(Q_0) - E_{S_1}(Q_0)}\right] \left\langle \chi^{S_2}_{v'_T} \middle| \chi^{S_1}_{v''_T} \right\rangle_{Q_T} \left\langle \chi^{S_2}_{v'_{\overline{T}}} \middle| Q_{\overline{T}} \middle| \chi^{S_1}_{v''_{\overline{T}}} \right\rangle_{Q_{\overline{T}}} \prod_{j \neq \overline{T} \neq T}^{3N-6} \left\langle \chi^{S_2}_{v'_j} \middle| \chi^{S_1}_{v''_j} \right\rangle_{Q_j}$$

$$\gamma = \left\langle \psi_{S_2}(q;Q_0) \middle| \left(\frac{\partial U(q,Q)}{\partial Q_{\overline{T}}}\right)_{Q_0} \middle| \psi_{S_1}(q;Q_0) \right\rangle_q$$

Jortner & Berry, *J. Chem. Phys.*, 1968, *48*, 2757. Sharf & Silbey, *Chem. Phys. Lett.*, 1971, *9*, 125. Scharf, *Chem. Phys.*, 1975, *7*, 478.

Finally...

Conclusion

- DPM possesses an excitonic splitting of only $123\,\mathrm{cm}^{-1}$.
- Due to this small splitting the S_2 electronic origin is immersed into a very sparse density of S_1 vibronic levels. As a result, the low-lying S_2 vibronic levels show mixed electronic state character due to internal mixing with near-degenerate S_1 levels.
- The quantum number changes in $\overline{T}$ upon internal mixing ($\Delta v_{\overline{\mathrm{T}}} = +1,\, +3,\, +5$) suggest that additional to the internal conversion transitions accounted for by the Jortner-Berry $\Delta v = \pm 1$ propensity rule higher order vibronic mechanisms have to be considered as well.

Scharf, *Chem. Phys.*, **1975**, *7*, 478.

Outlook

- Currently, CASSCF calculations of the S_1 and S_2 torsional PES are underway to elucidate intensity discrepancies we attribute to mechanical deformations of the PES.
- We currently pursue the study of other bichromophores in which the energy separation between S_1 and S_2 is varied systematically.

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