

Infrared and Ultraviolet Spectroscopy  
of Jet-Cooled 2-Benzylphenol:  
II. Duschinsky Normal Mode Mixing in the Excited State

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## 1 Duschinsky Analysis

- Fluorescence Excitation Spectrum
- SVLF Spectrum of the  $0^0$  Level
- SVLF Spectrum of the  $1^1$  Level ( $29\text{ cm}^{-1}$ )
- SVLF Spectrum of the  $2^1$  Level ( $41\text{ cm}^{-1}$ )

## 2 Rotationally Resolved Fluorescence Excitation Spectra of Different Vibronic Bands

## 3 Summary

- Can one understand the puzzling and counterintuitive intensity patterns within the Duschinsky framework?
- Is the band at  $41\text{ cm}^{-1}$  the origin of a second excited state conformer or  $2_0^1$ ?
- Can one account for the  $S_1$  electronic spectrum in terms of local excitation of the phenol moiety?

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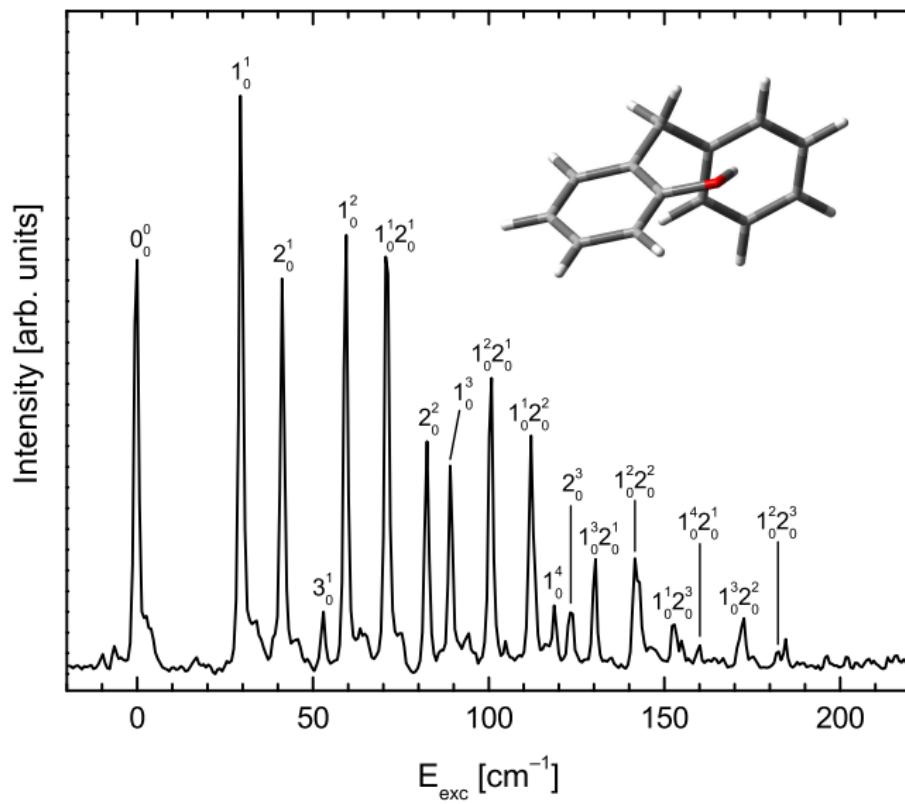
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# Fluorescence Excitation Spectrum

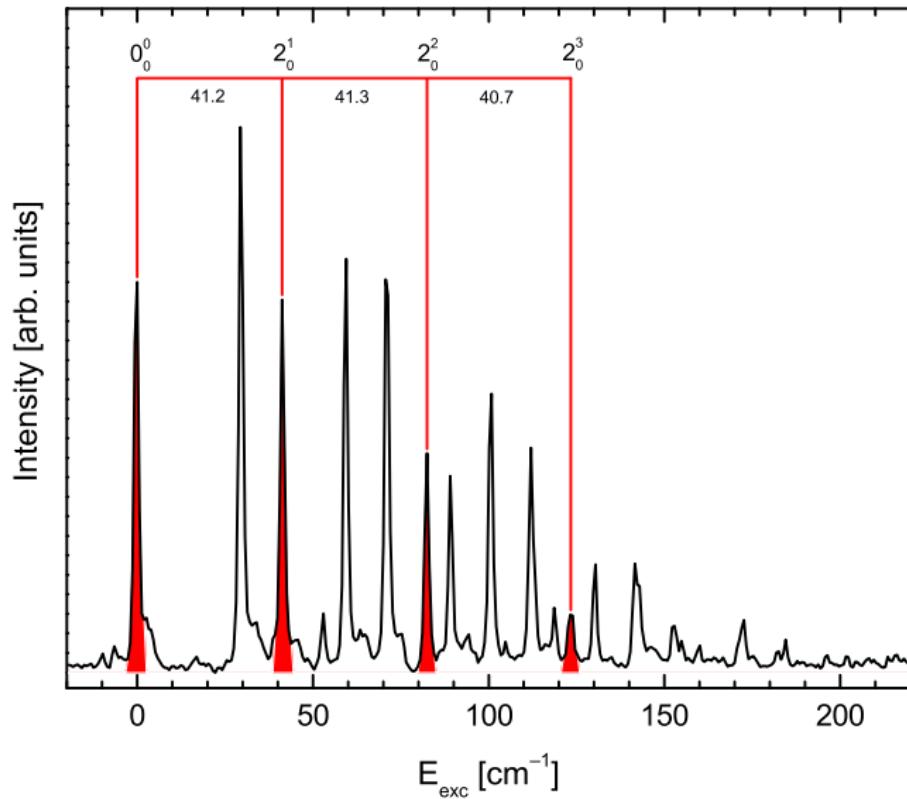
Assignment of the FE Spectrum requires only Two Normal Modes



