Duschinsky Mixing between Four Non-totally Symmetric Normal Coordinates in the S_1–S_0 Vibronic Structure of Phenylvinylacetylene

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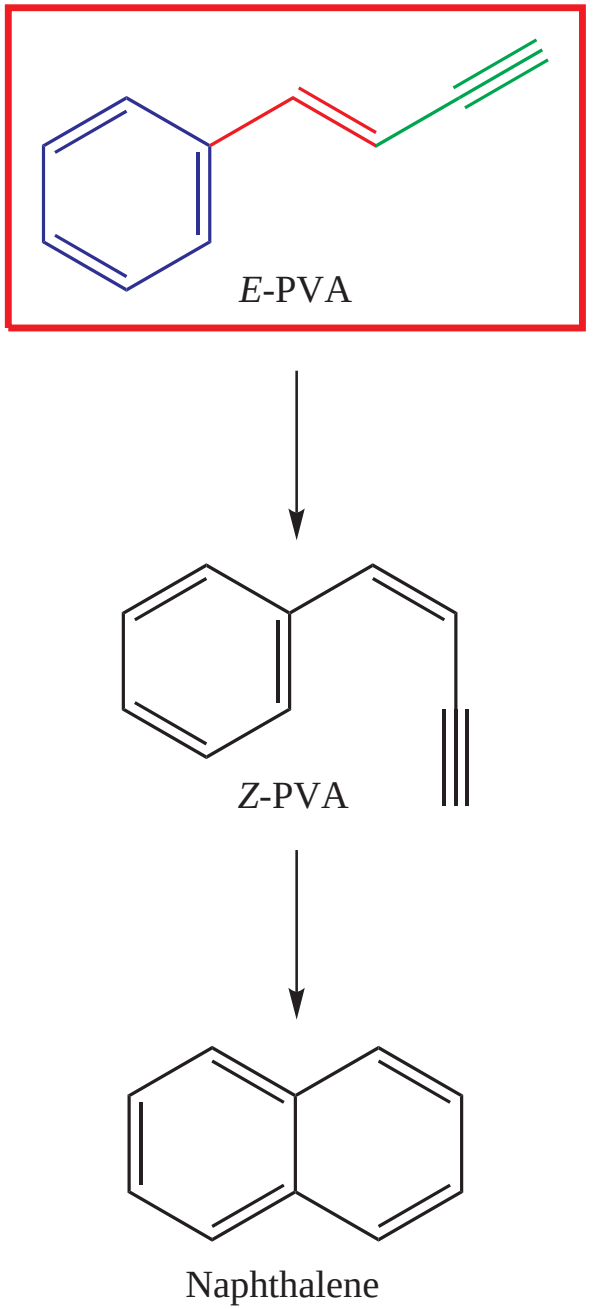
Phenylvinylacetylene

- Phenylvinylacetylene (PVA)
  or 1-phenyl-1-buten-3-yne
  (synthesized by Dr. Hsiupu D. Lee)
- Previously identified as a $C_{10}H_8$ product from the reaction of UV-excited diacetylene with ground state styrene* and in a benzene discharge**.
- Found to cycloisomerize thermally into naphthalene in flash vacuum pyrolysis studies***.
- Possible intermediate leading to naphthalene and higher-order polyaromatic hydrocarbons (PAHs) in Titan's atmosphere, sooting flames, discharges, and interstellar media.



* A. G. Robinson, P. R. Winter and T. S. Zwier, *J. Phys. Chem. A*, 2002, *106*, 5789.

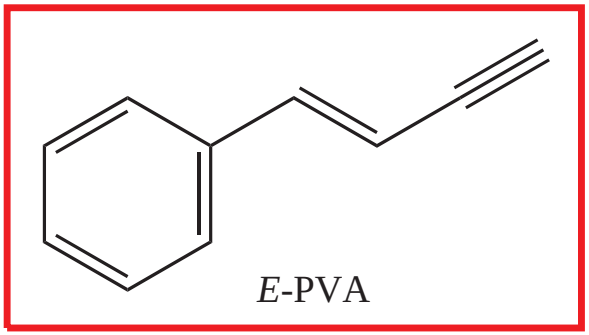
** F. Güthe, H. B. Ding, T. Pino and J. P. Maier, *Chem. Phys.*, 2001, *269*, 347.

*** K. Schulz, J. Hofmann, G. Zimmermann, *Liebigs Annalen – Recueil*, 1997, 2535.

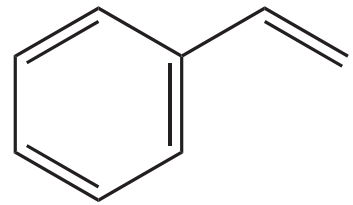
The UV-Spectroscopy of Phenylvinylacetylene

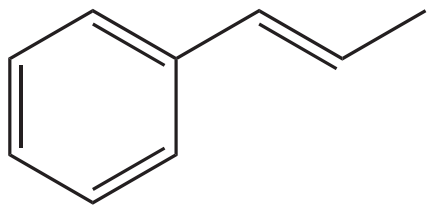
Forthcoming...

The detailed analysis of the $S_1 - S_0$ vibronic structure of *E*-PVA has recently been accepted at *J. Phys. Chem. A*.



- Much of the S_0 vibrational structure was assigned by comparison with styrene and *trans*-β-methylstyrene, assisted by calculations at the B3LYP/6-311++G(d,p) level of theory.
- *E*-PVA is planar in both the S_0 and S_1 state. The electronic transition is of the type $\tilde{A}\,^1A' \leftarrow \tilde{X}\,^1A'$.
- All in-plane fundamentals (a' modes $\nu_1 - \nu_{33}$) are allowed, whereas only even-quanta overtones and combination bands of the out-of-plane fundamentals (a'' modes $\nu_{34} - \nu_{48}$) possess non-vanishing intensity.


Styrene


trans-β-methylstyrene

Outline

1. Experimental Setup & Results
   - Fluorescence Excitation Spectroscopy
   - UV-UV Holeburning Spectroscopy
   - Single Vibronic Level Fluorescence (SVLF) Spectroscopy
   - Evidence for 4D-Duschinsky mixing in the SVLF spectra
2. What is Duschinsky mixing?
   - Duschinsky mixing in 2D
   - Duschinsky mixing in 4D
3. Duschinsky Simulations
   - Implementation
   - Simulation of the SVLF Spectra

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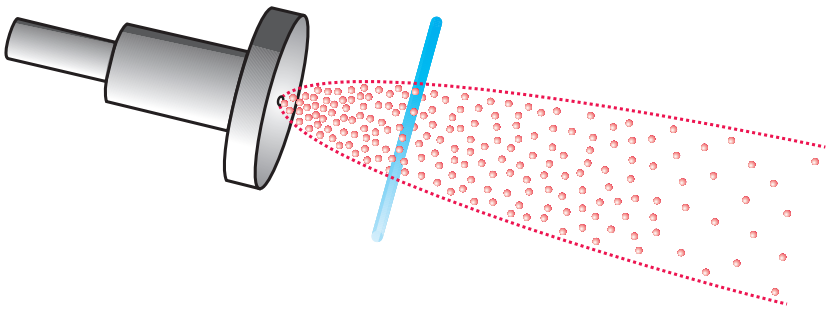
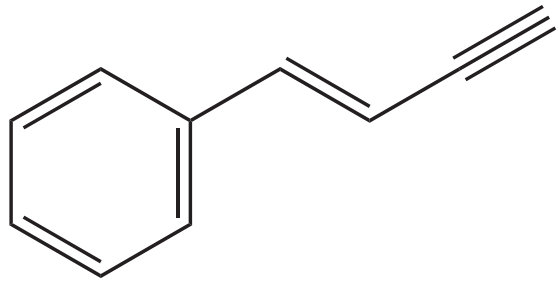
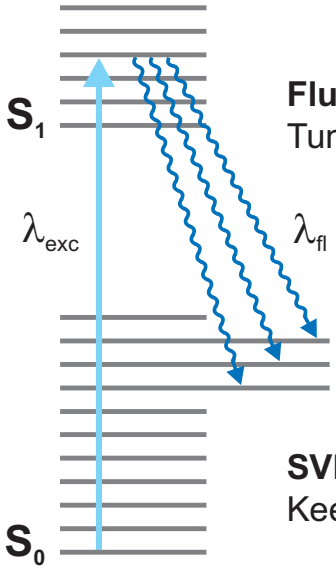
Fluorescence Excitation and SVLF Spectroscopy

Experimental Conditions







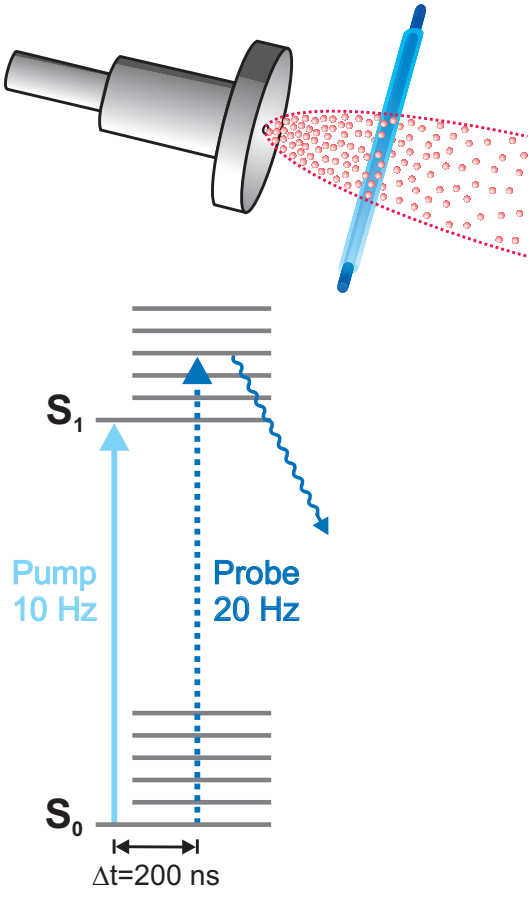
Fluorescence Excitation Spectroscopy
Tuning λ_{exc} and detecting total λ_{fl}

