RAMAN SPECTROSCOPY OF LASER-MATTER INTERACTIONS

Miklós Veres

veres.miklos@wigner.hu

Wigner Research Centre for Physics

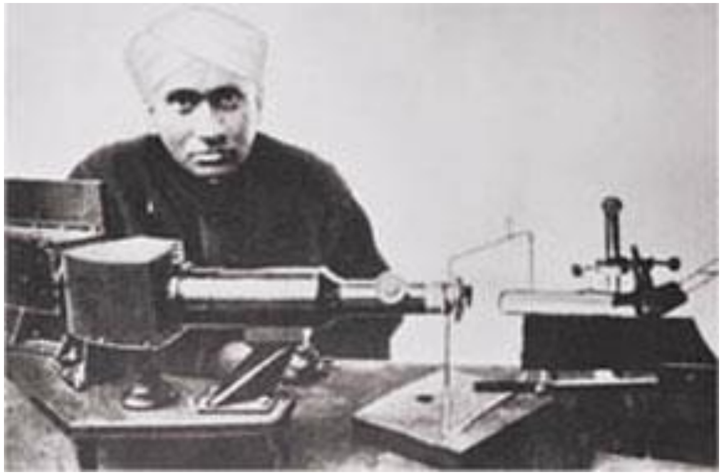
Budapest, Hungary

NAPLIFE

Nanoplasmonic Laser Fusion

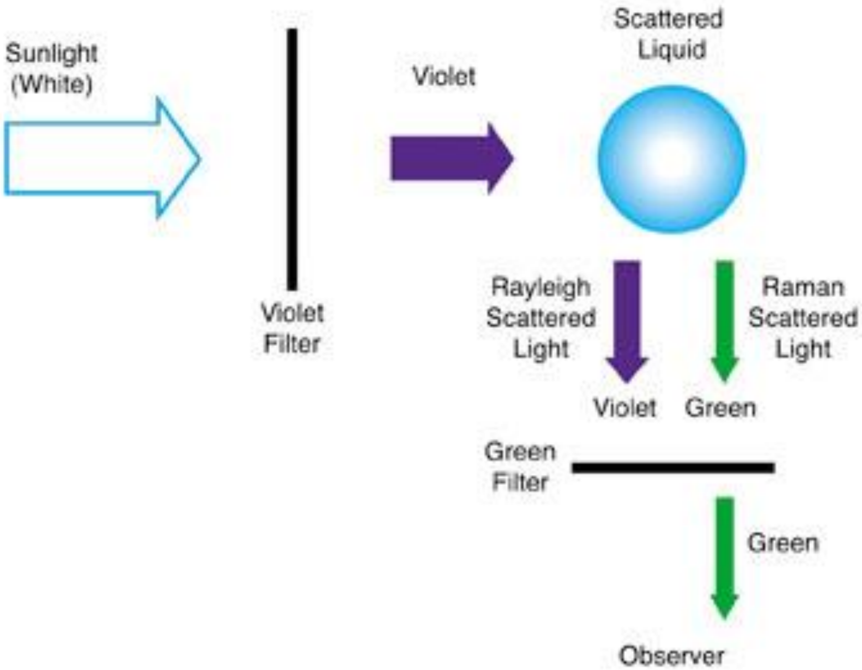
Raman scattering

C. V. Raman in 1928
Nobel Prize, 1930



Investigation of light scattering by water droplets with focused sunlight and filters

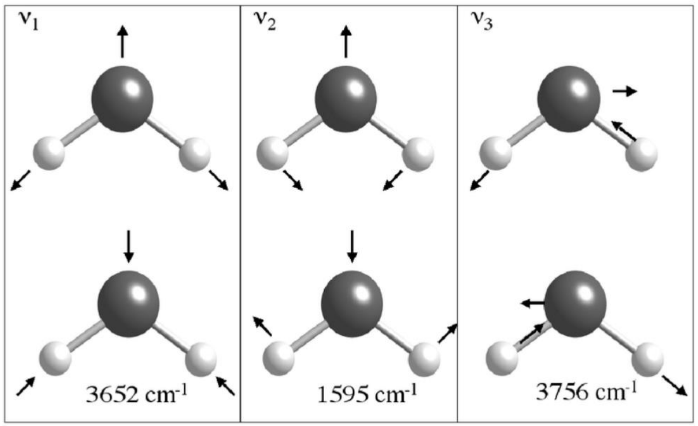
Appearance of a different (green) color in the scattered (violet) light, which had 10^{-7} times lower intensity