# Fluorescence Excitation Spectrum

$2_0^n$ -Progression built off of the  $0_0^0$ -Transition

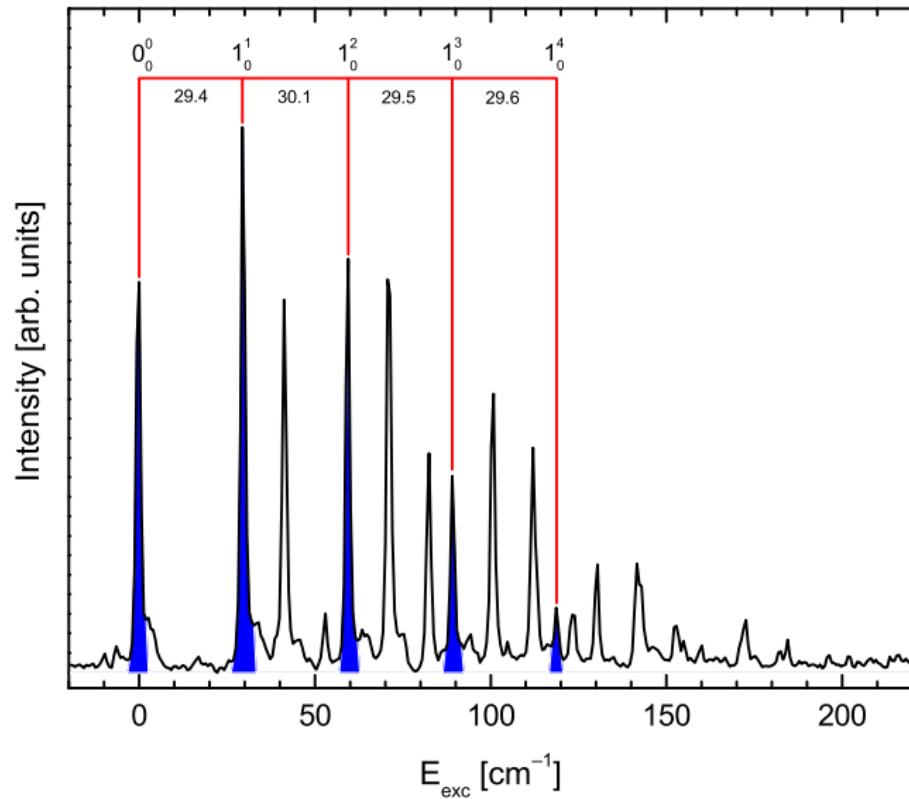
$41\text{ cm}^{-1}$ -Progression



# Fluorescence Excitation Spectrum

$1_0^n$ -Progression built off of the  $0_0^0$ -Transition

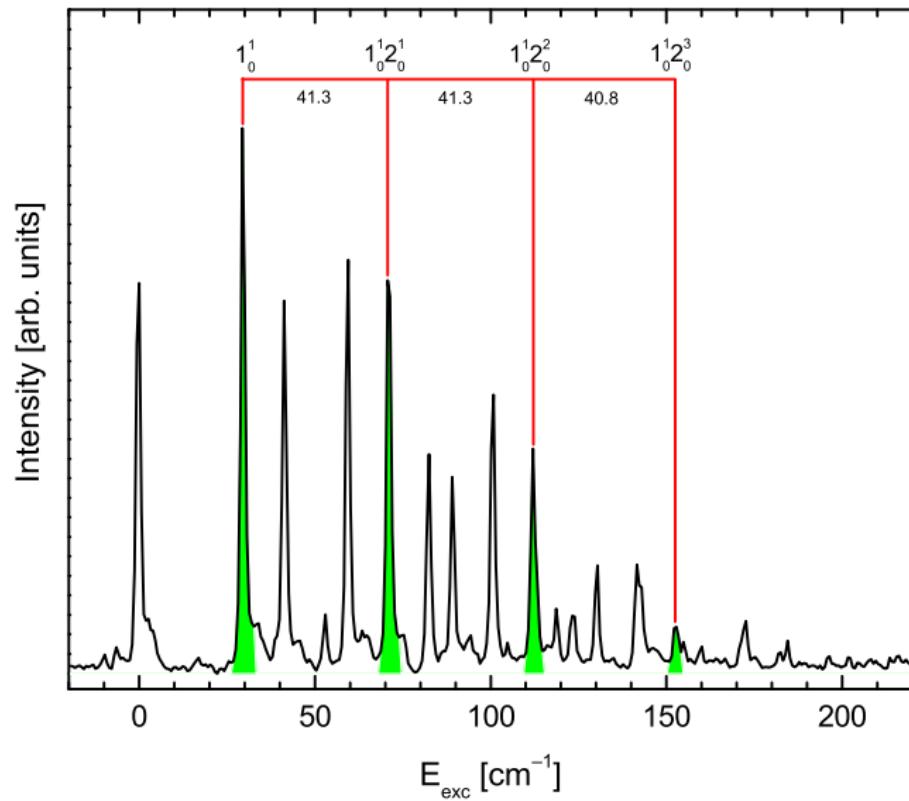
$29\text{ cm}^{-1}$ -Progression



# Fluorescence Excitation Spectrum

$2_0^n$ -Progression built off of the  $1_0^1$ -Transition

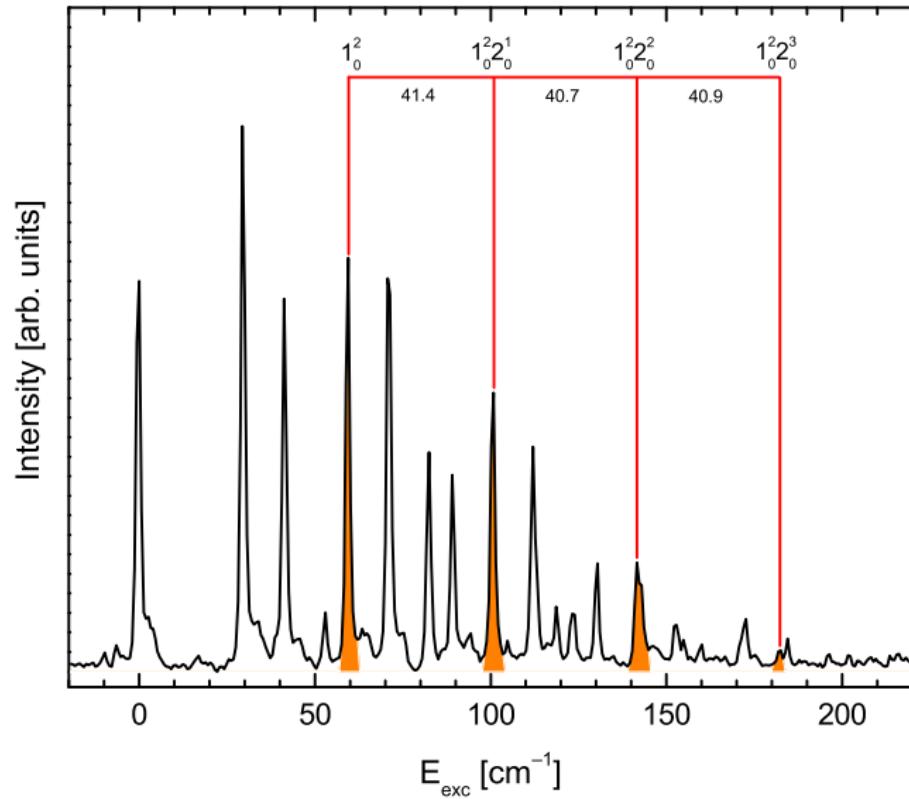
$41\text{ cm}^{-1}$ -Progression



# Fluorescence Excitation Spectrum

$2_0^n$ -Progression built off of the  $1_0^2$ -Transition

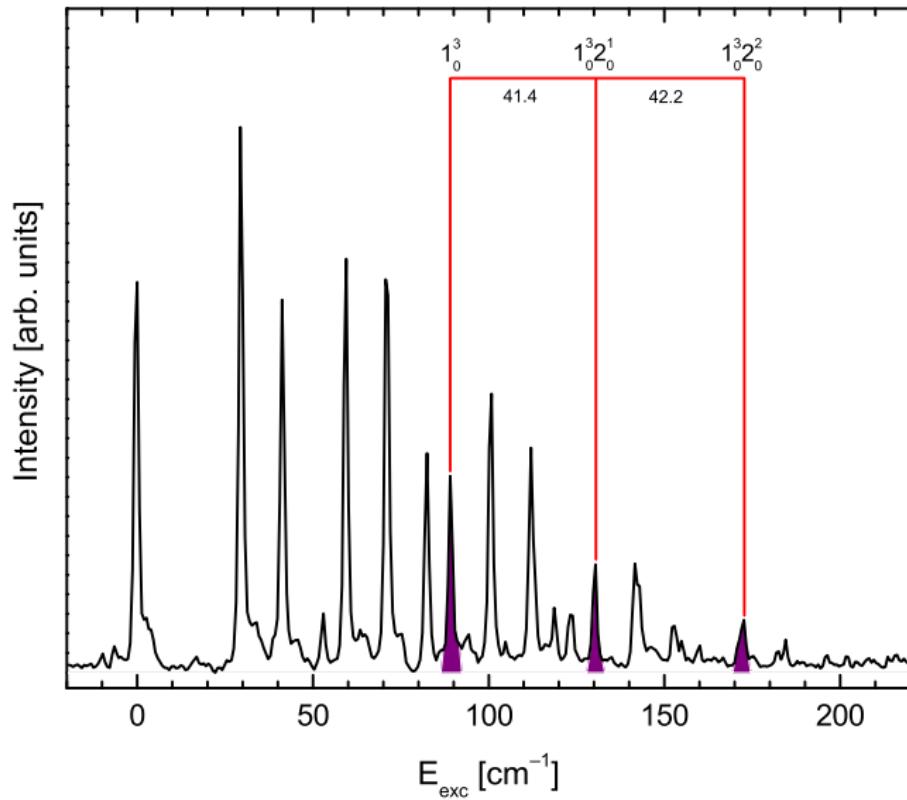
$41\text{ cm}^{-1}$ -Progression



# Fluorescence Excitation Spectrum

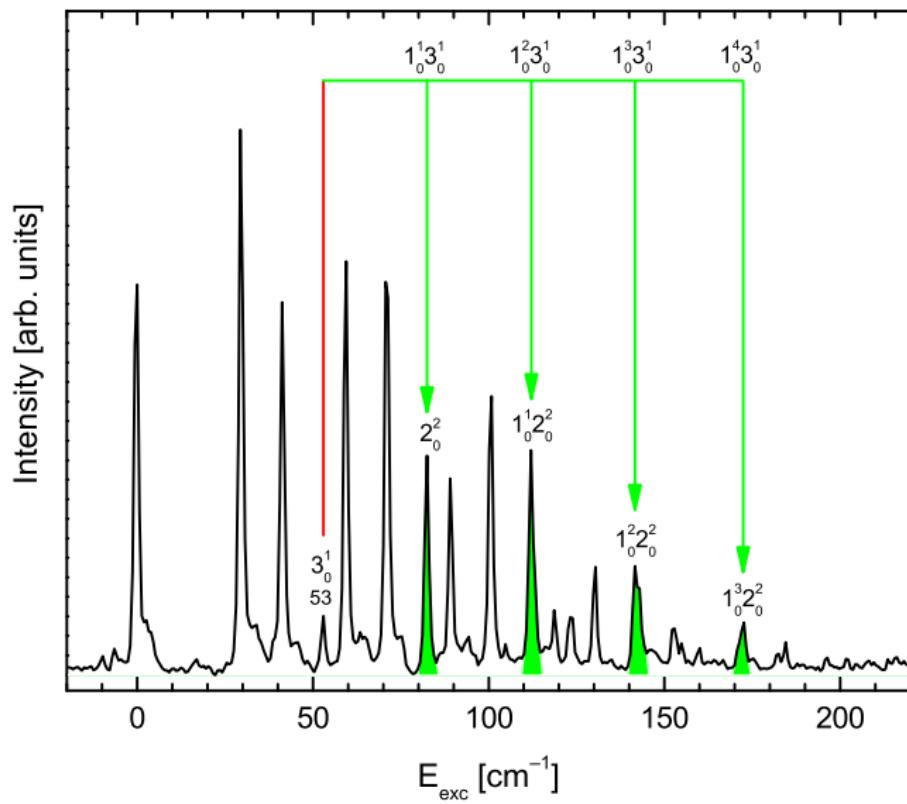
$2_0^n$ -Progression built off of the  $1_0^3$ -Transition