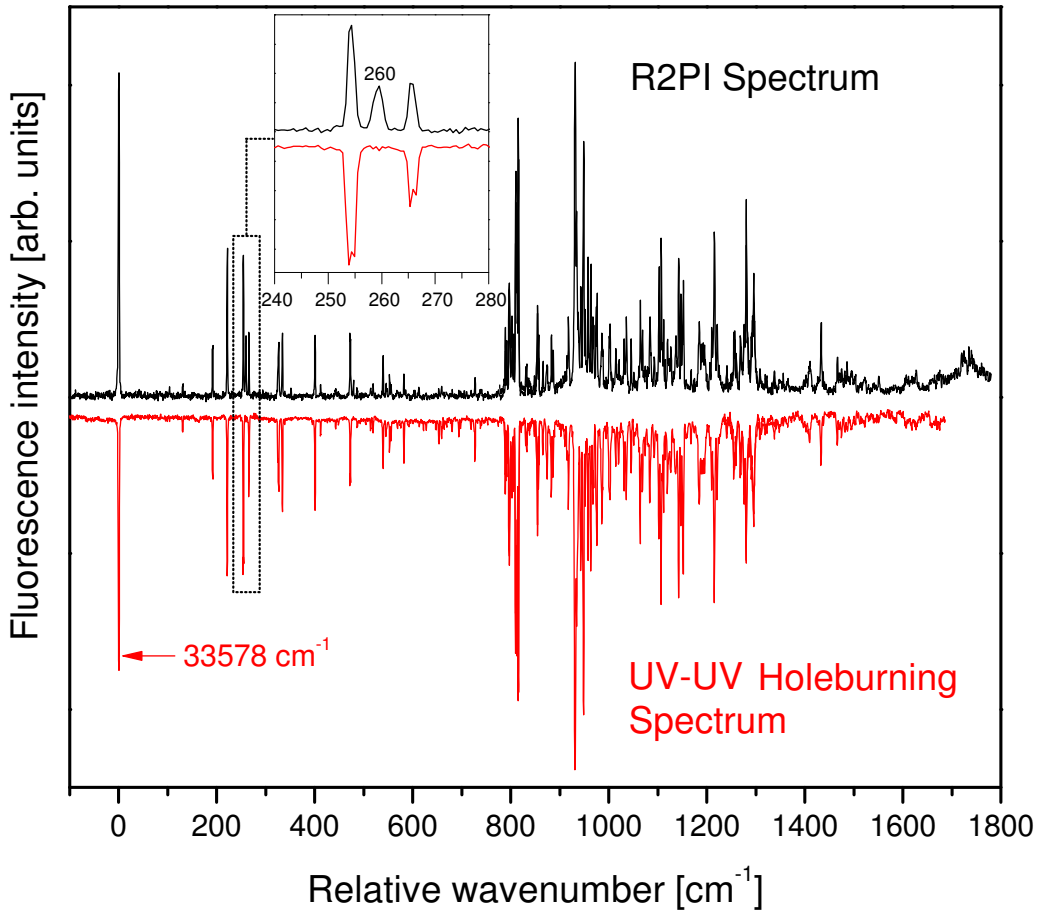
SVLF Spectroscopy
Keeping λ_{exc} constant and tuning through λ_{fl}

- Stagnation temperature: $21\,^{\circ}\mathrm{C}$
- Stagnation pressure: $3.6\,\mathrm{bar}$ of Helium
- Pulsed expansion: 20 Hz
- Nozzle orifice diameter: $d = 800\,\mu\mathrm{m}$
- FES resolution: $\sim 0.2\,\mathrm{cm}^{-1}$
- SVLF resolution: $\sim 8\,\mathrm{cm}^{-1}$

UV-UV Holeburning Spectroscopy

Conformation-specific Excitation Spectrum

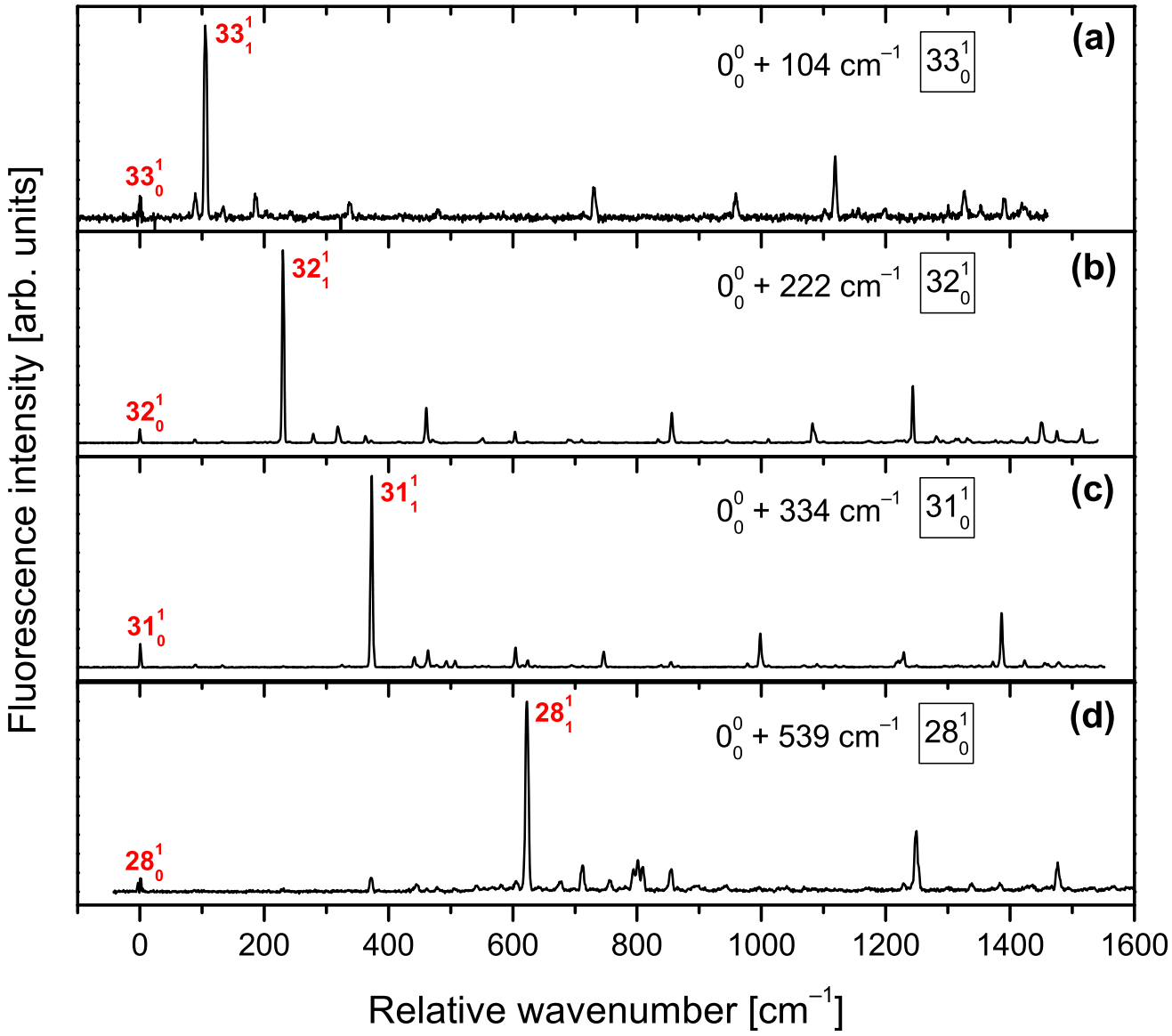




- All transitions (except for two) are due to one conformer, *E*-PVA.
- The transitions at $260\,\mathrm{cm}^{-1}$ and $351\,\mathrm{cm}^{-1}$ are due to *Z*-PVA.

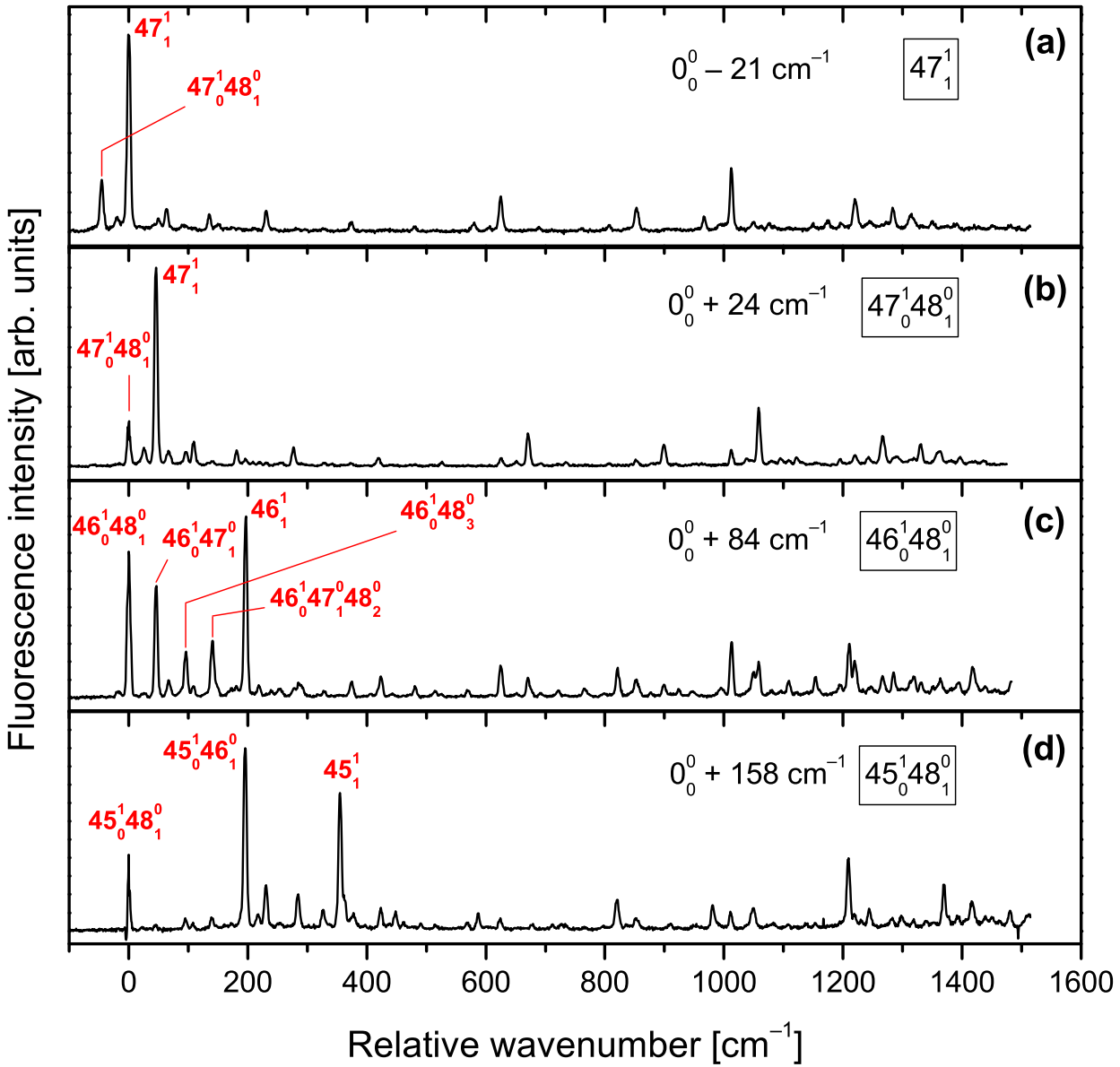
S_0 Vibrational Structure

Excitation of in-plane normal modes



S_0 Vibrational Structure

SVLF Spectra of Hot Bands



Evidence for...