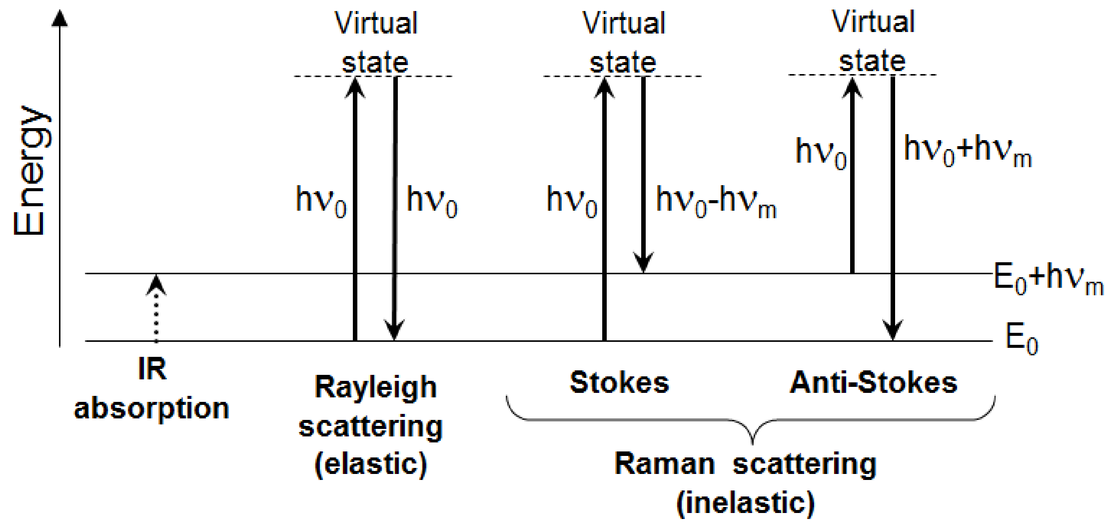
G. Landsberg, L. Mandelstam
Combinatorial scattering in crystals

Raman scattering

Inelastic light scattering due to the interaction of the incident light with matter.



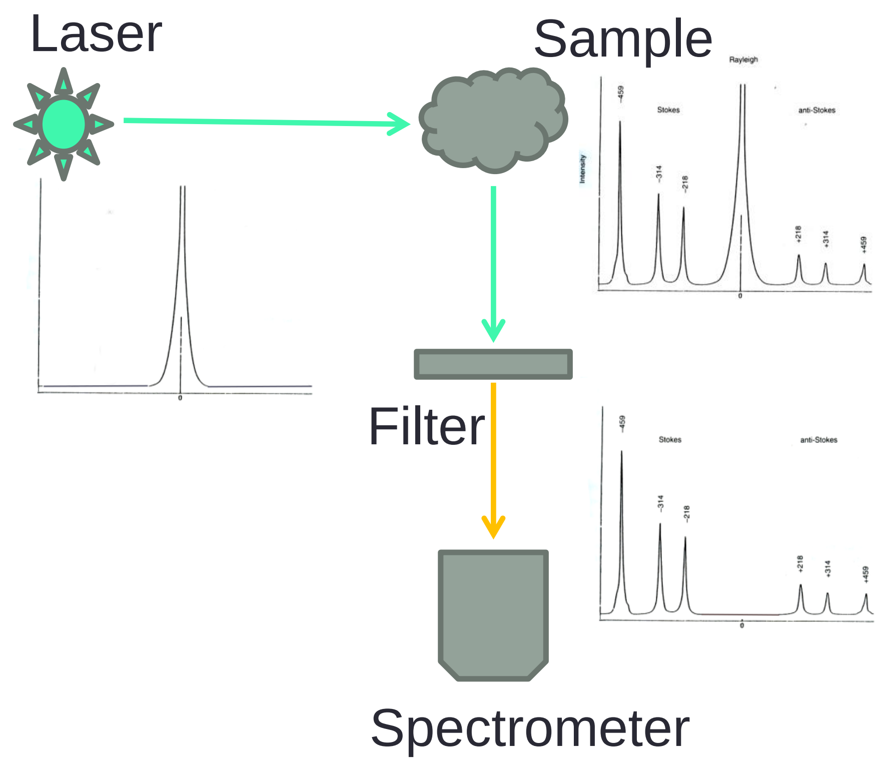
Vibrations of a water molecule



The energy difference of the excitation and Raman scattered light equals to the energy of a normal vibration of the medium (molecule, crystal).