$41\text{ cm}^{-1}$ -Progression

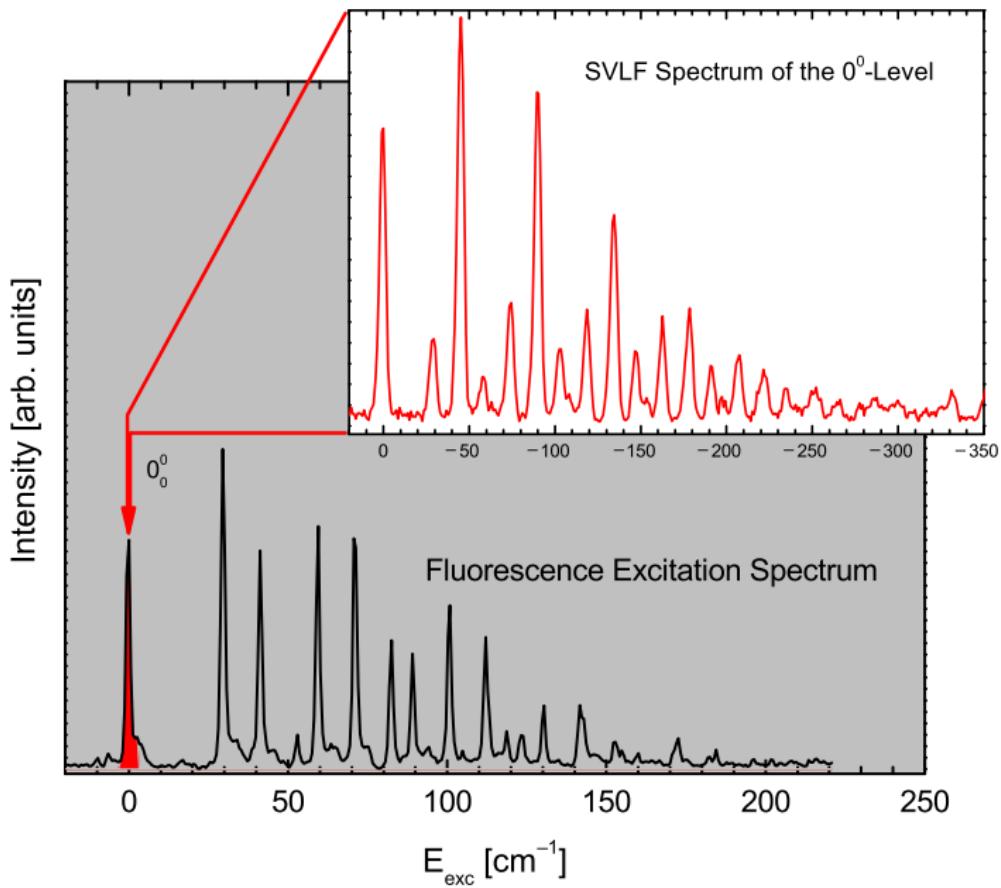


# Fluorescence Excitation Spectrum

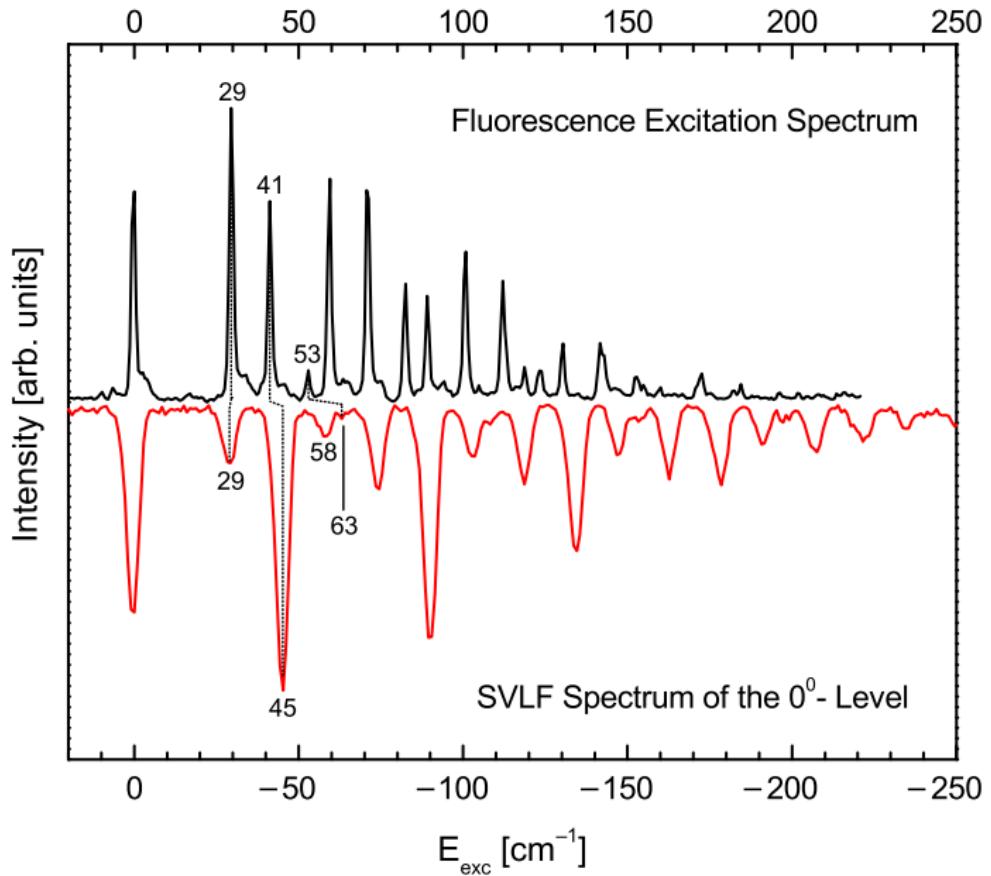
Expected Perturbations in  $S_1$  due to Fermi Resonances