2-Mode-Mixing
47 – 48

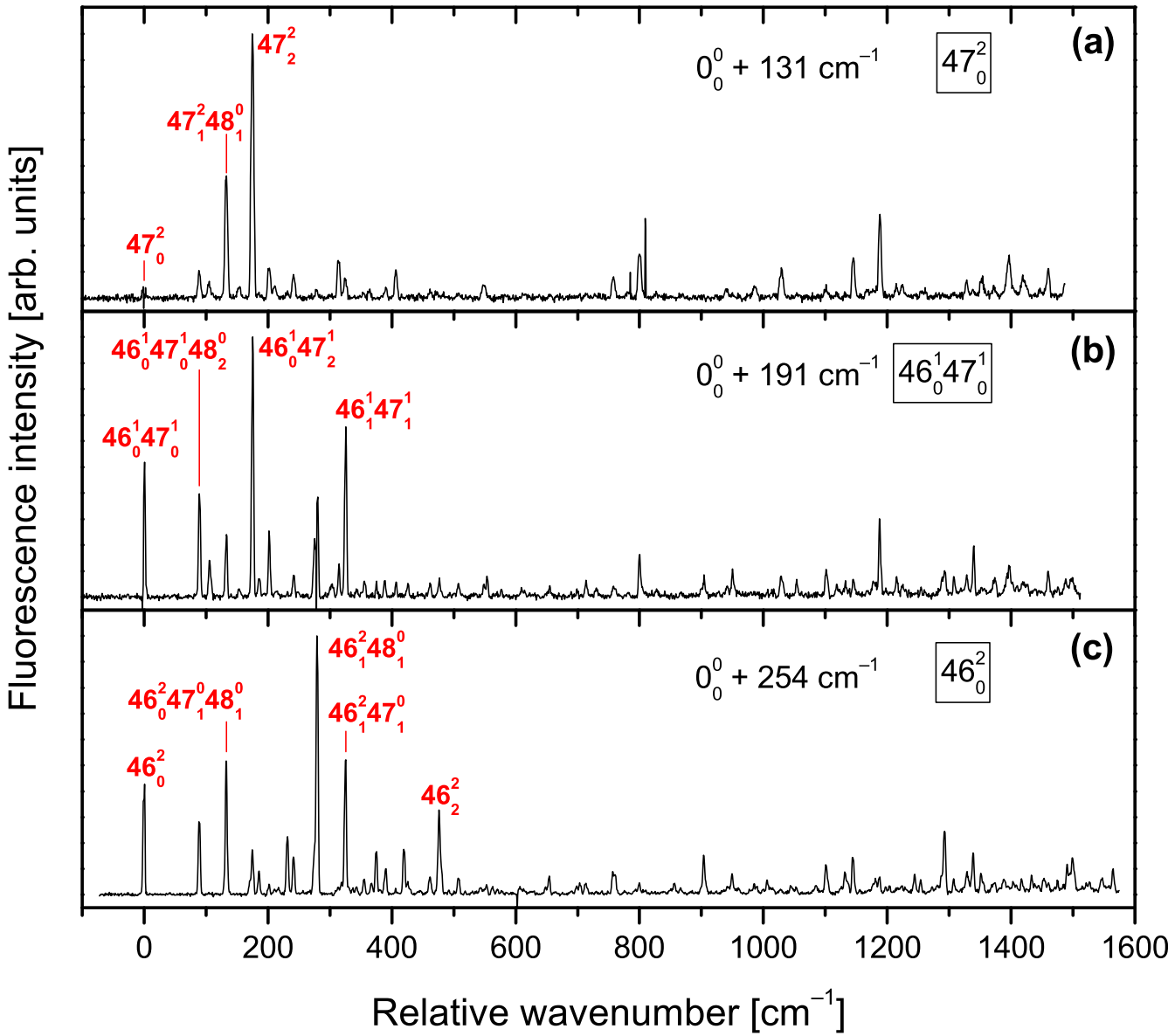
2-Mode-Mixing
47 – 48

3-Mode-Mixing
46 – 47 – 48

3-Mode-Mixing
45 – 46 – 48

S_0 Vibrational Structure

Excitation of out-of-plane normal modes



Evidence for...

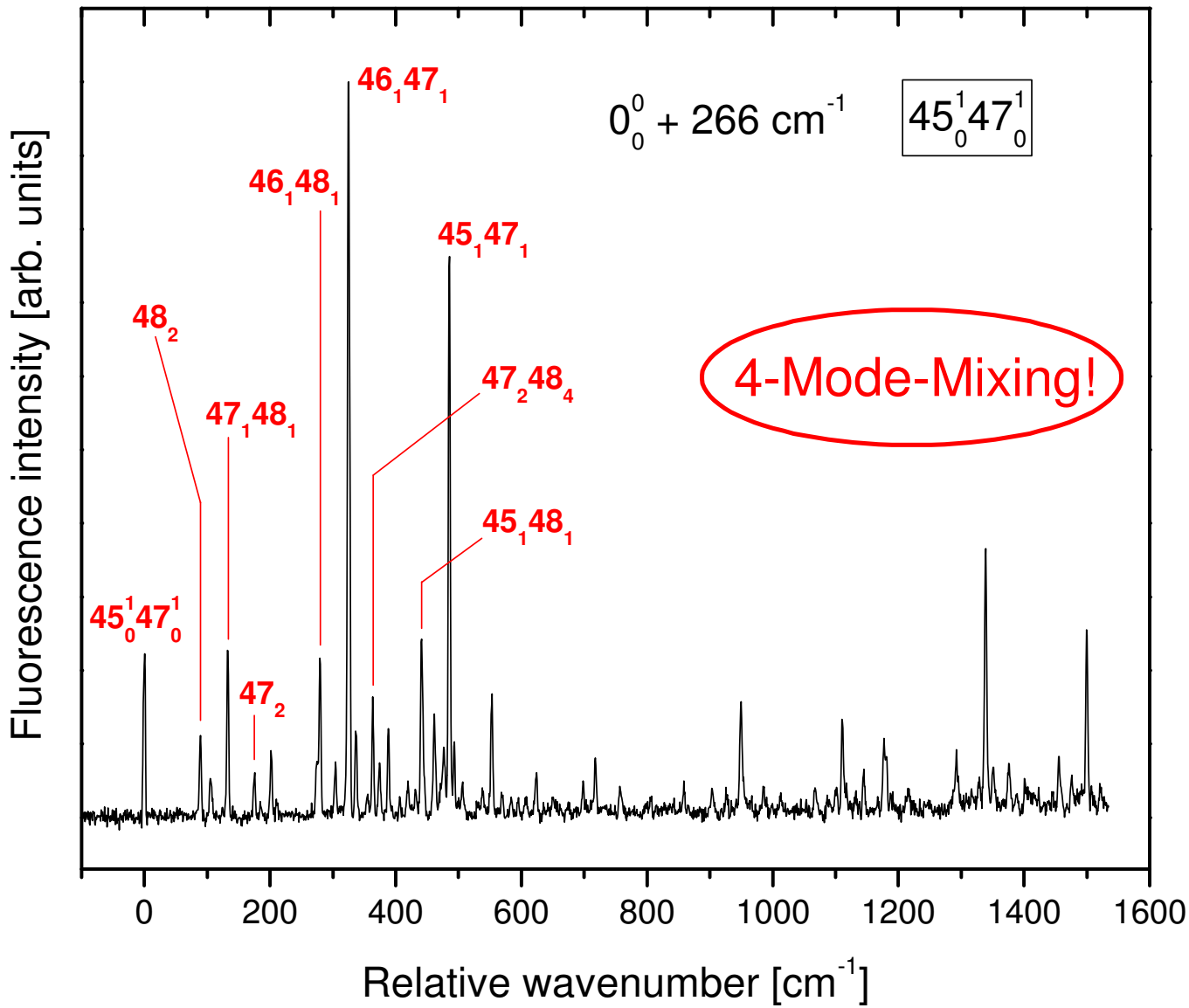
2-Mode-Mixing
47 – 48

3-Mode-Mixing
46 – 47 – 48

3-Mode-Mixing
46 – 47 – 48

S_0 Vibrational Structure

Excitation of out-of-plane normal modes



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The Original Article by Duschinsky

1937 ACTA PHYSICOCHIMICA U.R.S.S. VOL. VII. No. 4

Zur Deutung der Elektronenspektren mehratomiger Moleküle

I. Über das Franck-Condon-Prinzip

Von *F. Duschinsky*

Nach einer Einleitung (§ 1) werden die beim Elektronensprung eines mehratomigen Moleküls möglichen Änderungen der Normalkoordinaten und Eigenvektoren diskutiert (§ 2) und für deren allgemeinst mögliche Änderung werden in Verallgemeinerung einer Rechnung von Herzberg und Teller Intensitätsregeln für antisymmetrische Schwingungen abgeleitet (§ 3). In § 4 wird der Begriff „Kombinationsübergänge" diskutiert und eine einfache Intensitätsregel angegeben. In § 5 wird eine vereinfachte graphische Darstellung des Franck-Condon-Prinzipes beschrieben.