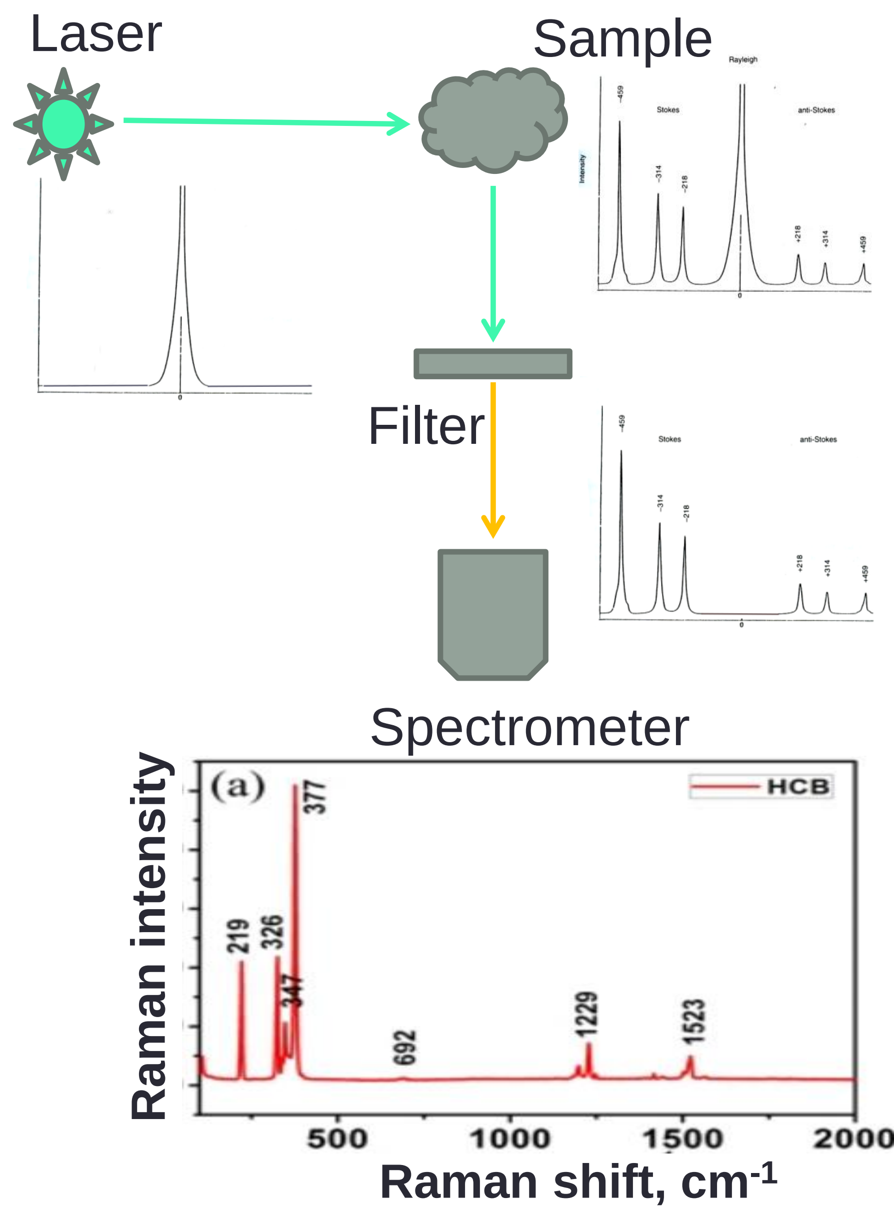
Raman spectroscopy

- Inelastic light scattering
- Excitation with a monochromatic light source (laser)
- Recording the spectrum of the scattered light in wavelength region different from the excitation



