



PROJECT OUTLINE

Our research interest

- during photosynthesis chlorophyll adopts different functions (absorption, energy transfer, charge separation)
- studying non-radiative relaxation for deeper understanding of photosynthesis

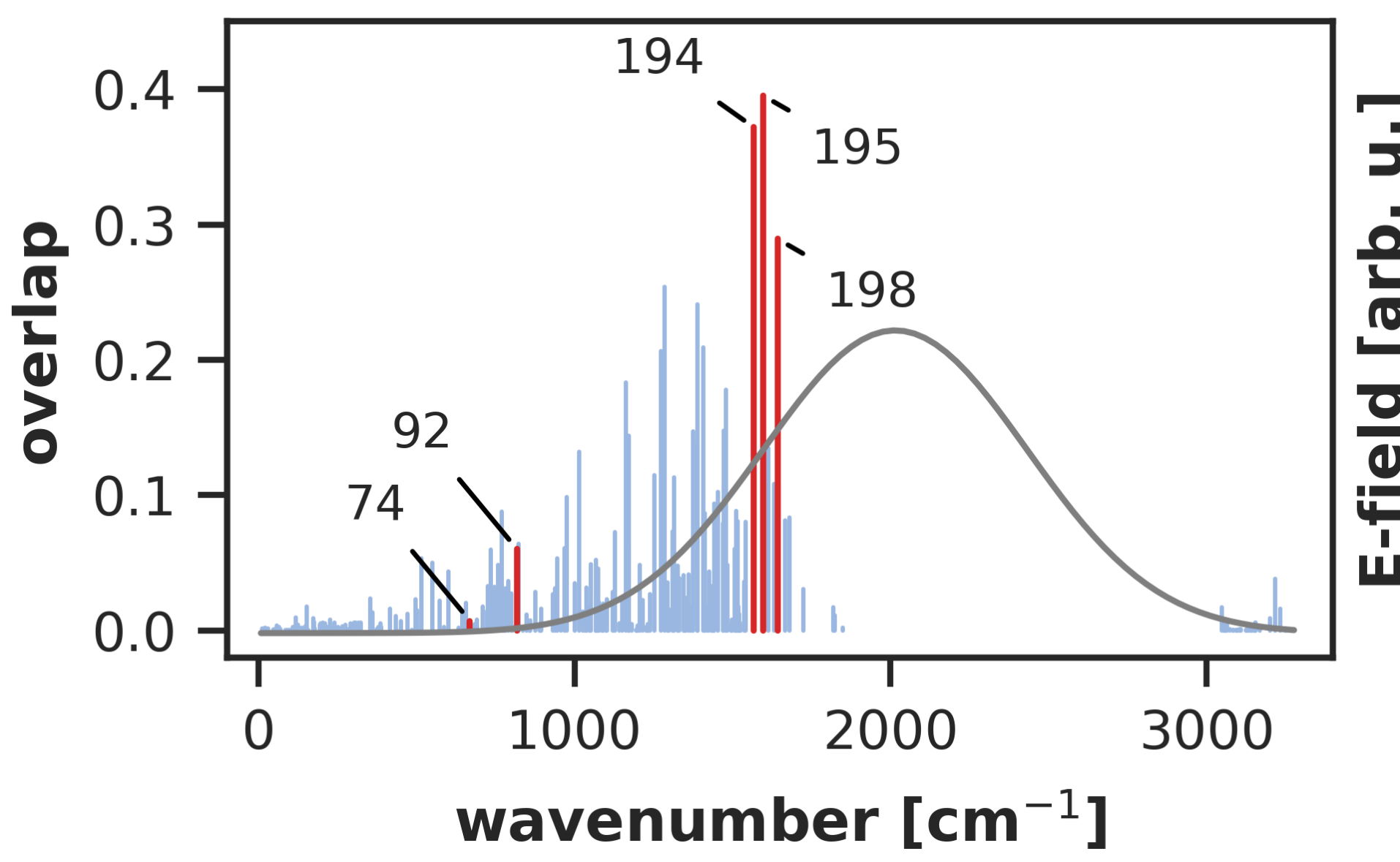
The challenge

- discussion about assignment of Q_x in literature
- CASPT2 energy difference $|Q_y - Q_x|$ depending on IPEA and imaginary shift
- benchmark of different applied shifts
- high dimensional system challenging for wavepacket dynamics