§ 1. Einleitung

Vorliegende Arbeit ist der Anfang einer ursprünglich in drei Abschnitten geplanten Untersuchung über die Elektronenspektren mehratomiger Moleküle. Der erste Abschnitt sollte einige theoretische, bisher noch nicht geklärte Fragen behandeln und die Gesichtspunkte darstellen, nach denen im zweiten die derzeit vorliegende Literatur diskutiert werden sollte. Für den dritten Abschnitt waren experimentelle Untersuchungen über die aufgeworfenen Fragen beabsichtigt. Da die vollständige Durchführung dieses Programms aus äusseren Gründen auf ungewisse Zeit aufgeschoben werden muss, seien hier nur einige Überlegungen des ersten Abschnittes mitgeteilt. Den Umständen entsprechend stellen auch diese teilweise mehr ein Programm als eine ausgearbeitete Theorie dar. Trotzdem glaubten wir, dass sie vielleicht auch schon in diesem Zustand einen Beitrag zum Verständnis der Elektronenspektren mehratomiger Moleküle liefern könnten, und teilen sie deshalb (in 3 Teilen) mit.

Fig. 3 zeigt ein Beispiel für die Anwendung des Franck-Condon-Prinzipes auf ein System mit den Frequenzen 1000 und 445 im Grundzustand, bzw. 830 und 310 im angeregten Zustand. Fluoreszenz aus dem mit 3 Quanten der Frequenz 830 und 1 Quant der Frequenz 310 angeregten Zustand wird mit grösster Wahrscheinlichkeit aus der Umgebung der 4 Punkte *A*, *B*, *C*, *D* erfolgen, und wie man sieht, folgenden Übergängen entsprechen:

$$\begin{pmatrix}3&1\\13&8\end{pmatrix}\begin{pmatrix}3&1\\30&0\end{pmatrix}\begin{pmatrix}3&1\\2&0\end{pmatrix}\begin{pmatrix}3&1\\0&3\end{pmatrix}$$

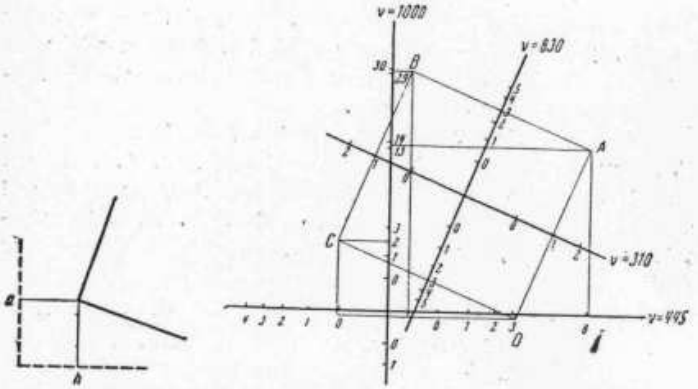


Fig. 2.
Eigenvektoren im Grundzustand (ausgezogene Achsen) und im angeregten Zustand (gestrichelte Achsen). Aus dem Grundzustand wird vorzugsweise eine Frequenz absorbiert, die den Amplituden *a* resp. *b* im angeregten Zustand entspricht.

Fig. 3.
Aus dem mit 3 Quanten der Frequenz 830 und 1 Quant der Frequenz 310 angeregten oberen Zustand werden mit grösster Wahrscheinlichkeit die den Gegenden grösster Verweilzeit *A*, *B*, *C*, *D* entsprechenden Amplituden des unteren Zustandes (mit den Frequenzen 1000 bzw. 445) angeregt. Die Emission entspricht also den Übergängen $\begin{pmatrix}3&1\\13&8\end{pmatrix}$, $\begin{pmatrix}3&1\\30&0\end{pmatrix}$, $\begin{pmatrix}3&1\\2&0\end{pmatrix}$, $\begin{pmatrix}3&1\\0&3\end{pmatrix}$, welche zu den folgenden tieferen Niveaus 17280, 30722, 2722, 2060 führen.

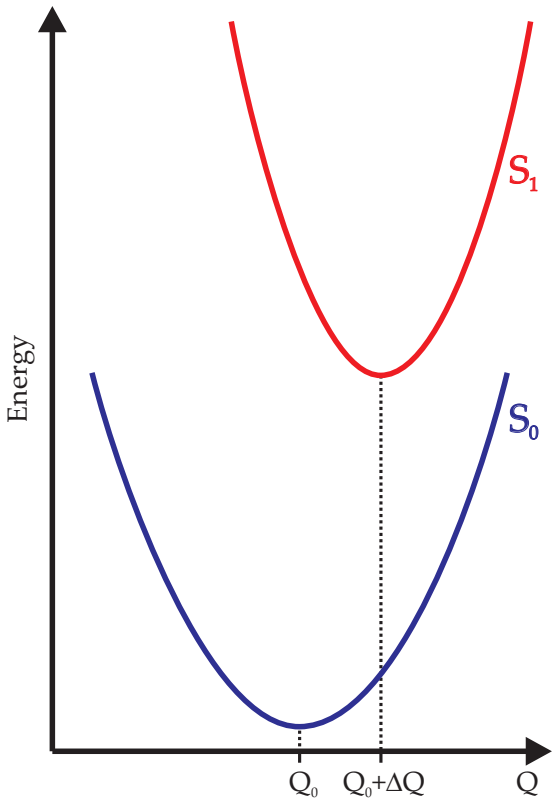
Die Übergänge erfolgen also nach den vier, in Frequenzen ausgedrückten unteren Energieniveaus: 17 280, 30 722, 2 722, 2 060. Auf gegeneinander nicht verschobene, aber verdrehte Systeme angewandt lässt unsere Darstellung qualitativ, aber anschaulich die Resultate von § 3 erkennen. Der „Umkehrpunkt" der zum nullten Schwingungsquant gehörigen Bewegung ist hier zwar nicht ein Punkt maximaler Aufenthaltsdauer, aber doch ein relatives Mass

⇒ English translation now available at
http://www.chem.purdue.edu/zwier/pubs/Duschinsky.pdf

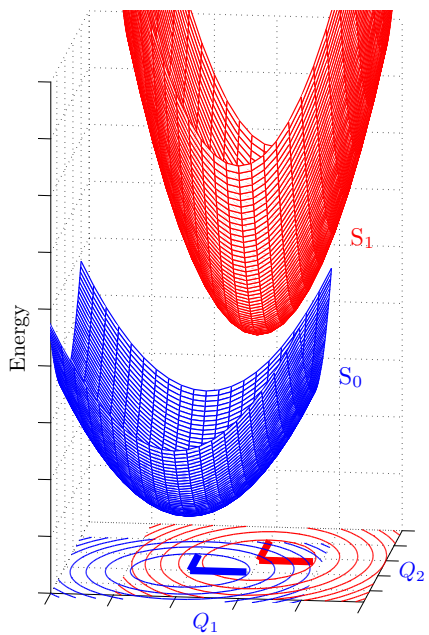
The Duschinsky Effect

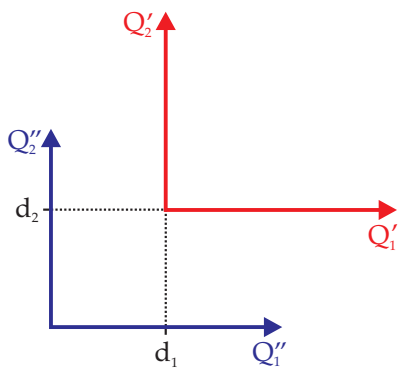
Duschinsky rotation in 2D

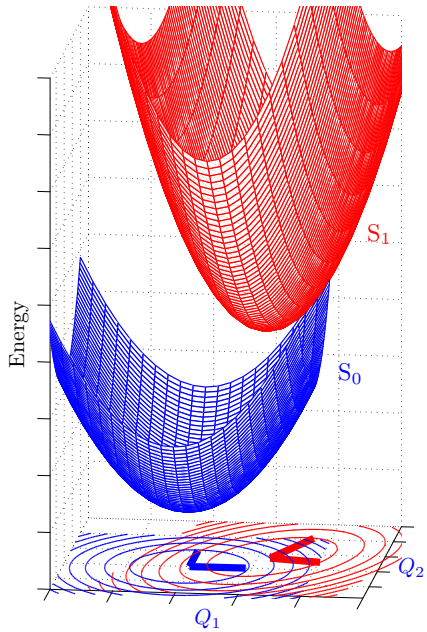
1D

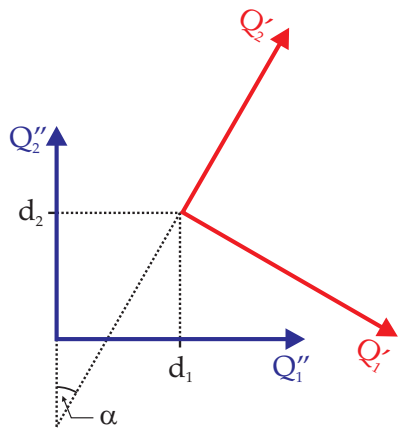


2D



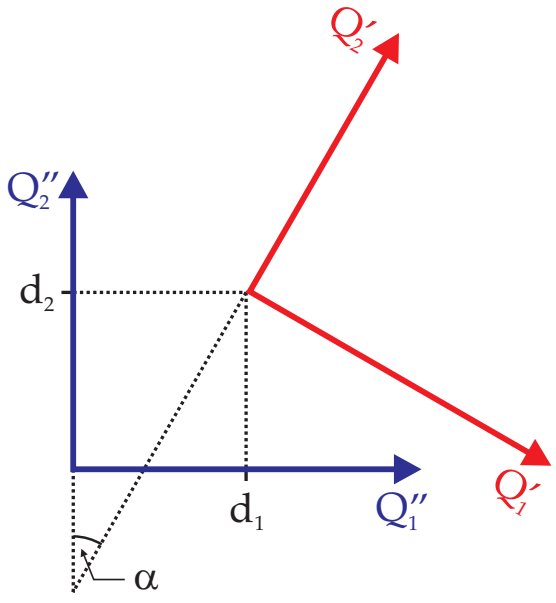






The Duschinsky Effect

Duschinsky rotation in 2D



If both electronic states have the same nuclear symmetry:

$$\mathbf{Q}'_i = \sum_{k=1}^{r} D_{ik}\,\mathbf{Q}''_k + \mathbf{d}_i$$

for the r totally symmetric vibrations

$$\mathbf{Q}'_i = \sum_{k=1}^{s_\alpha} D_{ik}\,\mathbf{Q}''_k$$

for the s_α non-totally symmetric vibrations of symmetry species α

F. Duschinsky, *Acta Physicochim. U.R.S.S.*, **1937**, *7*, 551.

Duschinsky mixing between 2 totally symmetric normal coordinates

$$\begin{pmatrix}\mathbf{Q}'_1\\ \mathbf{Q}'_2\end{pmatrix} = \underbrace{\begin{pmatrix}\cos\alpha & -\sin\alpha\\ \sin\alpha & \cos\alpha\end{pmatrix}}_{\text{Duschinsky matrix}} \begin{pmatrix}\mathbf{Q}''_1\\ \mathbf{Q}''_2\end{pmatrix} + \begin{pmatrix}\mathbf{d_1}\\ \mathbf{d_2}\end{pmatrix} \qquad (1)$$