# SVLF Spectrum of the $0^0$ -Level



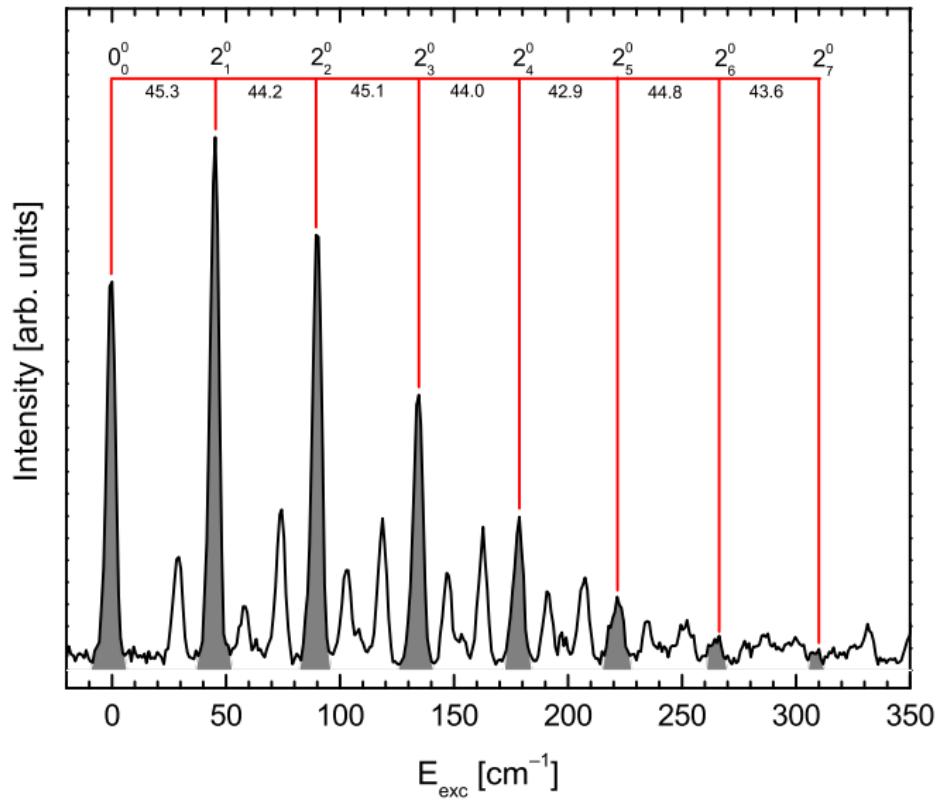
# Mirror Symmetry Breakdown



# SVLF Spectrum of the $0^0$ -Level

$2^0_n$ -Progression built off of the  $0^0_0$ -Transition

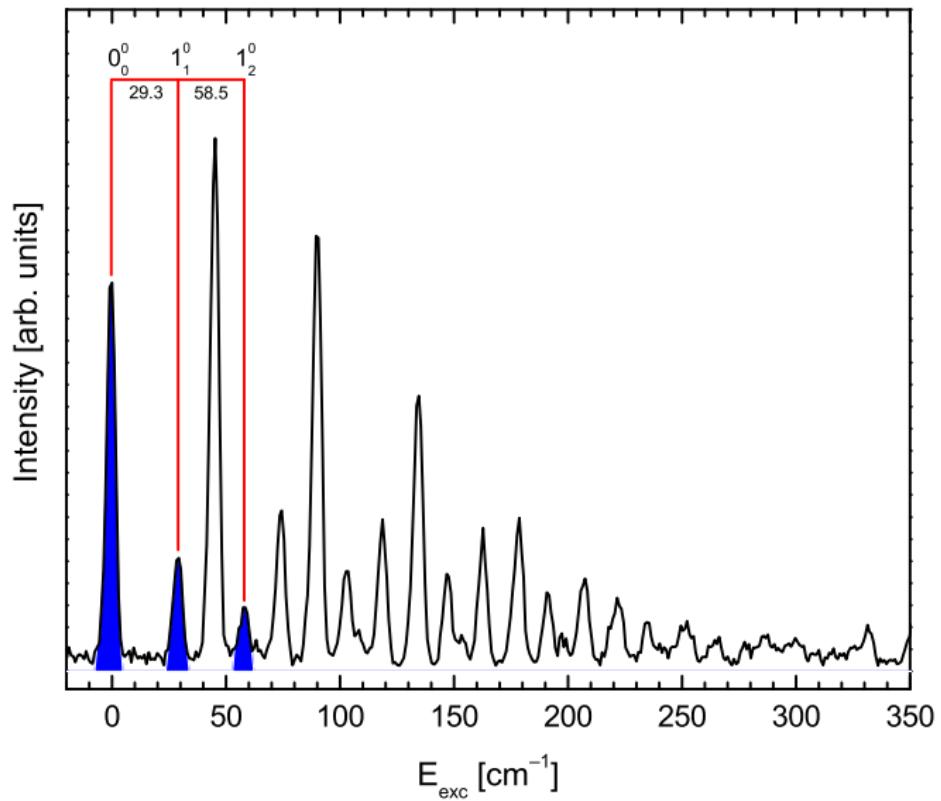
$45\text{ cm}^{-1}$ -Progression



# SVLF Spectrum of the $0^0$ -Level

$1^0_n$ -Progression

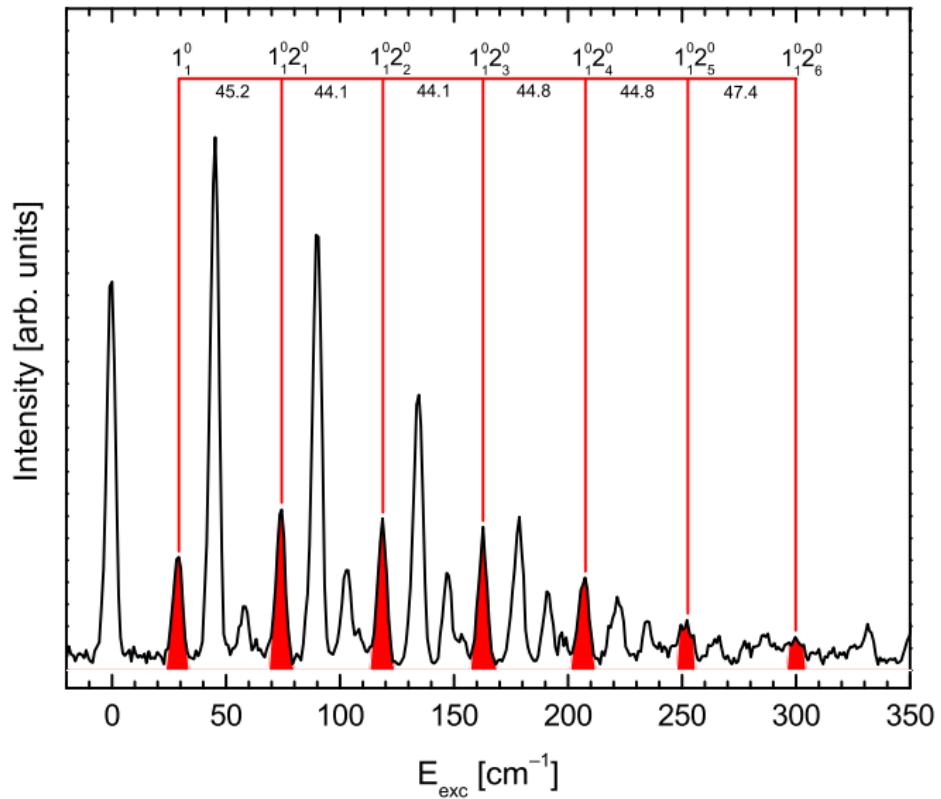
$29\text{ cm}^{-1}$ -Progression



# SVLF Spectrum of the $0^0$ -Level

$2^0_n$ -Progression built off of the  $1^0_1$ -Transition

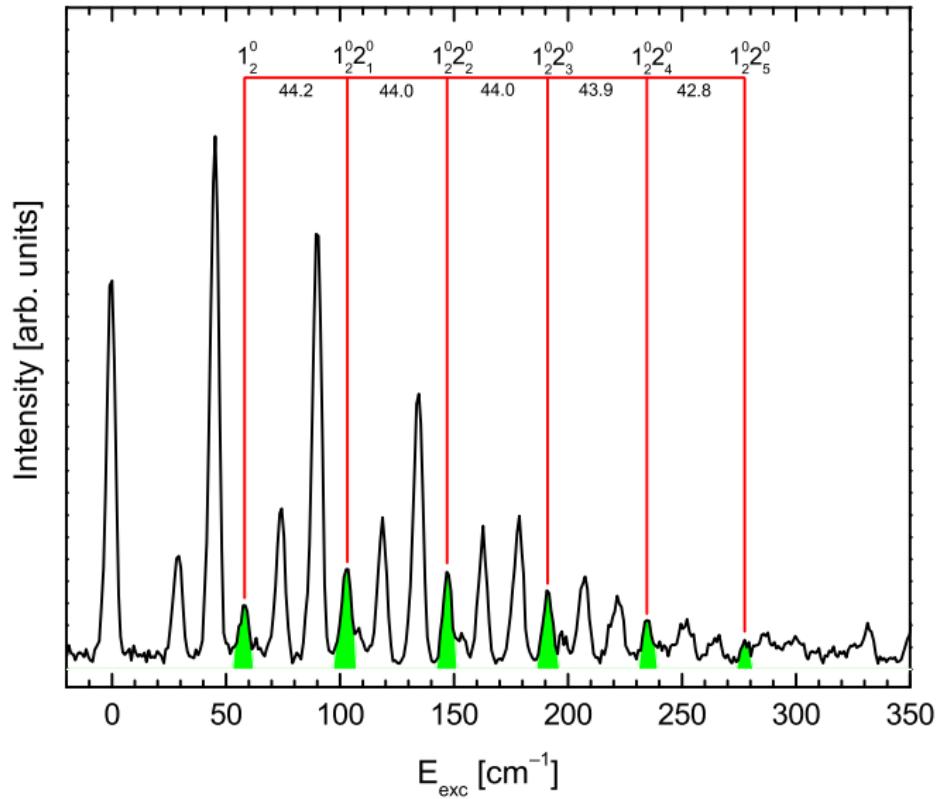
$45\text{ cm}^{-1}$ -Progression



# SVLF Spectrum of the $0^0$ -Level

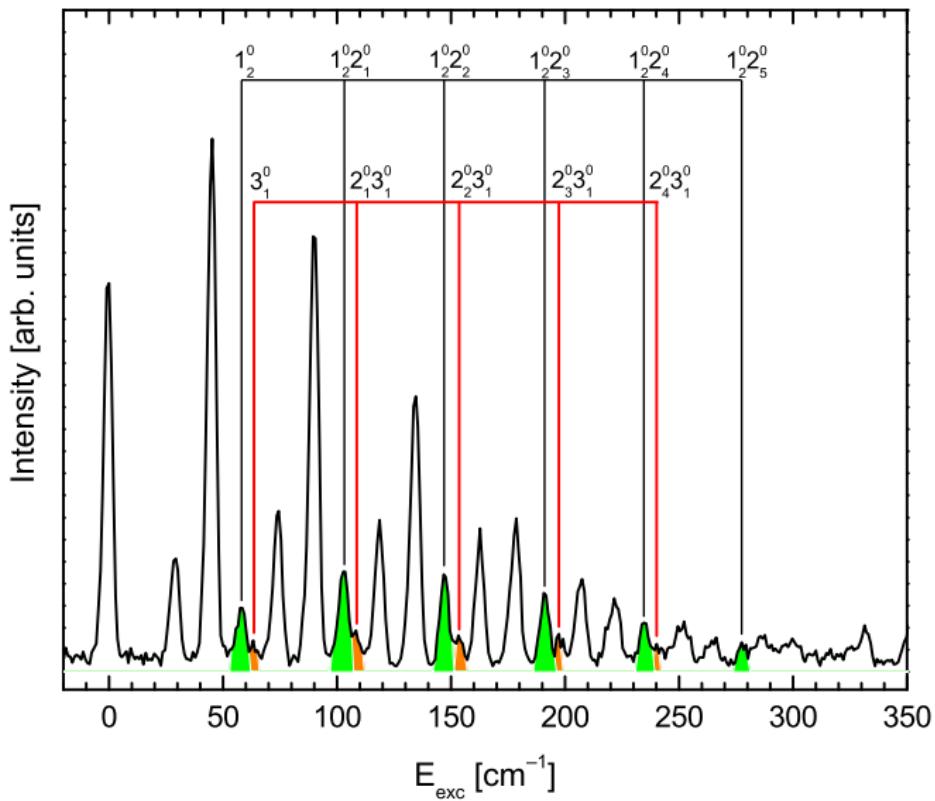
$2^0_n$ -Progression built off of the  $1^0_2$ -Transition