What we present

- procedure to determine relevance of coordinates
- wavepacket dynamics of laser-excited chlorophyll
- coupled nuclear and electron dynamics

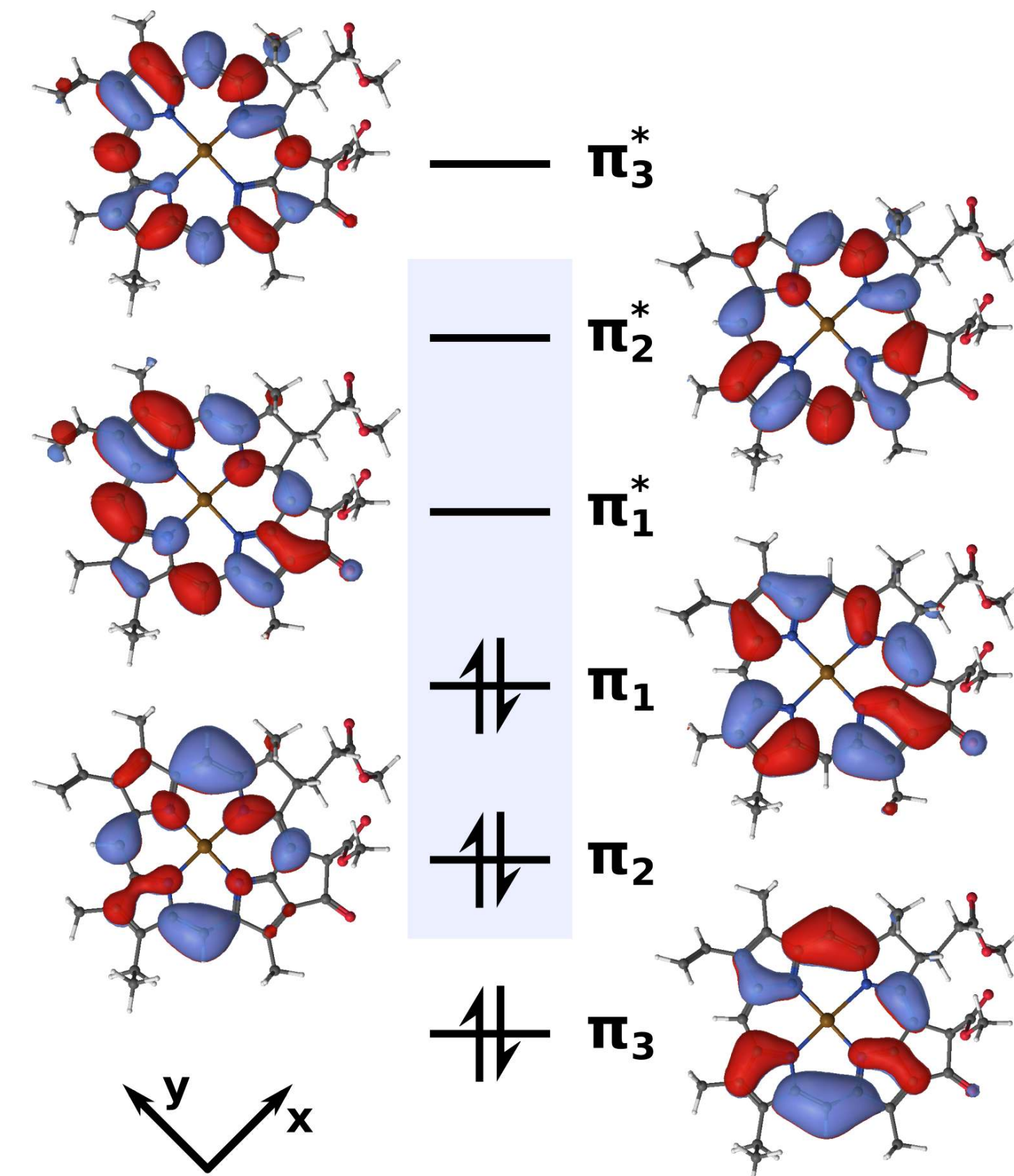
COORDINATE SELECTION



- overlap of normal modes with coupling vector at FC point
- multiple modes involved in coupling