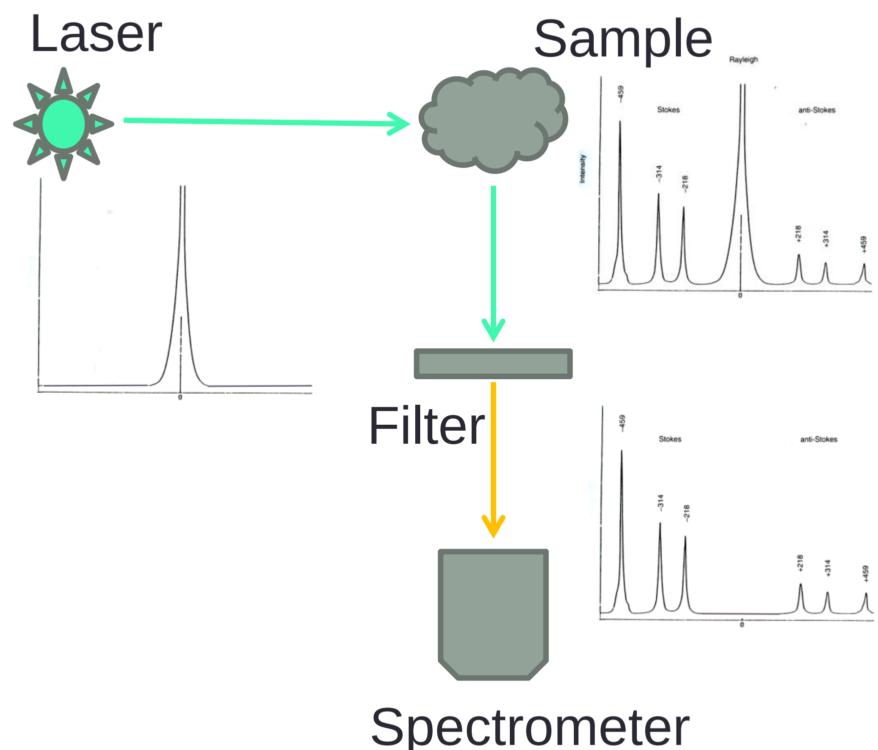
Raman spectroscopy

- Inelastic light scattering
- Excitation with a monochromatic light source (laser)
- Recording the spectrum of the scattered light in wavelength region different from the excitation