$45\text{ cm}^{-1}$ -Progression

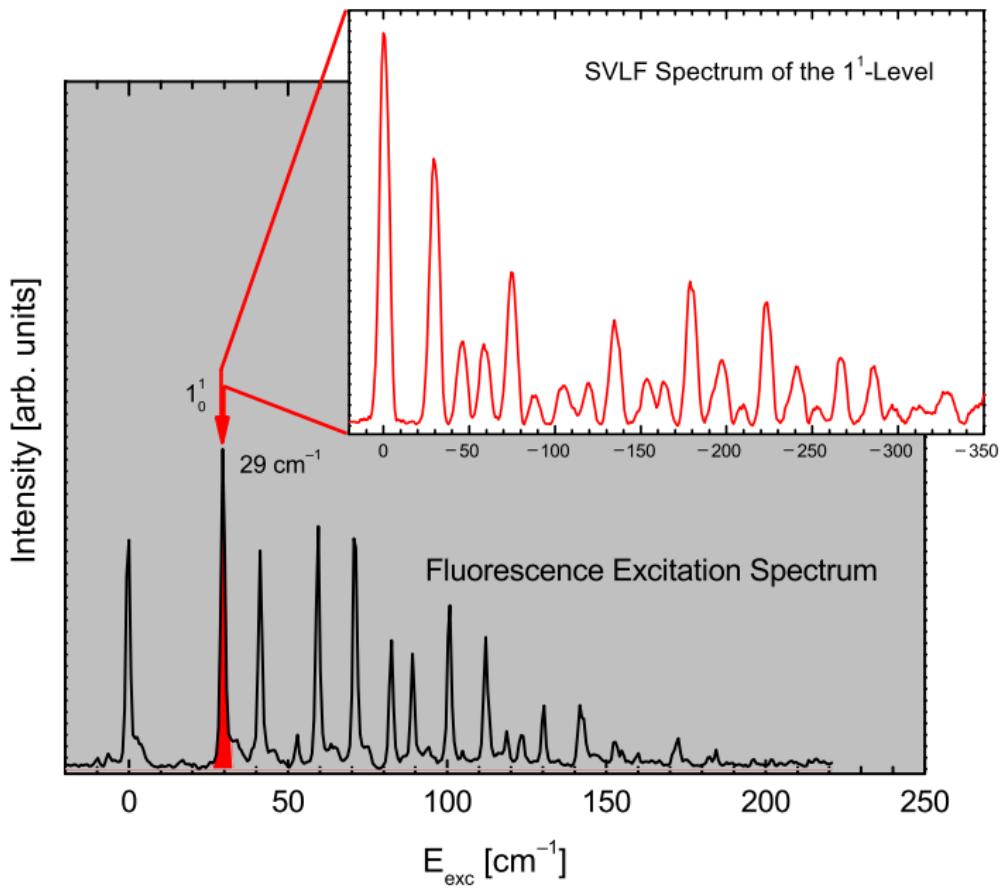


# SVLF Spectrum of the $0^0$ -Level

Expected Perturbations in  $S_0$  due to Fermi Resonances



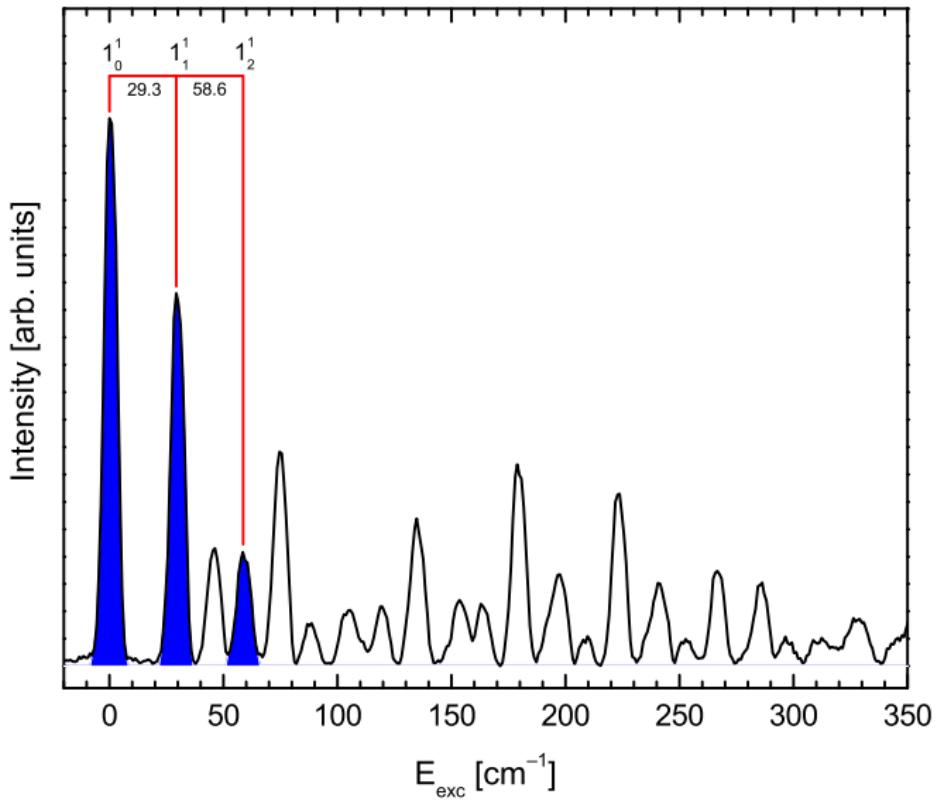
# SVLF Spectrum of the $1^1$ -Level



# SVLF Spectrum of the $1^1$ -Level

$1^1_n$ -Progression

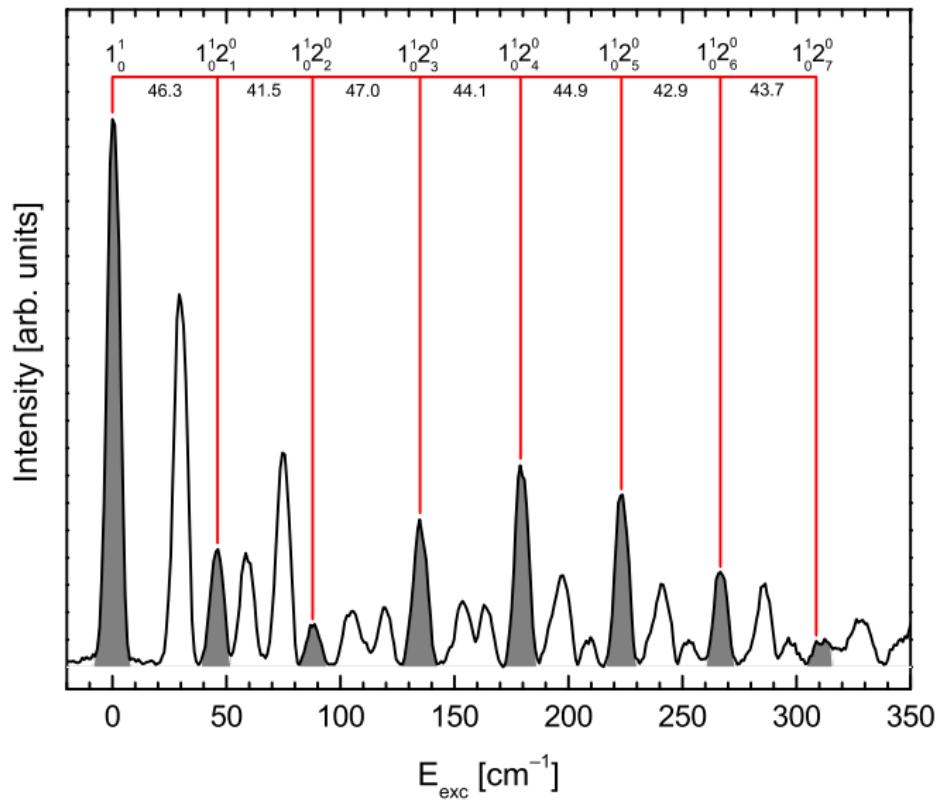
$29\text{ cm}^{-1}$ -Progression



# SVLF Spectrum of the $1^1$ -Level

$2^0_n$ -Progression built off of the  $1^1_0$ -Transition

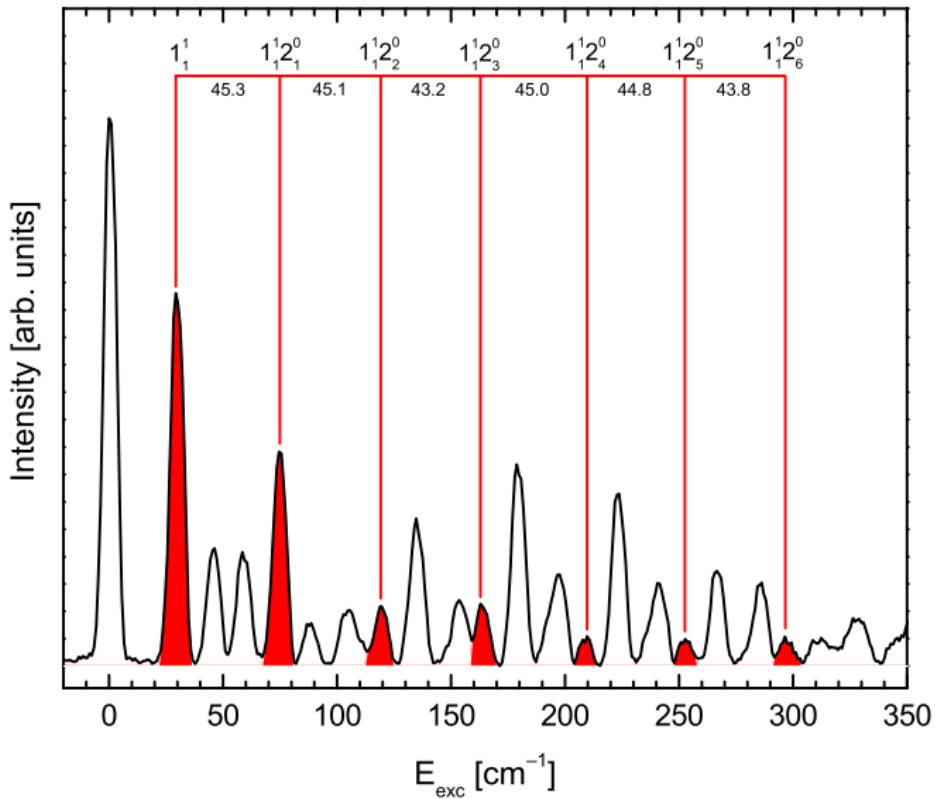
$45\text{ cm}^{-1}$ -Progression



# SVLF Spectrum of the $1^1$ -Level

$2^0_n$ -Progression built off of the  $1^1_1$ -Transition

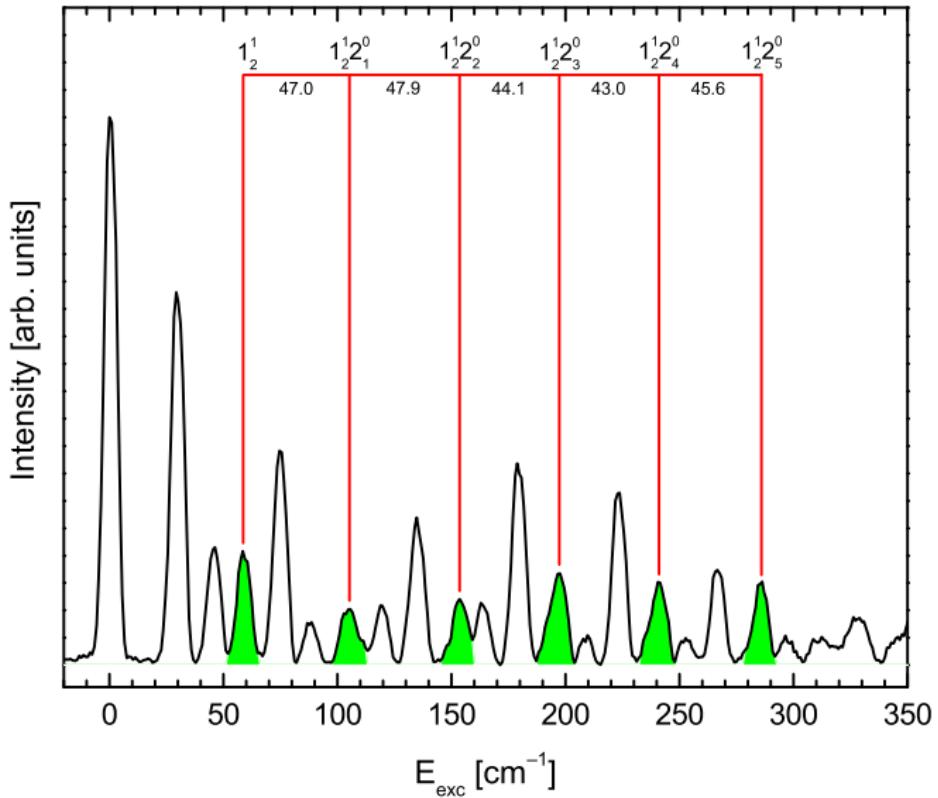
$45\text{ cm}^{-1}$ -Progression



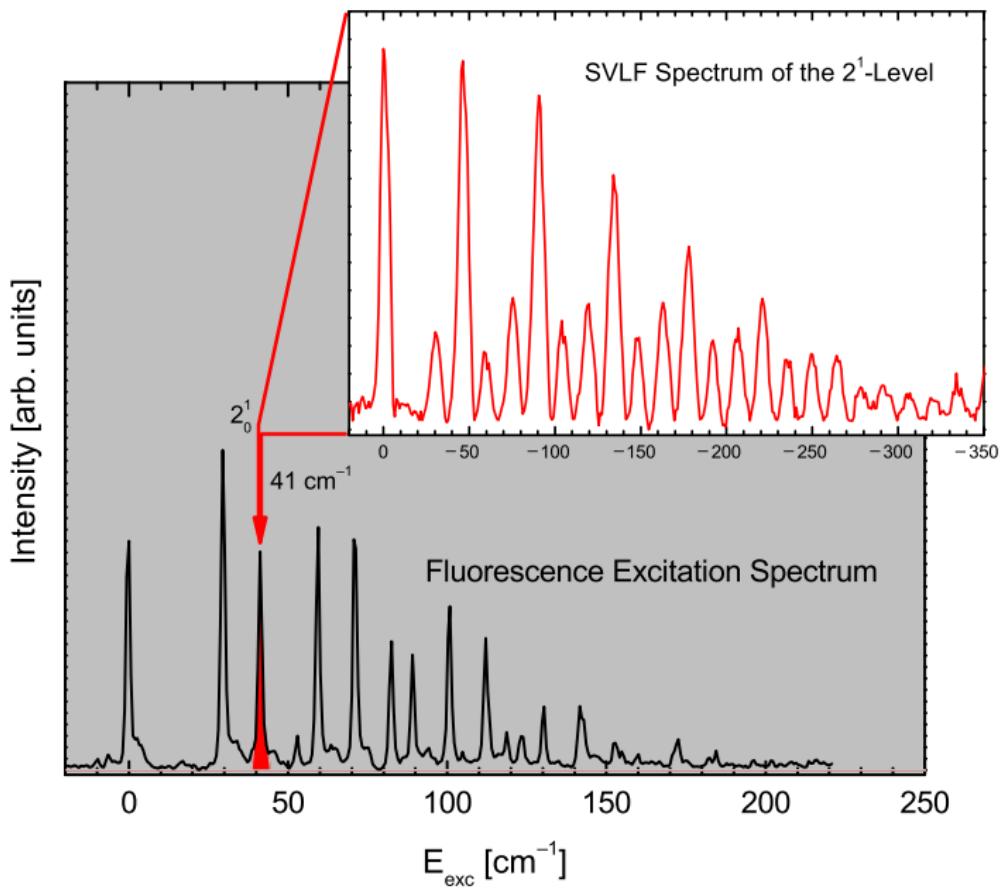
# SVLF Spectrum of the $1^1$ -Level

$2_n^0$ -Progression built off of the  $1_2^1$ -Transition