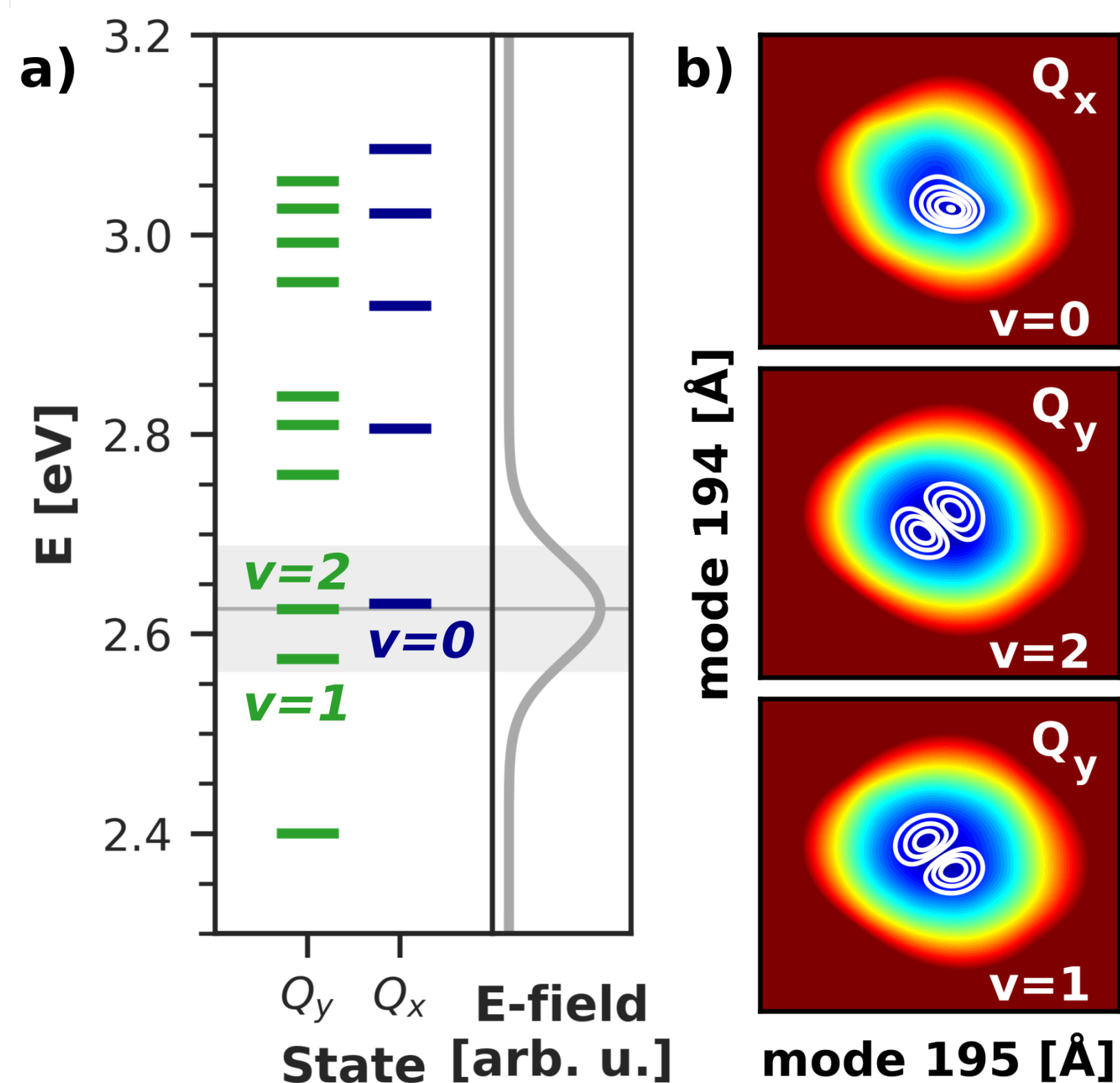
- 2D-space spanned by modes of highest overlap
- for comparison: using modes of descending overlap
- determine relevance of weakly coupled modes