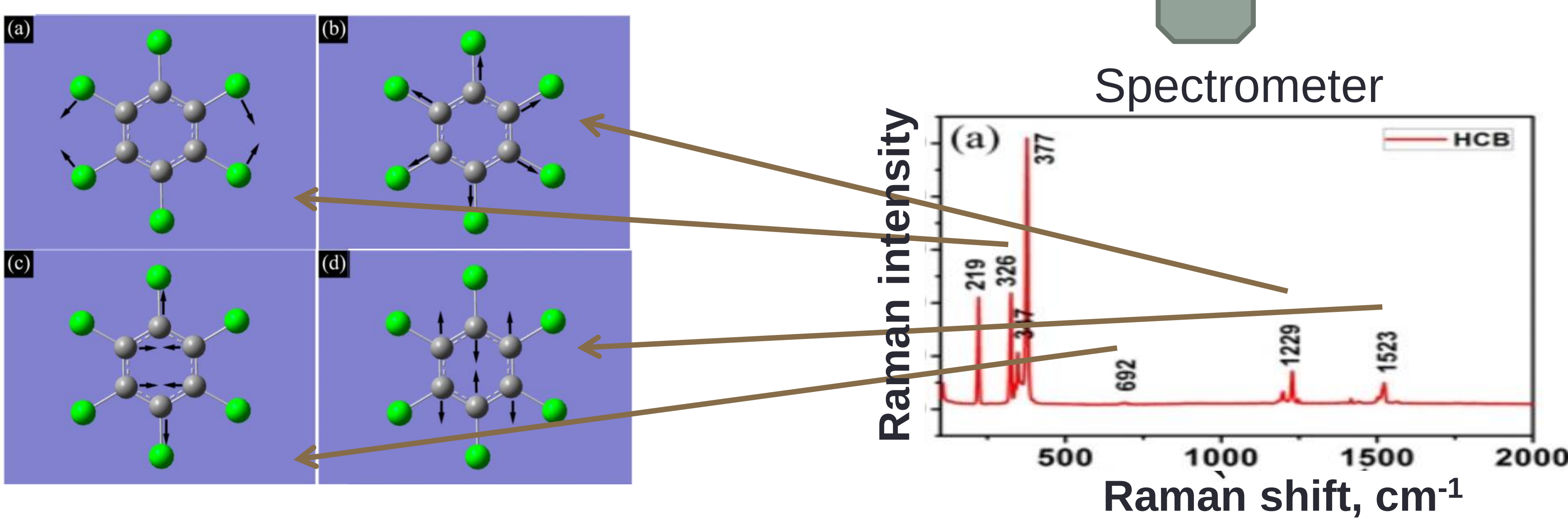


Raman spectroscopy

- Inelastic light scattering
- Excitation with a monochromatic light source (laser)
- Recording the spectrum of the scattered light in wavelength region different from the excitation



Hexachlorobenzene



Applications

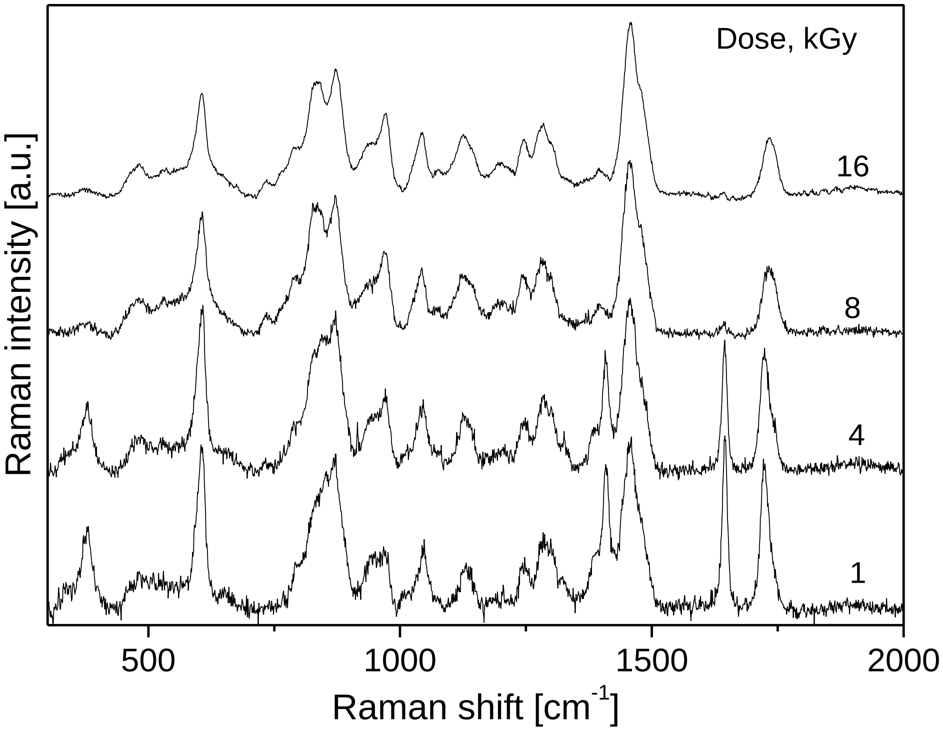
Information related to the vibrations of the medium

- Composition
- Conformation of the molecule
- Crystal lattice
- Crystal orientation
- Presence of isotopes
- Trace elements and defects
- Temperature
- Internal stress

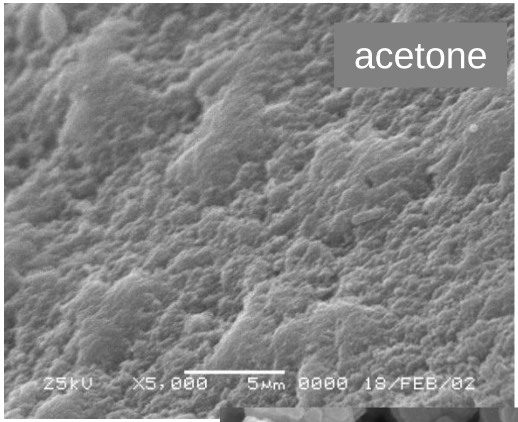
Journal of Raman Spectroscopy **keyword cloud**