$45\text{ cm}^{-1}$ -Progression

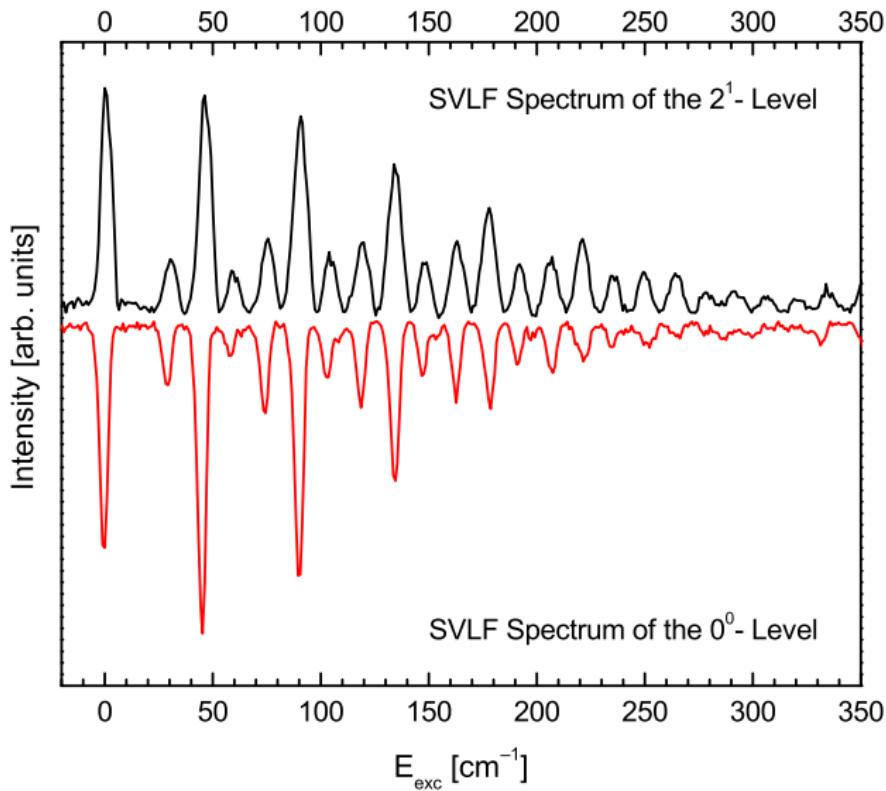


# SVLF Spectrum of the $2^1$ -Level

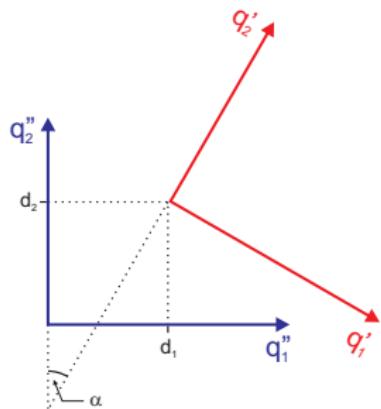


# SVLF Spectrum of the $2^1$ -Level

Puzzling Similarity between the  $2^1$  and  $0^0$  SVLF Spectra



# The Duschinsky Effect



$$\mathbf{q}_i' = \sum_{k=1}^r A_{ik} \mathbf{q}_k'' + \mathbf{d} \quad \text{for the } r \text{ totally symmetric vibrations}$$
$$\mathbf{q}_i'' = \sum_{k=1}^{s_\alpha} A_{ik} \mathbf{q}_k'' \quad \text{for the } s_\alpha \text{ non-totally symmetric vibrations of symmetry species } \alpha$$

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

## Implementation

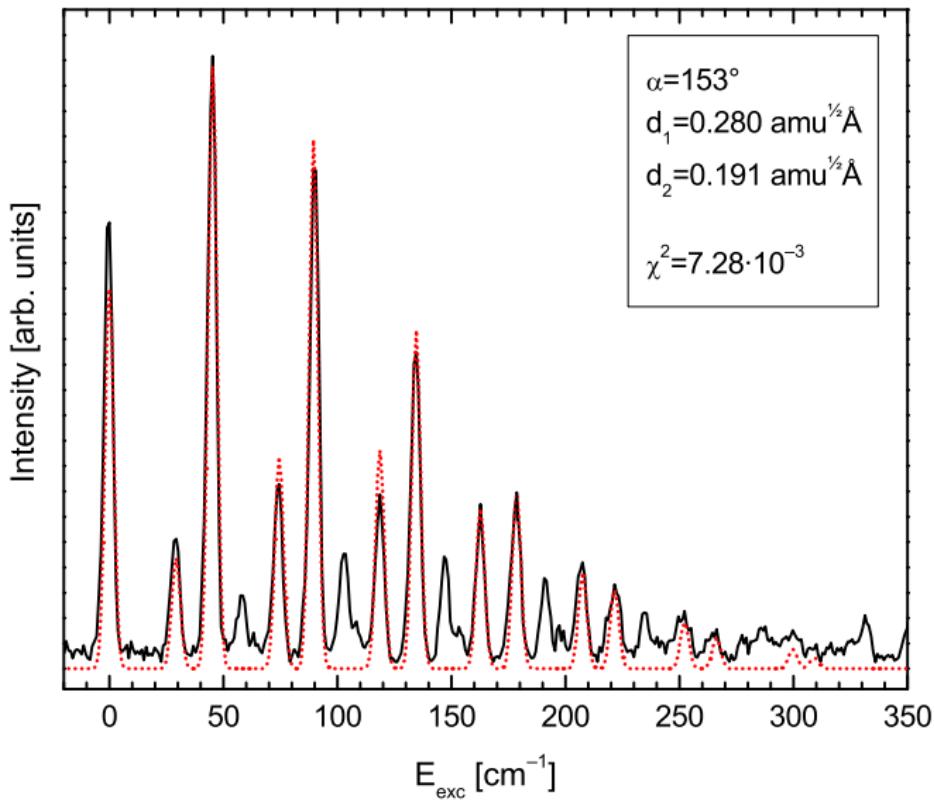
- Calculation of two-dimensional Franck-Condon overlap integrals by using recursion relations involving harmonic oscillator wave functions