ACTIVE SPACE



- CASSCF(6/6) consisting of Gouterman orbitals (highlighted in blue) and additional π and π^* orbital

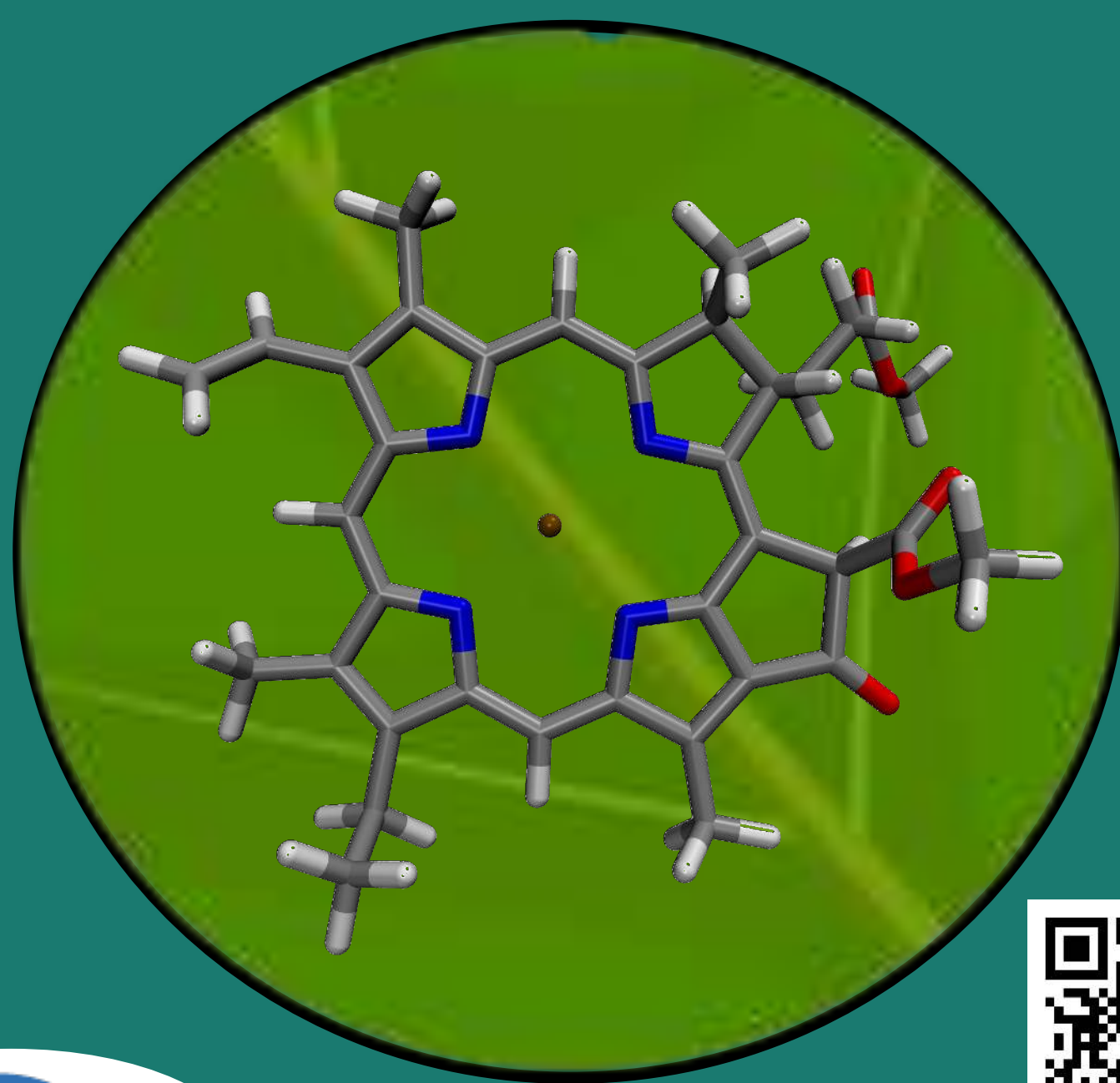
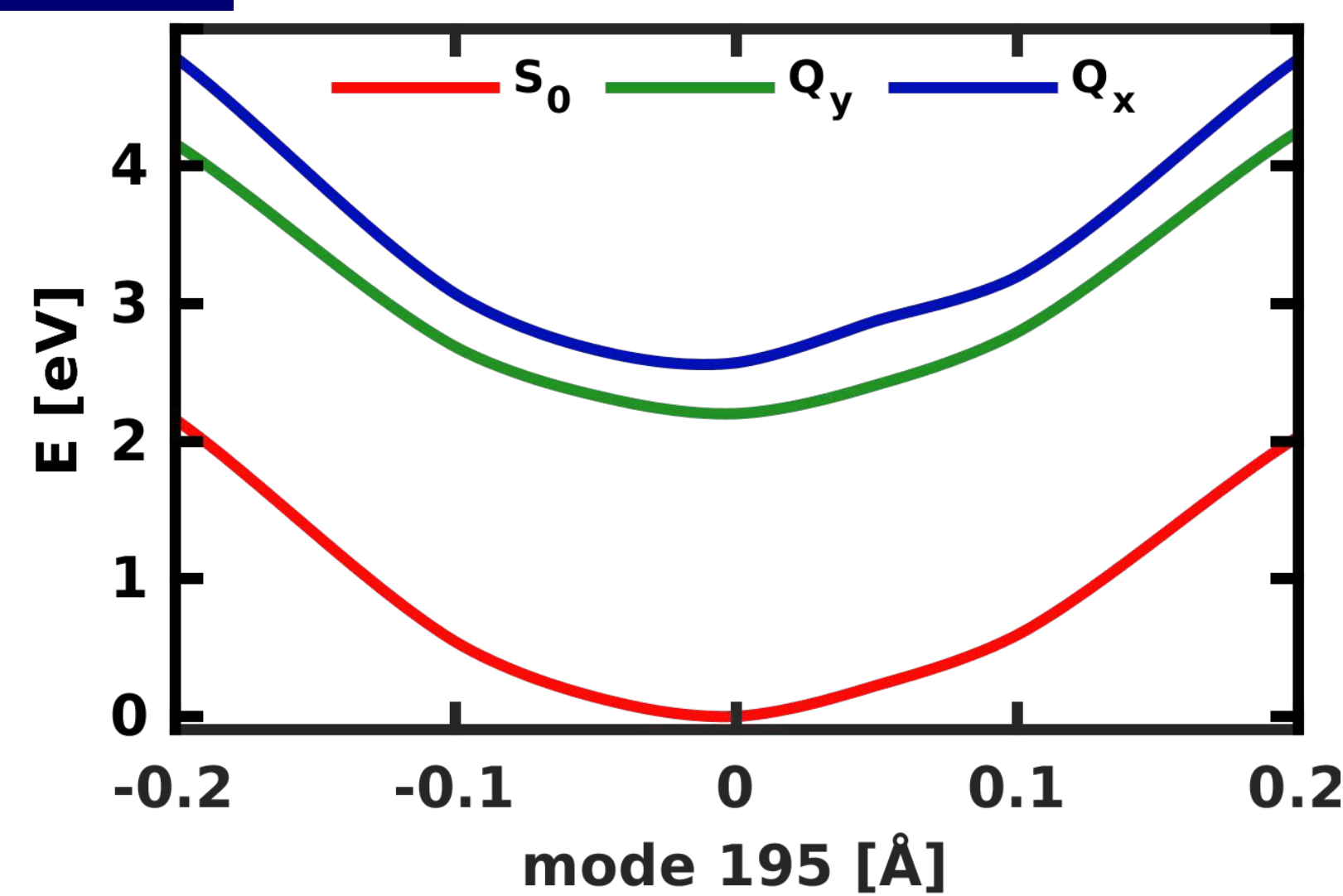
Q_x/Q_y COUPLING