Duschinsky rotation in 4D

Resolution of the 4×4 Duschinsky rotation matrix into pairwise contributions:

$$\mathbf{D} = \mathbf{D}_{12} \cdot \mathbf{D}_{13} \cdot \mathbf{D}_{14} \cdot \mathbf{D}_{23} \cdot \mathbf{D}_{24} \cdot \mathbf{D}_{34} \tag{2}$$

$$\mathbf{D}_{12} = \begin{pmatrix} \cos\alpha & -\sin\alpha & 0 & 0 \\ \sin\alpha & \cos\alpha & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \qquad \mathbf{D}_{23} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & \cos\delta & -\sin\delta & 0 \\ 0 & \sin\delta & \cos\delta & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

$$\mathbf{D}_{13} = \begin{pmatrix} \cos\beta & 0 & -\sin\beta & 0 \\ 0 & 1 & 0 & 0 \\ \sin\beta & 0 & \cos\beta & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \qquad \mathbf{D}_{24} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & \cos\epsilon & 0 & -\sin\epsilon \\ 0 & 0 & 1 & 0 \\ 0 & \sin\epsilon & 0 & \cos\epsilon \end{pmatrix}$$

$$\mathbf{D}_{14} = \begin{pmatrix} \cos\gamma & 0 & 0 & -\sin\gamma \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ \sin\gamma & 0 & 0 & \cos\gamma \end{pmatrix} \qquad \mathbf{D}_{34} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & \cos\zeta & -\sin\zeta \\ 0 & 0 & \sin\zeta & \cos\zeta \end{pmatrix}$$

Duschinsky rotation in 4D

Matrix elements of the 4×4 Duschinsky rotation matrix:

$$d_{11} = \cos\alpha\ \cos\beta\ \cos\gamma \tag{3}$$

$$d_{12} = -\sin\alpha\ \cos\delta\ \cos\epsilon - \cos\alpha\ \sin\beta\ \sin\delta\ \cos\epsilon - \cos\alpha\ \cos\beta\ \sin\gamma\ \sin\epsilon \tag{4}$$

$$d_{13} = \sin\alpha\ \sin\delta\ \cos\zeta - \cos\alpha\ \sin\beta\ \cos\delta\ \cos\zeta + \sin\alpha\ \cos\delta\ \sin\epsilon\ \sin\zeta + \cos\alpha\ \sin\beta\ \sin\delta\ \sin\epsilon\ \sin\zeta - \cos\alpha\ \cos\beta\ \sin\gamma\ \cos\epsilon\ \sin\zeta \tag{5}$$

$$d_{14} = -\sin\alpha\ \sin\delta\ \sin\zeta + \cos\alpha\ \sin\beta\ \cos\delta\ \sin\zeta + \sin\alpha\ \cos\delta\ \sin\epsilon\ \cos\zeta + \cos\alpha\ \sin\beta\ \sin\delta\ \sin\epsilon\ \cos\zeta - \cos\alpha\ \cos\beta\ \sin\gamma\ \cos\epsilon\ \cos\zeta \tag{6}$$

$$d_{21} = \sin\alpha\ \cos\beta\ \cos\gamma \tag{7}$$

$$d_{22} = \cos\alpha\ \cos\delta\ \cos\epsilon - \sin\alpha\ \sin\beta\ \sin\delta\ \cos\epsilon - \sin\alpha\ \cos\beta\ \sin\gamma\ \sin\epsilon \tag{8}$$

$$d_{23} = -\cos\alpha\ \sin\delta\ \cos\zeta - \sin\alpha\ \sin\beta\ \cos\delta\ \cos\zeta - \cos\alpha\ \cos\delta\ \sin\epsilon\ \sin\zeta + \sin\alpha\ \sin\beta\ \sin\delta\ \sin\epsilon\ \sin\zeta - \sin\alpha\ \cos\beta\ \sin\gamma\ \cos\epsilon\ \sin\zeta \tag{9}$$

$$d_{24} = \cos\alpha\ \sin\delta\ \sin\zeta + \sin\alpha\ \sin\beta\ \cos\delta\ \sin\zeta - \cos\alpha\ \cos\delta\ \sin\epsilon\ \cos\zeta + \sin\alpha\ \sin\beta\ \sin\delta\ \sin\epsilon\ \cos\zeta - \sin\alpha\ \cos\beta\ \sin\gamma\ \cos\epsilon\ \cos\zeta \tag{10}$$

$$d_{31} = \sin\beta\ \cos\gamma \tag{11}$$

$$d_{32} = \cos\beta\ \sin\delta\ \cos\epsilon - \sin\beta\ \sin\gamma\ \sin\epsilon \tag{12}$$

$$d_{33} = \cos\beta\ \cos\delta\ \cos\zeta - \cos\beta\ \sin\delta\ \sin\epsilon\ \sin\zeta - \sin\beta\ \sin\gamma\ \cos\epsilon\ \sin\zeta \tag{13}$$

$$d_{34} = -\cos\beta\ \cos\delta\ \sin\zeta - \cos\beta\ \sin\delta\ \sin\epsilon\ \cos\zeta - \sin\beta\ \sin\gamma\ \cos\epsilon\ \cos\zeta \tag{14}$$

$$d_{41} = \sin\gamma \tag{15}$$

$$d_{42} = \cos\gamma\ \sin\epsilon\,, \tag{16}$$

$$d_{43} = \cos\gamma\ \cos\epsilon\ \sin\zeta \tag{17}$$

$$d_{44} = \cos\gamma\ \cos\epsilon\ \cos\zeta\,. \tag{18}$$

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S_0 Vibrational Levels accounted for in the Intensity Fits

S_0 level	$\tilde{\nu}_{exp}$ [cm^{-1}]
48_2	89
$47_1 48_1$	133
47_2	175
48_4	201
$47_1 48_3$	231
$47_2 48_2$	275
$46_1 48_1$	280
$47_3 48_1$	313
$46_1 47_1$	326
$47_2 48_4$	355
$46_1 48_3$	375
$46_1 47_1 48_2$	419
$45_1 48_1$	441
$46_1 47_2 48_1$	461
46_2	476
$45_1 47_1$	486
$45_1 48_3$	538
$46_2 48_2$	563
$45_1 47_1 48_2$	570
$45_1 46_1$	636
$46_2 48_4$	649
$46_2 47_2$	654
$45_1 46_1 48_2$	728
$46_3 48_1$	757
45_2	795
$46_3 47_1$	799

S_0 state

$\tilde{\nu}''_{45} = 398\,cm^{-1}$
$\tilde{\nu}''_{46} = 238\,cm^{-1}$
$\tilde{\nu}''_{47} = 88\,cm^{-1}$
$\tilde{\nu}''_{48} = 45\,cm^{-1}$

S_1 state

$\tilde{\nu}'_{45} = 201\,cm^{-1}$
$\tilde{\nu}'_{46} = 127\,cm^{-1}$
$\tilde{\nu}'_{47} = 67\,cm^{-1}$
$\tilde{\nu}'_{48} = ?$

Duschinsky Simulations

- 10 SVLF spectra, each containing 26 bands, and the FE spectrum were fit.
- All 62 bands possible (up to $v = 4$) in each SVLF spectrum are plotted.

Franck-Condon integrals

- Calculation of four-dimensional Franck-Condon overlap integrals by using recursion relations involving harmonic oscillator wave functions.

P. T. Ruhoff, *Chem. Phys.*, 1994, *186*, 355.

Fit Parameters

- 6 Duschinsky angles and the S_1 frequency of normal mode ν_{48} were fitted simultaneously.

Fit Function & Search Algorithm

- Unweighted least-squares sum fit function

$$F_{\mathrm{I}} = \sum_{i=1}^{N} \left[I_i^{\mathrm{calc}} - I_i^{\mathrm{exp}} \right]^2$$

was minimized using a Pattern Search algorithm.

Equivalent Parameter Sets

- For any N-dimensional Duschinsky mixing between *totally symmetric vibrations* there are

$$2 \cdot 2^N$$

mathematically equivalent sets of parameters, in the case of *non-totally symmetric vibrations*

$$2^N$$

mathematically and physically equivalent parameter sets.

