g) characteristics of the $S_0 \rightarrow S_1$ absorption and $S_1 \rightarrow S_0$ emission
geometry relaxation in $S_1$ of PPV5

in very long oligomers: $S_1$ geometry relaxation over ~ 25 Å
absorption

the most intense transition is the vertical one

electronic excited state $S_1$

electronic ground state $S_0$
because of the difference in equilibrium geometry between the ground state and excited state, the emission and absorption curves are displaced with respect to one another!

emission takes place from the lowest vibrational state of the electronic excited state
absorption and emission in oligophenylene vinylenes

- analysis of the vibronic progression using the displaced harmonic oscillator model

\[ \mu_{\text{tot}} (S_i \rightarrow S_j; \nu_m \rightarrow \nu_n) = \mu_{\text{elect.}} (S_i \rightarrow S_j) \times F_{mn} \]
experimental absorption and emission spectra of oligophenylene vinylenes

77K in inert PMMA matrix (Los Alamos)
simulation of absorption

theory

experiment (D.D.C. Bradley)

$S_1$ relaxation energy decreases as chain grows
Simulation of emission

$S_1$ relaxation energy:
from $\sim 0.27$ eV in stilbene to $\sim 0.15$ eV in long chains
h) the metal-on-polymer interface

in UHV ($\sim 10^{-10} - 10^{-11}$ Torr)
principle of photoemission spectroscopy
the aluminum/polyacetylene interface
diphenylpolyenes (DPn):
analysis of the C(1s) shake-ups

“looking at \( \pi \rightarrow \pi^* \) transitions with XPS”

in DP7:
separate contributions from:

- the polyene chain
- the phenyl rings
AI /DP7 interface

- The polyene electronic structure is strongly modified.
- The phenyl rings remain unaffected.
aluminum / polyene interface

- Al-C covalent bond formation
- sp³-carbons; reduced conjugation
sodium on diphenylpolyenes

$DP_{1\rightarrow 7}$
pristine $DP_x$
the shake-up due to the polyene part remains strong upon Na metallization in contrast to the Al case
the XPS core-level data indicate:

* \( \text{Na}^{+} \)
* two sodiums per \( \text{DP}_x \)
sodium – doped DP\textsubscript{x}
electronic-structure evolution due to chemistry at the interface
low workfunction metal atoms on surfaces of conjugated polymers:

in context of polymer-based LED’s

- **Al**: forms covalent bonds electrode
- **Na**: acts as dopant Na⁺
- **Ca**: acts as dopant for clean PPV Ca⁺⁺
  but as electrode material on oxidized PPV surfaces

there is always an interfacial region between the metal and the polymer

→ needs to be incorporated in the physics of these devices