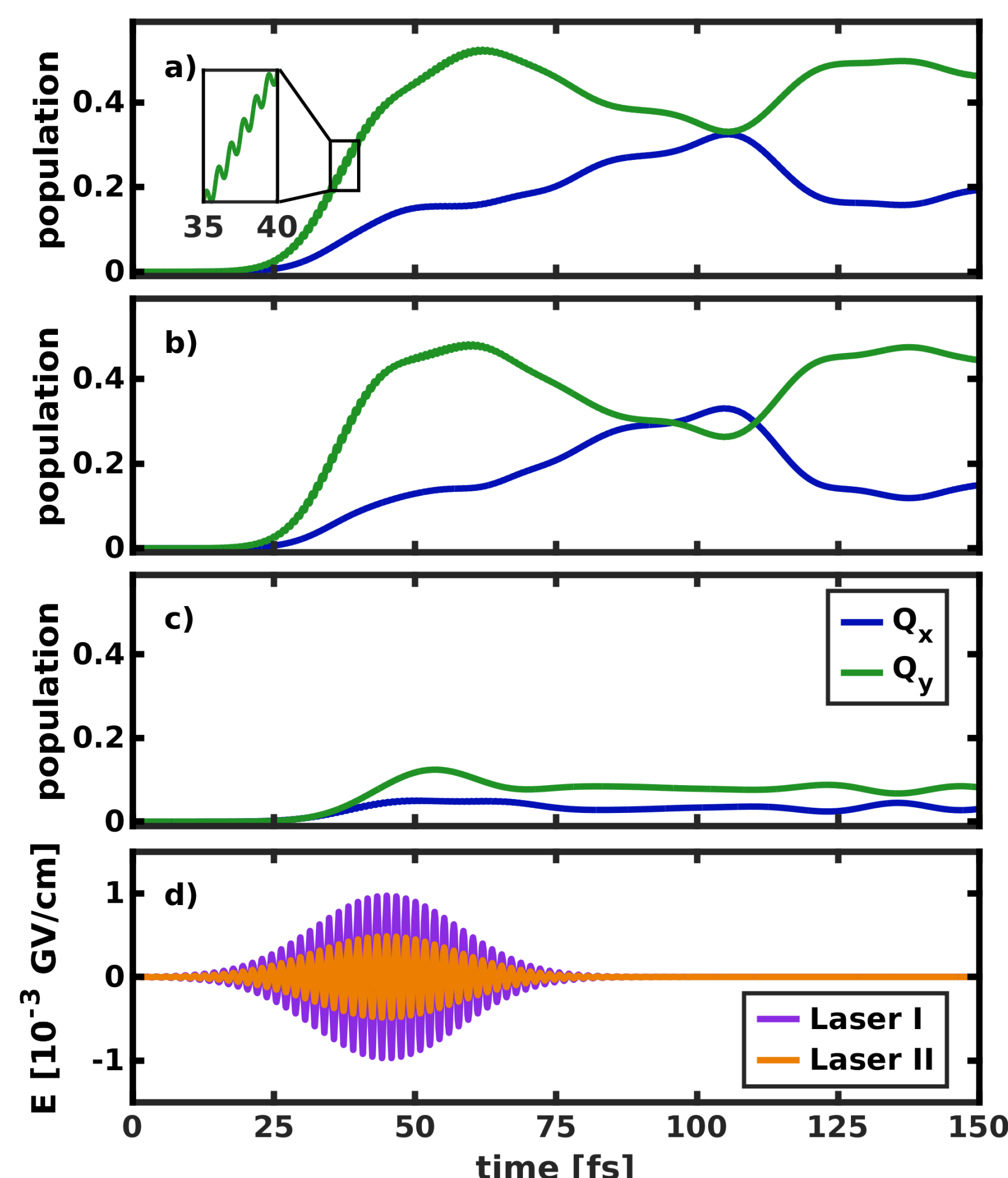
Vibrational energy levels (a) show almost degeneracy between some vibrational eigenfunctions (b) of Q_x and Q_y gray: optimized excitation laser pulse