E. g. 2D mixing between non-totally symmetric modes:

$$\alpha_1 = 50^\circ \qquad \alpha_2 = 50^\circ + 180^\circ = 230^\circ$$
$$\alpha_3 = 360^\circ - 50^\circ = 310^\circ \qquad \alpha_4 = 360^\circ - 50^\circ - 180^\circ = 130^\circ$$

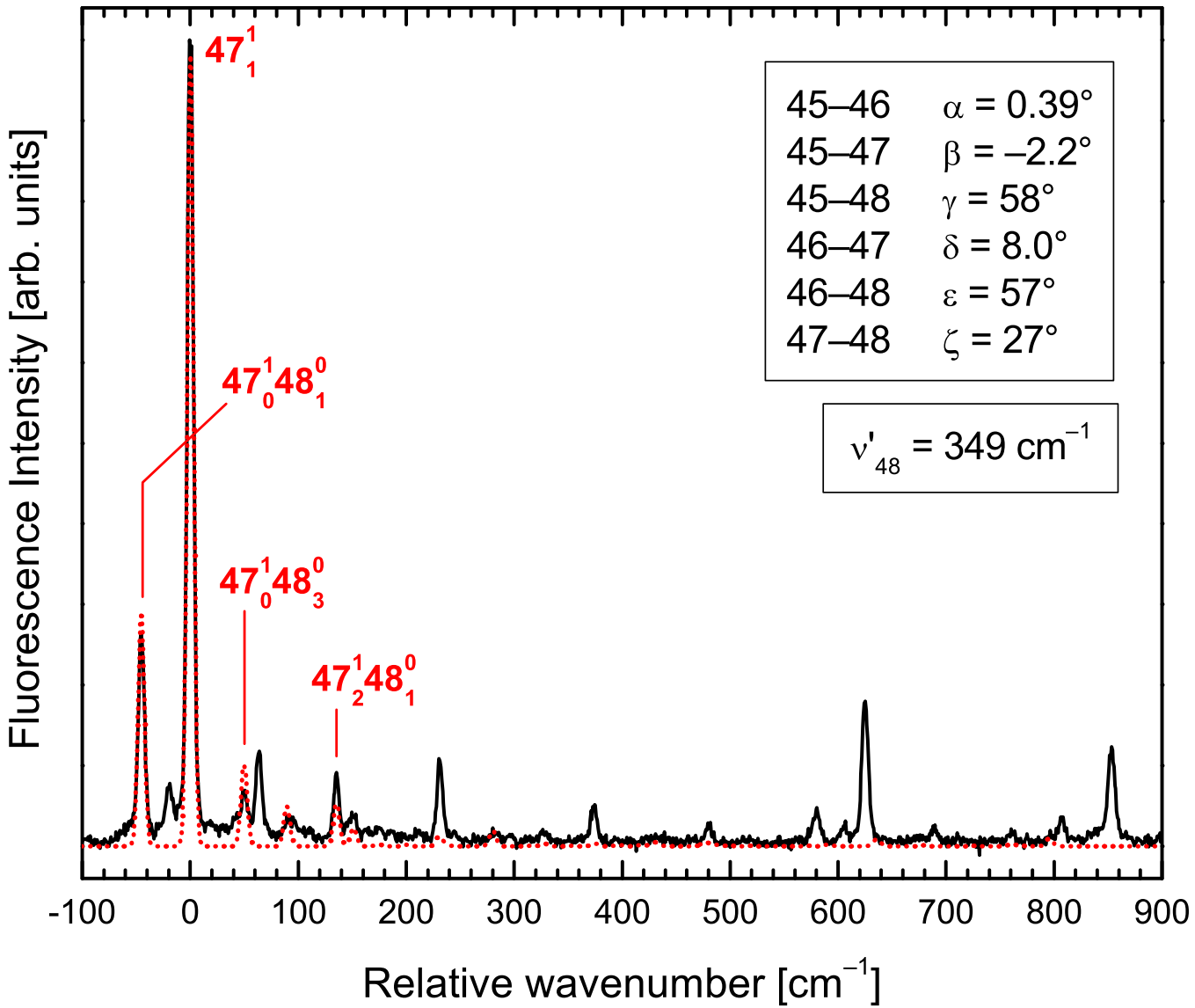
Fitting Procedure

- SVLF spectra were fitted according to *prima facie* increasing complexity

2-Mode-Mixing $\rightarrow$ 3-Mode-Mixing $\rightarrow$ 4-Mode-Mixing

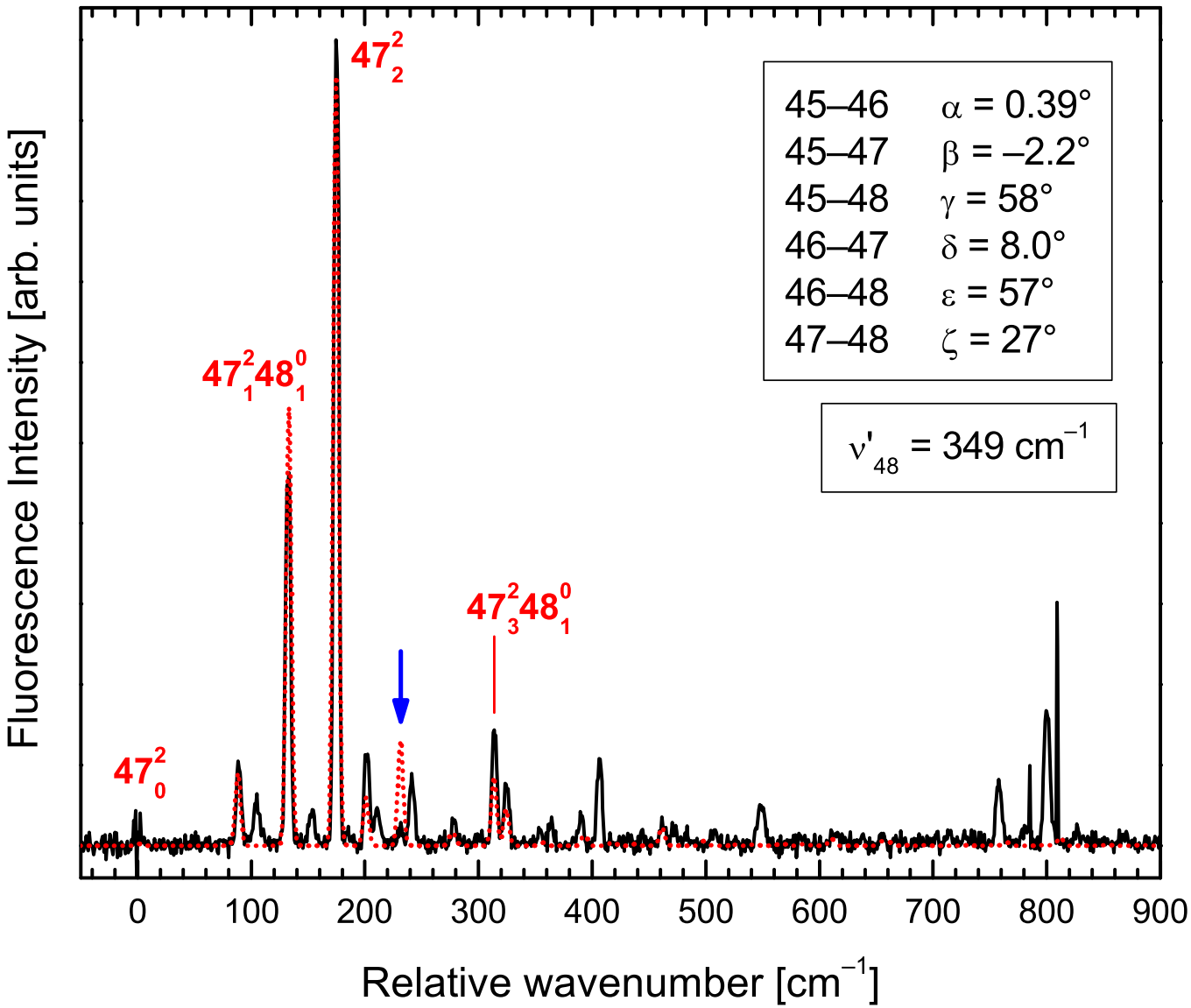
47_1^1 SVLF spectrum

2-Mode-Mixing



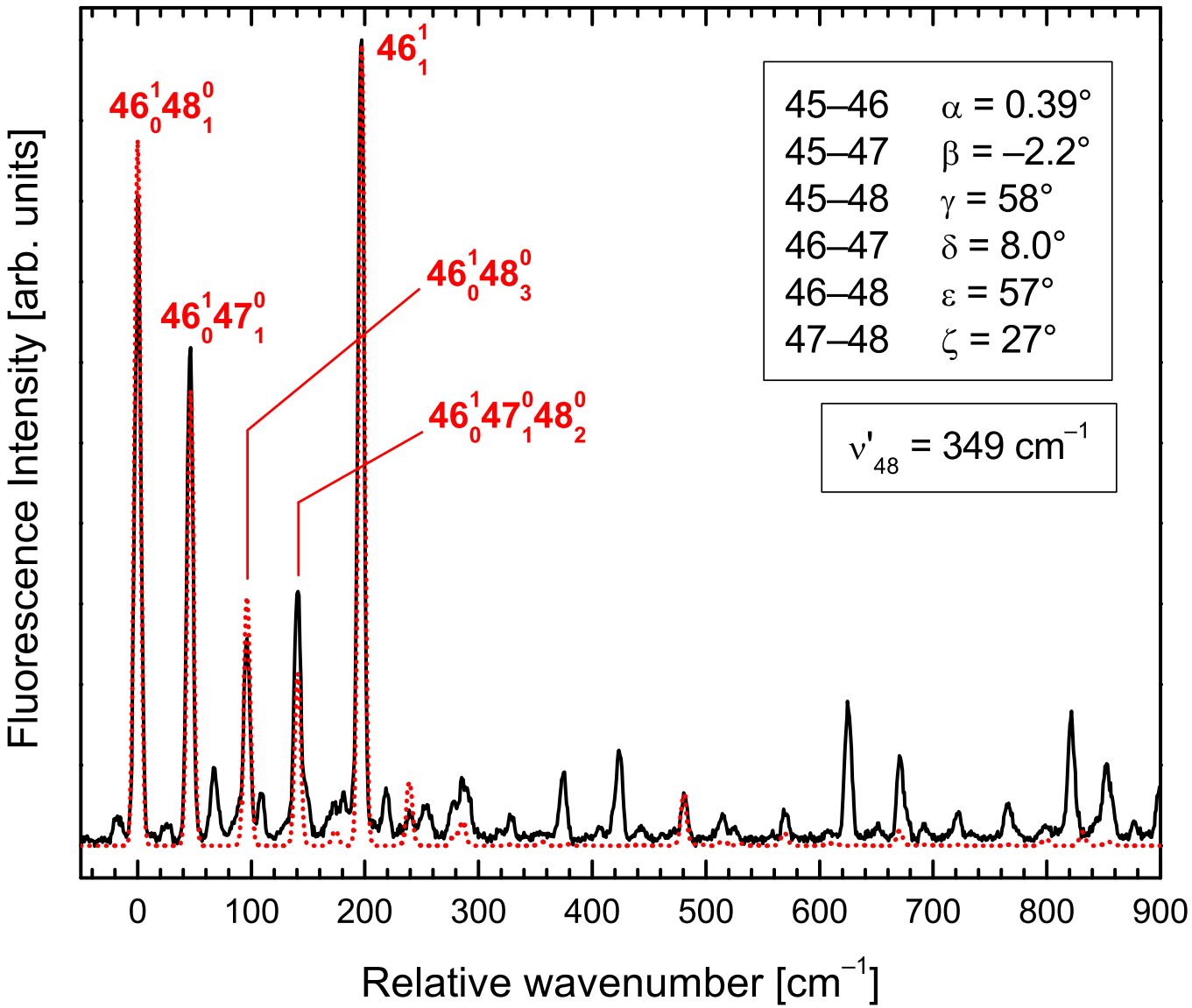
47_0^2 SVLF spectrum

2-Mode-Mixing



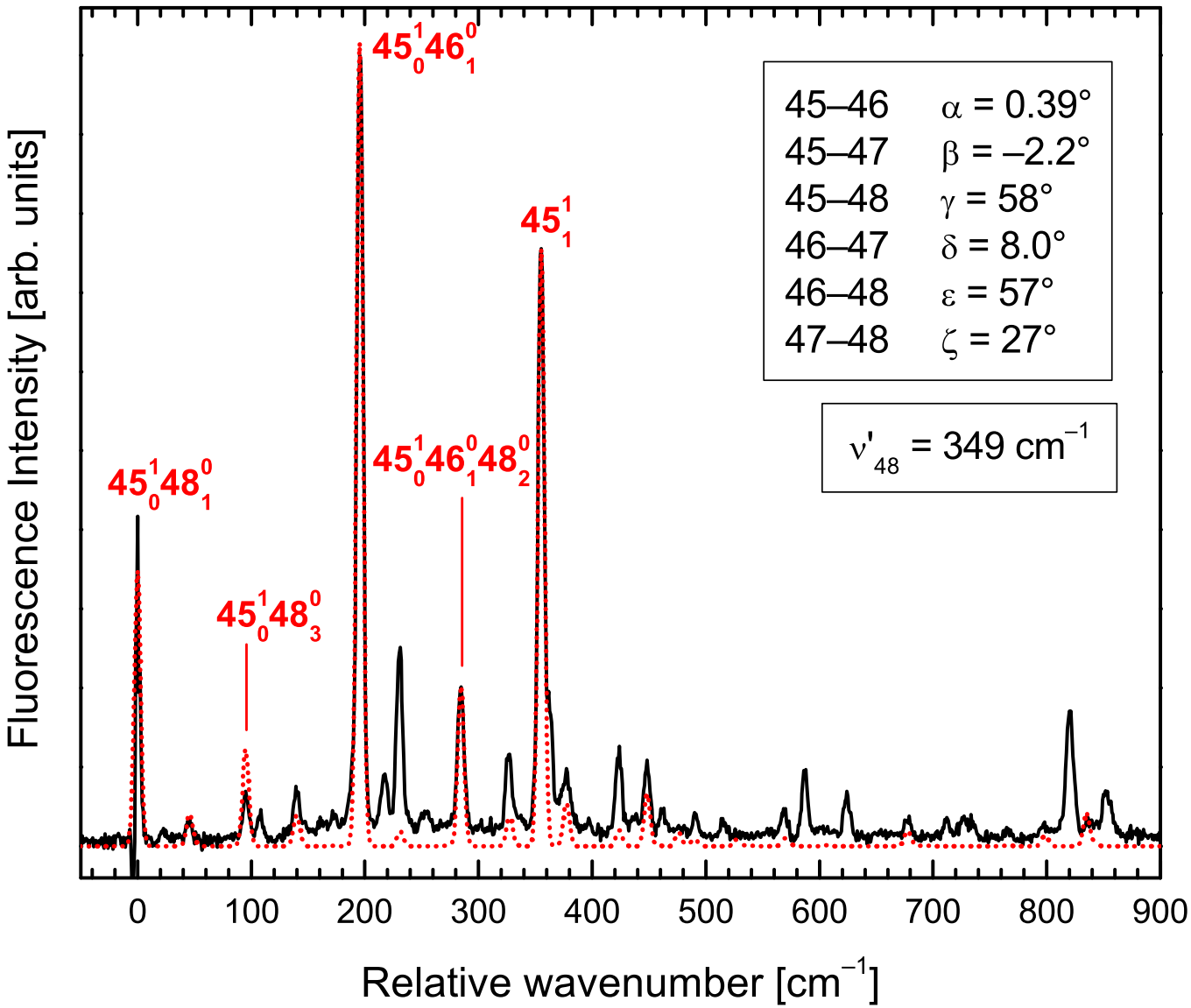
$46_0^1 48_1^0$ SVLF spectrum

3-Mode-Mixing