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

- Least-squares fitting procedure using the Nelder-Mead search algorithm

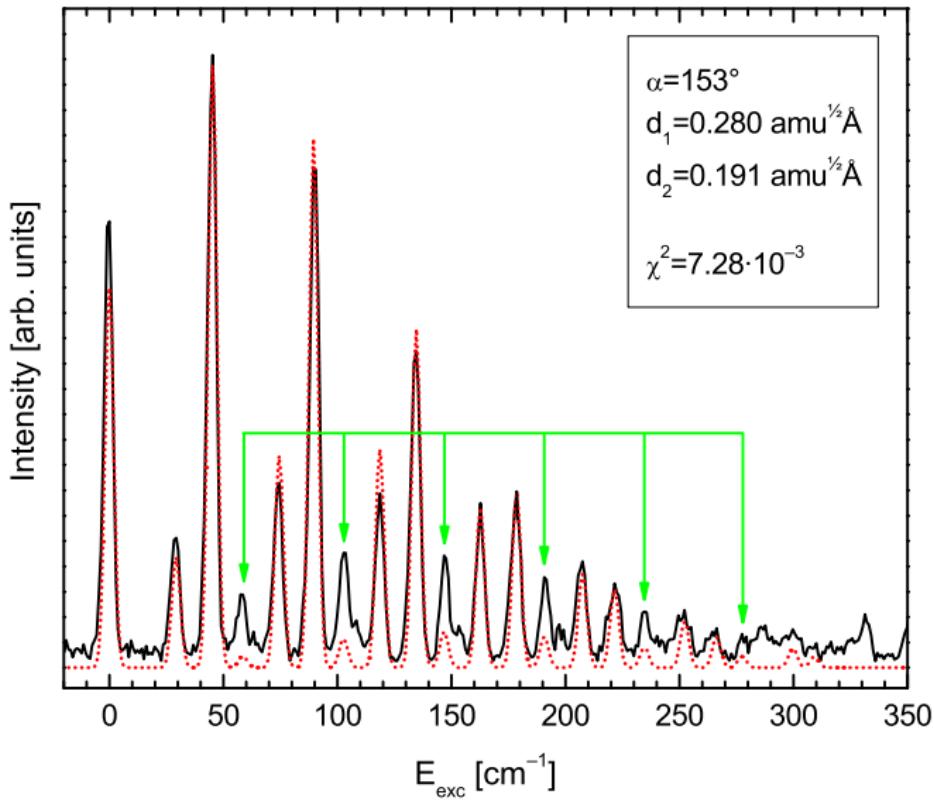
# SVLF Spectrum of the $0^0$ -Level

Best joint fit of the  $0^0$  SVLF Spectrum & the FE Spectrum



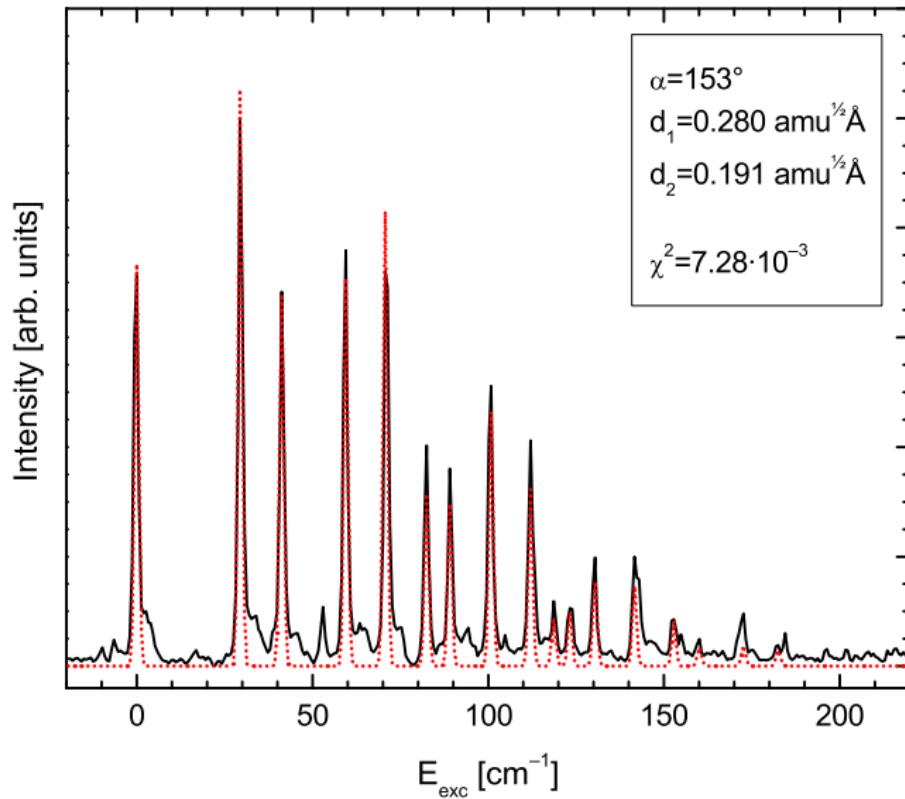
# SVLF Spectrum of the $0^0$ -Level

Including the  $1_2^0 2_n^0$ -Progression: Evidence for Perturbation



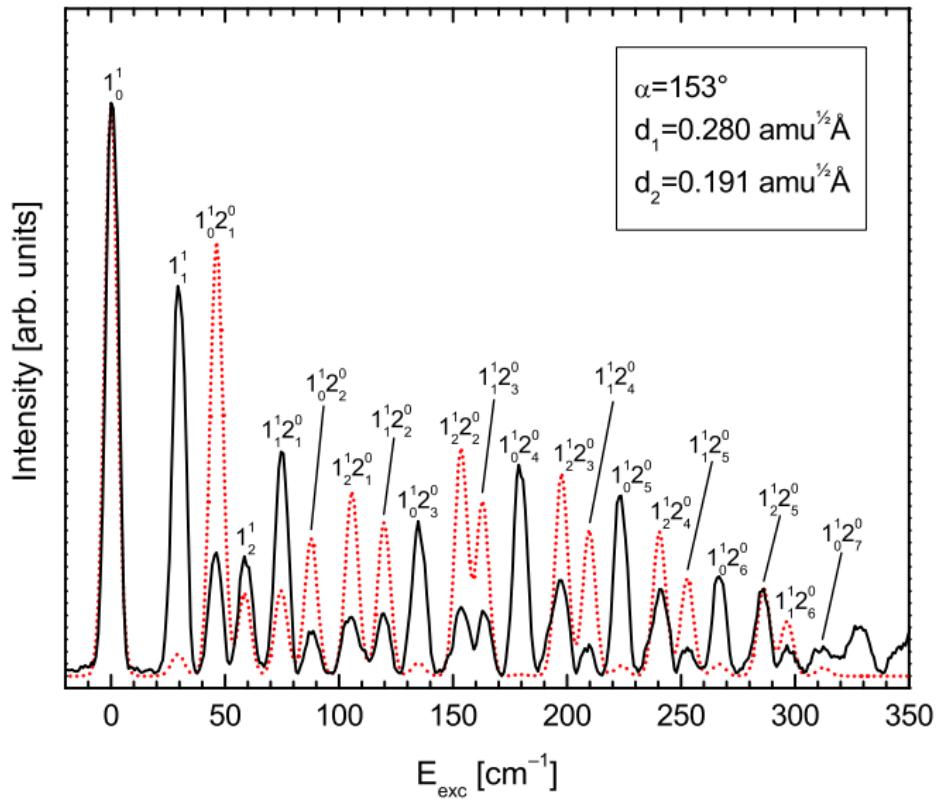
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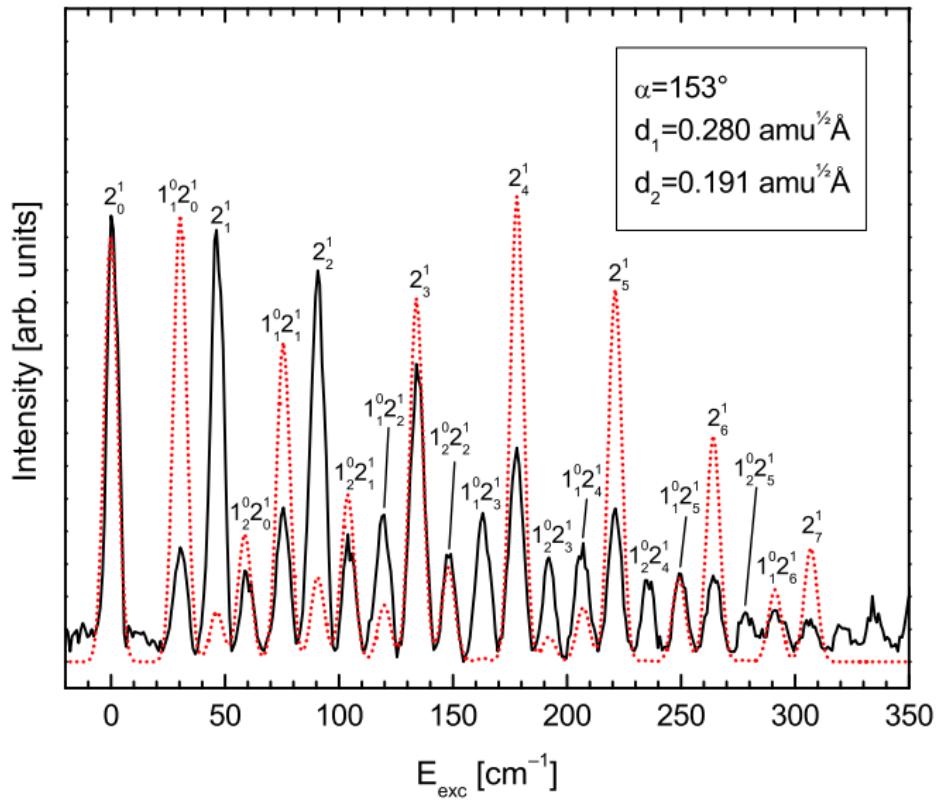
# SVLF Spectrum of the $1^1$ -Level

Using the Best-Fit Parameters to the  $0^0$  SVLF Spectrum & the FE Spectrum



# SVLF Spectrum of the $2^1$ -Level

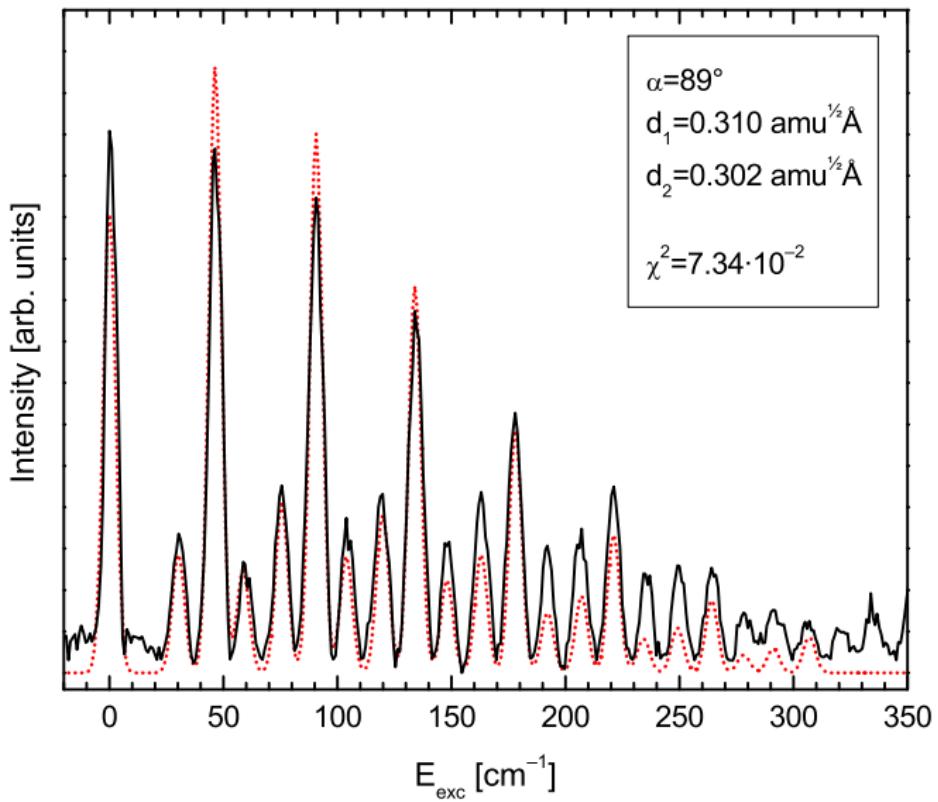
Using the Best-Fit Parameters to the  $0^0$  SVLF Spectrum & the FE Spectrum



# SVLF Spectrum of the $2^1$ -Level

Best fit

+ $41\text{ cm}^{-1}$ -Band



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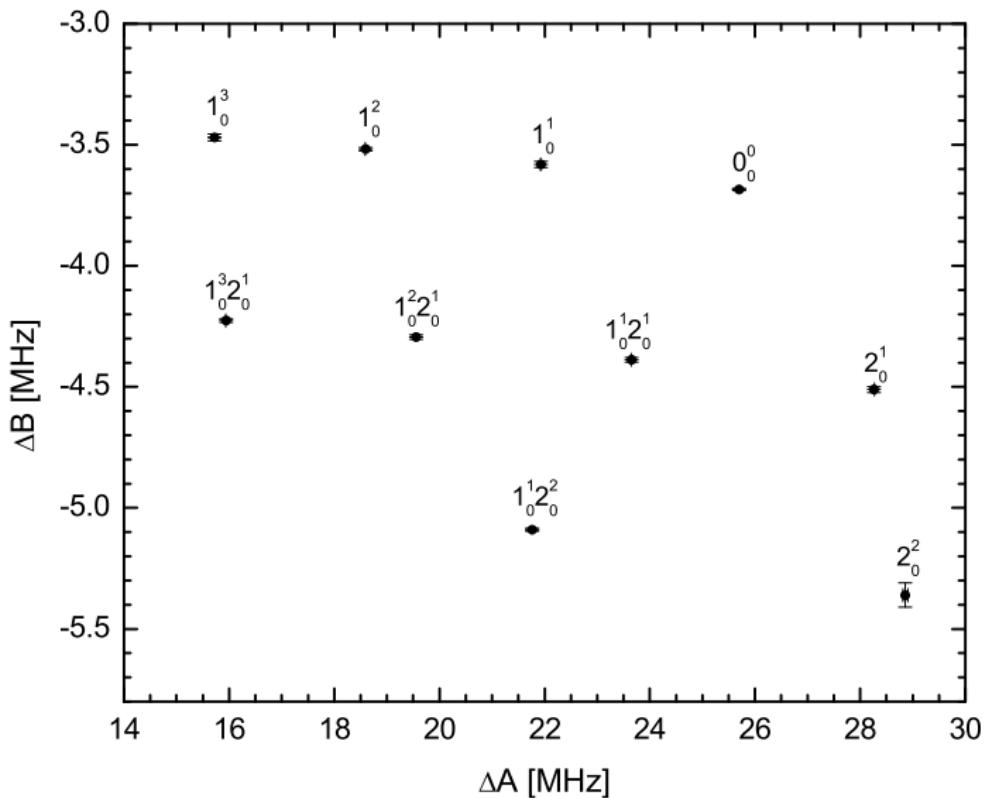
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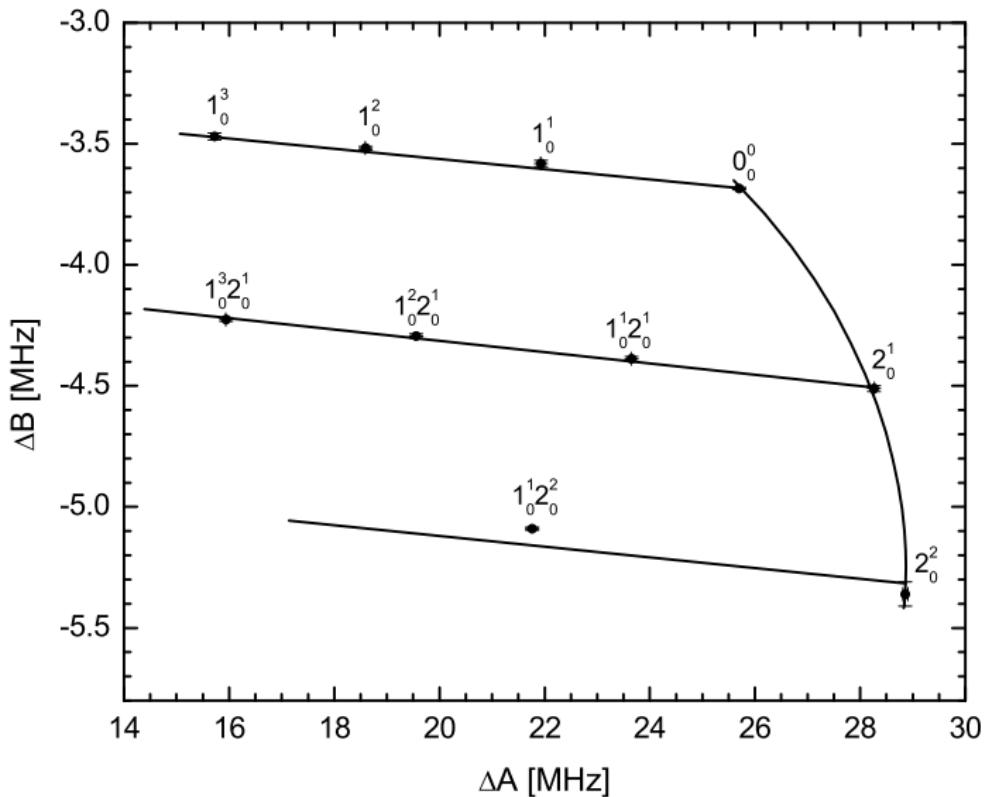
# Rotationally Resolved FE Spectra