- strong coupling between Q_x and Q_y
- ultrafast population transfer

1D-PES

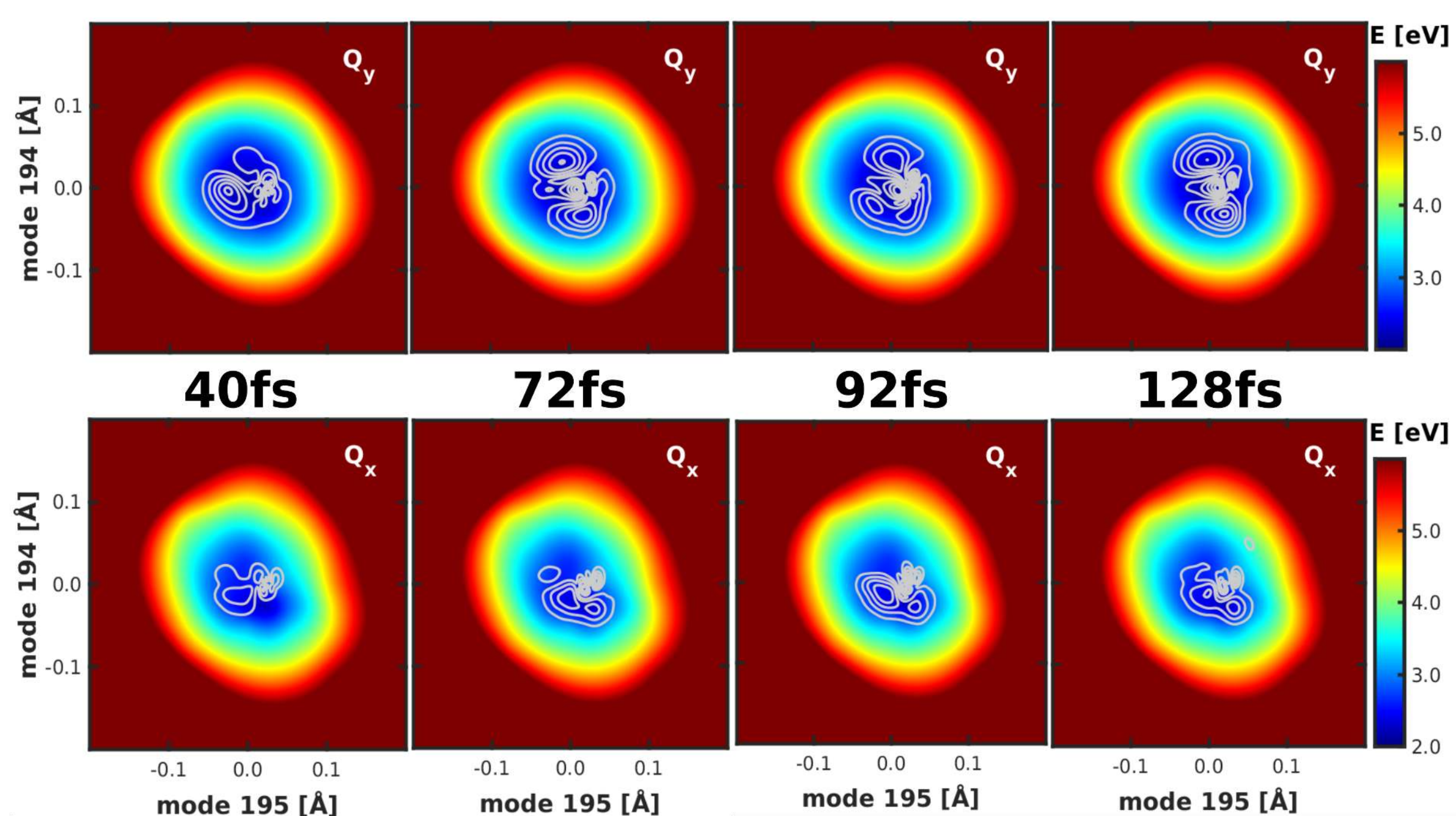


QUANTUM DYNAMICS



- a) excitation into both Q_x and Q_y
- b) excitation only into Q_y
- c) excitation only into Q_x
- immediate population transfer between Q_x and Q_y visible

NUCLEAR WAVEPACKET DYNAMICS



- propagation with excitation pulse into Q_x and Q_y
- 40fs, 92fs: wavepacket resembles $v=2$ eigenfunction of Q_y and $v=0$ of Q_x
- 72fs: wavepacket rotates to resemble $v=1$ of Q_y
- rotation stops around 130fs

COUPLED NEMOL DYNAMICS

NEMol

simulation without explicit excitation pulse
NEMol: determination, visualization of coupled nuclear and electron dynamics
induced dipole moment: experimental observable for electronic coherence