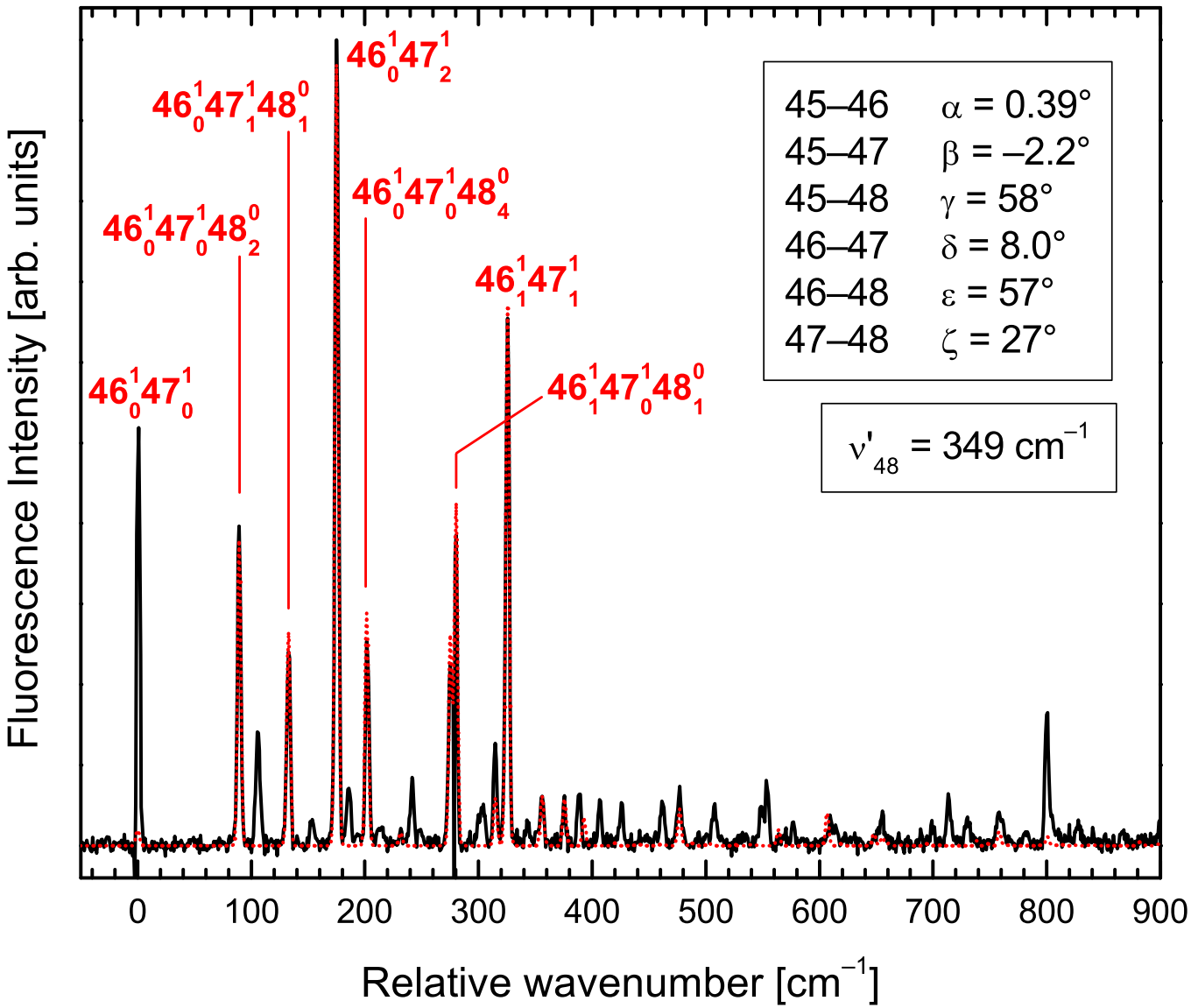
$45_0^1 48_1^0$ SVLF spectrum

3-Mode-Mixing



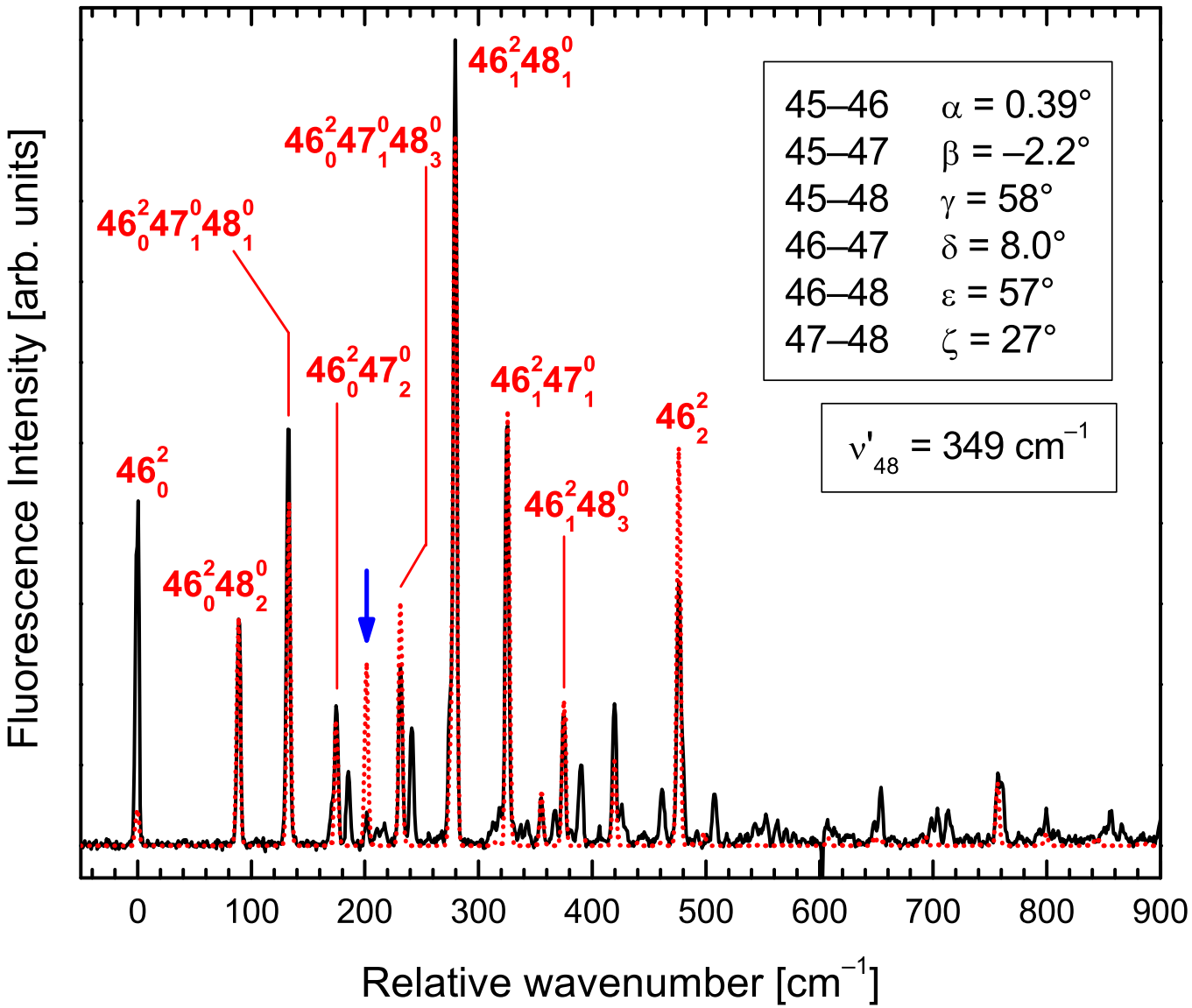
$46_0^1 47_0^1$ SVLF spectrum

3-Mode-Mixing



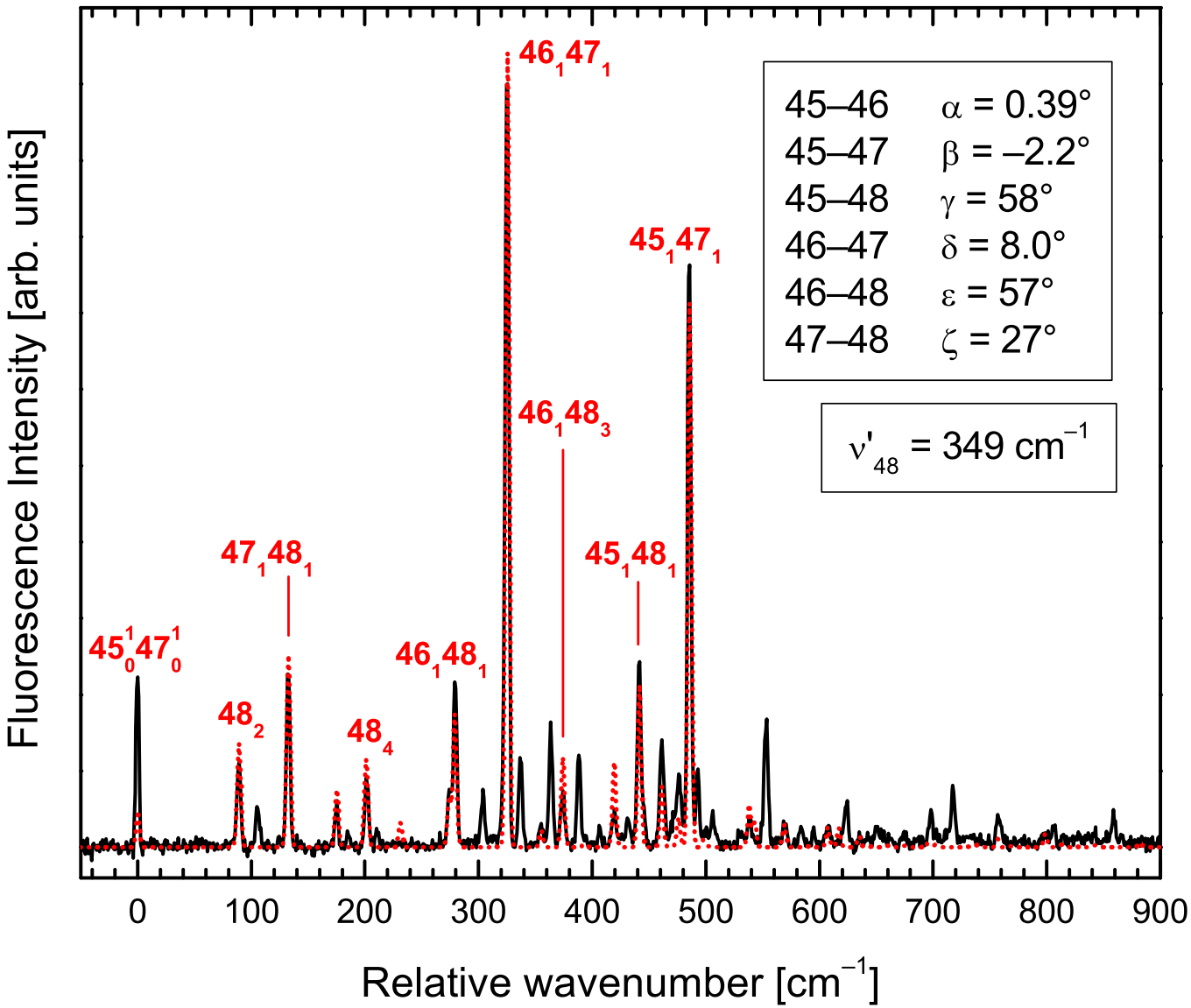
46_0^2 SVLF spectrum

3-Mode-Mixing



$45_0^1 47_0^1$ SVLF spectrum

4-Mode-Mixing



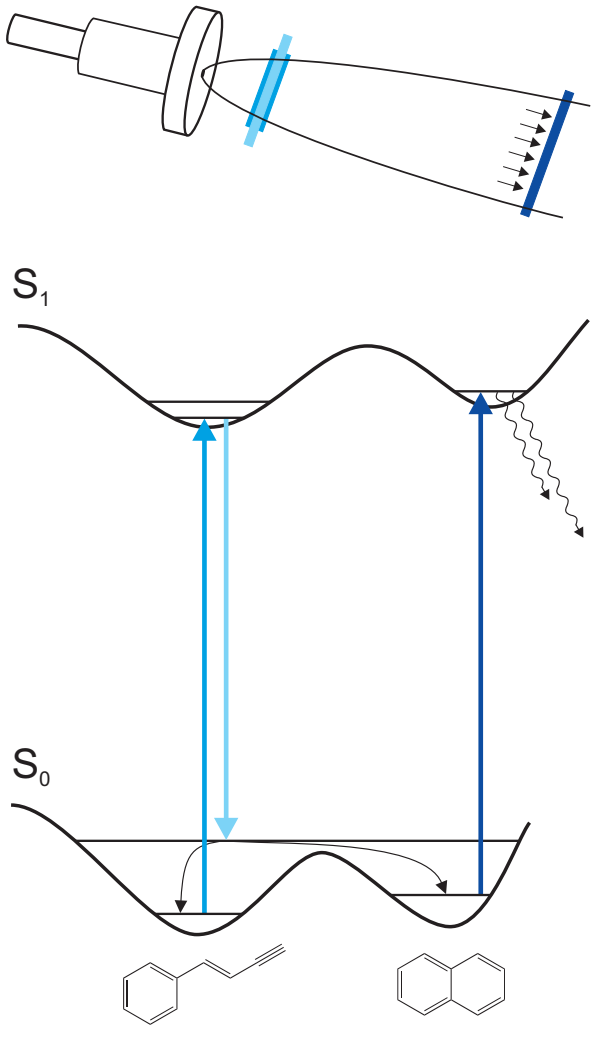
Finally...

Conclusion

- The intensities of ~ 280 overtone and combination transitions of 4 non-totally symmetric vibrations in 10 SVLF spectra and the flourescence excitation spectrum were fit in an automated least-squares fitting procedure with 7 Parameters to determine the amount of Duschinsky mixing between them.
- As a consistency check, all ~ 640 vibronic bands (up to $v = 4$) were simulated. These simulations yielded astonishingly consistent results.

Outlook

- Currently, CASSCF calculations for the S_0 and S_1 state are underway to elucidate the Duschinsky analysis in light of the $\pi - \pi^*$ transition involved in the electronic excitation.
- Eventually, Stimulated Emission Pumping Population Transfer experiments will be carried to determine the energy differences between conformers and the barriers to coformational isomerization.



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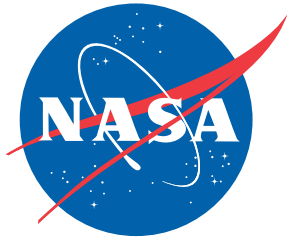
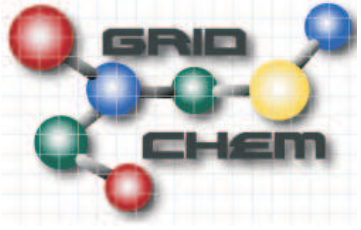
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