Changes of the Rotational Constants:  $\Delta B$  vs.  $\Delta A$  for different vibronic bands



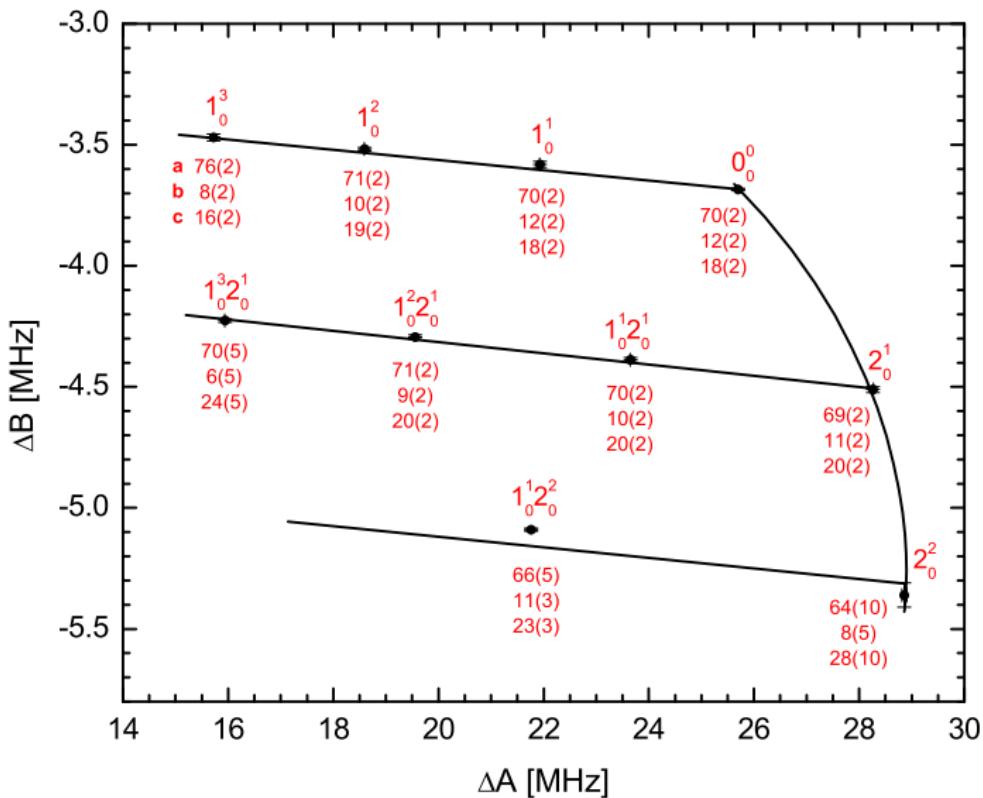
# Rotationally Resolved FE Spectra

Linear vs. Curved Dependence of the Changes of the Rotational Constants



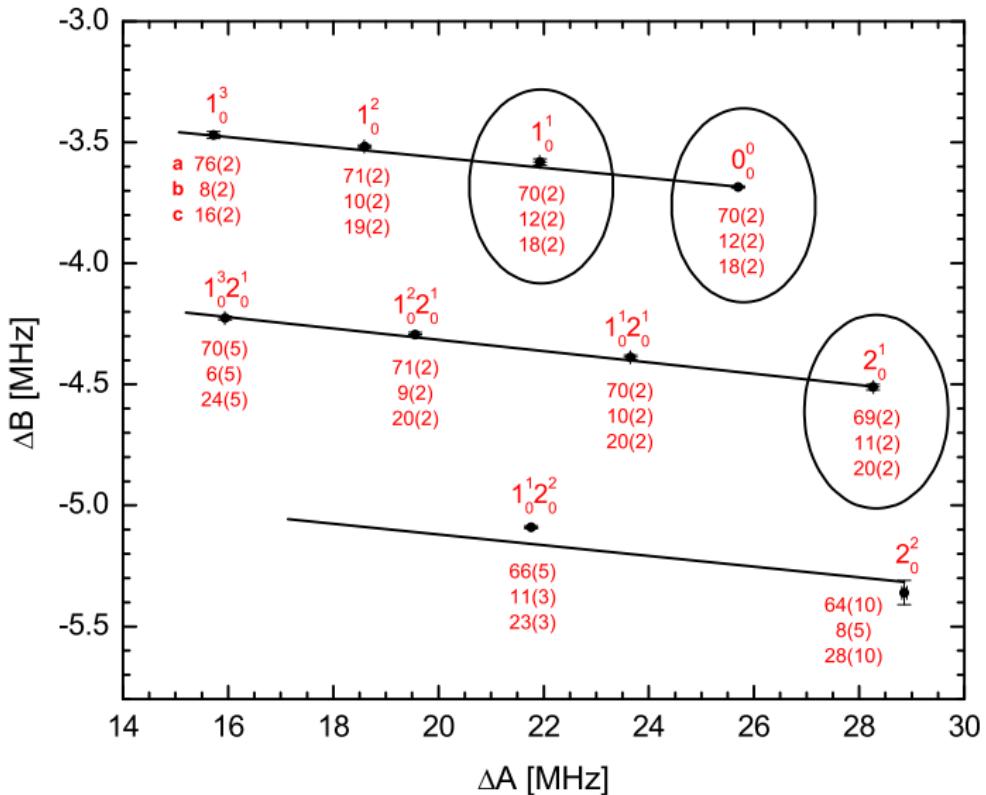
# Rotationally Resolved FE Spectra

## Directions of the Transition Dipole Moments



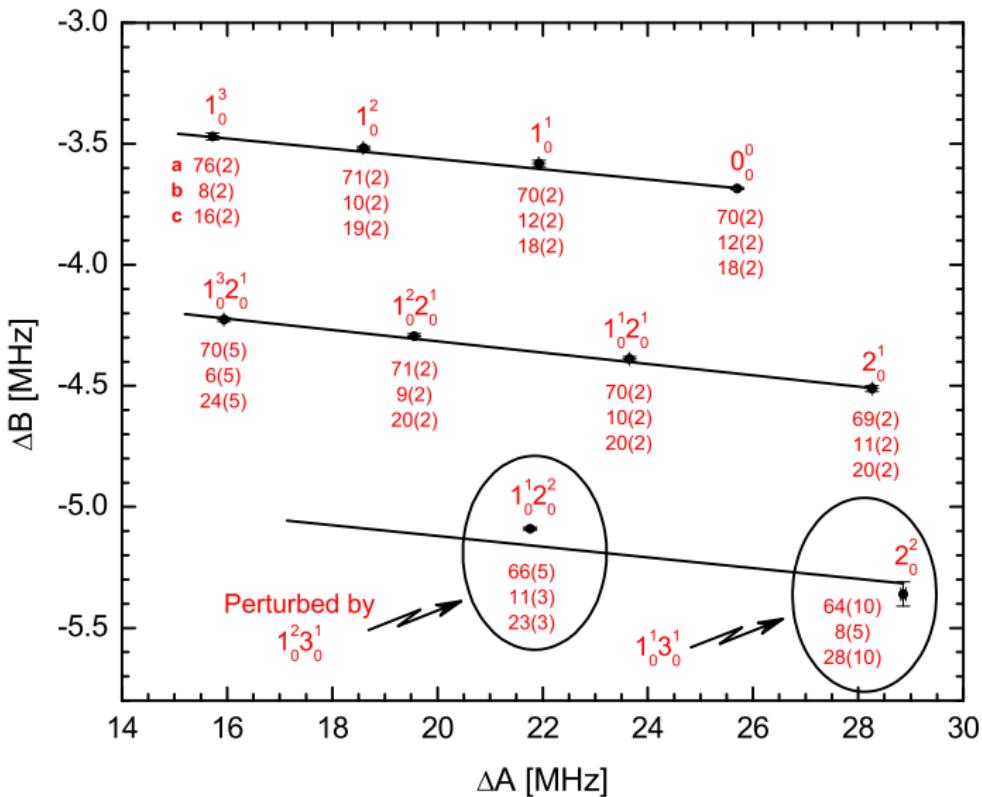
# Rotationally Resolved FE Spectra

The Electronic Origin & the Fundamentals  $1_0^1$  and  $2_0^1$



# Rotationally Resolved FE Spectra

## Perturbations caused by Fermi Resonance



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## Conclusion: Duschinsky Analysis

- Mirror symmetry breakdown between FE spectrum and  $0^0$  SVLF spectrum can be accounted for by **Duschinsky mixing**.
- **Fermi resonance** between  $1_2^0$  and  $3_1^0$  in  $S_0$  and/or **vibronic coupling** to higher electronic states could cause a perturbation of the  $1_2^0 2_n^0$ -progression in the  $0^0$  SVLF spectrum.

G. J. Small, *J. Chem. Phys.*, 1971, 54, 3300.

- Intensity pattern of  $2^1$  SVLF spectrum ( $41\text{ cm}^{-1}$  band) can be accounted for by a *different* set of parameters (state-specific Duschinsky mixing due to vibronic coupling?).
- Intensity pattern of  $1^1$  SVLF spectrum ( $29\text{ cm}^{-1}$  band) *cannot* be accounted for by a single set of parameters.

## Conclusion: Rotationally Resolved FE Spectra

- The band at  $41\text{ cm}^{-1}$  is *not* the electronic origin of a second excited state conformer, but  $2_0^1$ .
- The  $0_0^0$  transition dipole moment direction indicates that the electronic excitation can be conceived of as being localized on the phenol moiety.
- **Fermi resonance** between  $1_0^1 3_0^1$  and  $2_0^2$  in  $S_1$  which causes a perturbation of rovibronic eigenenergies in the rotationally resolved FE spectra.

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