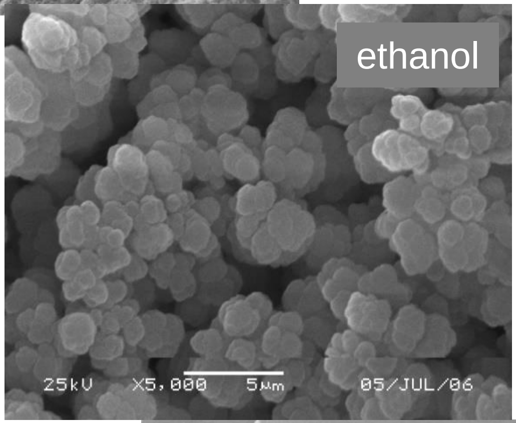
Study of polymerization kinetics

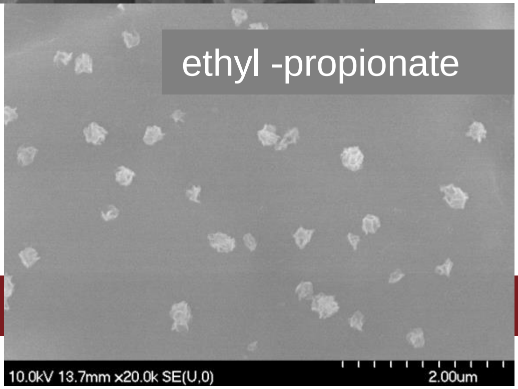
Gamma radiation induced precipitation polymerization of diethylene glycol dimethacrylate (DEGDMA) in different solvents.



Raman spectrum of the monomer mixture polymerized with different doses.

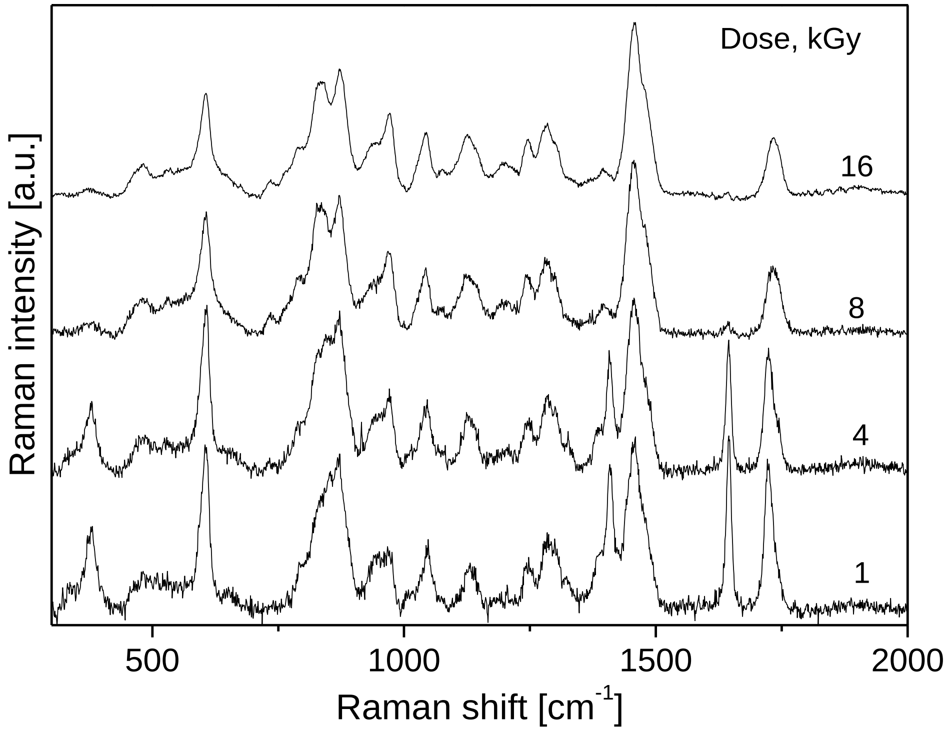




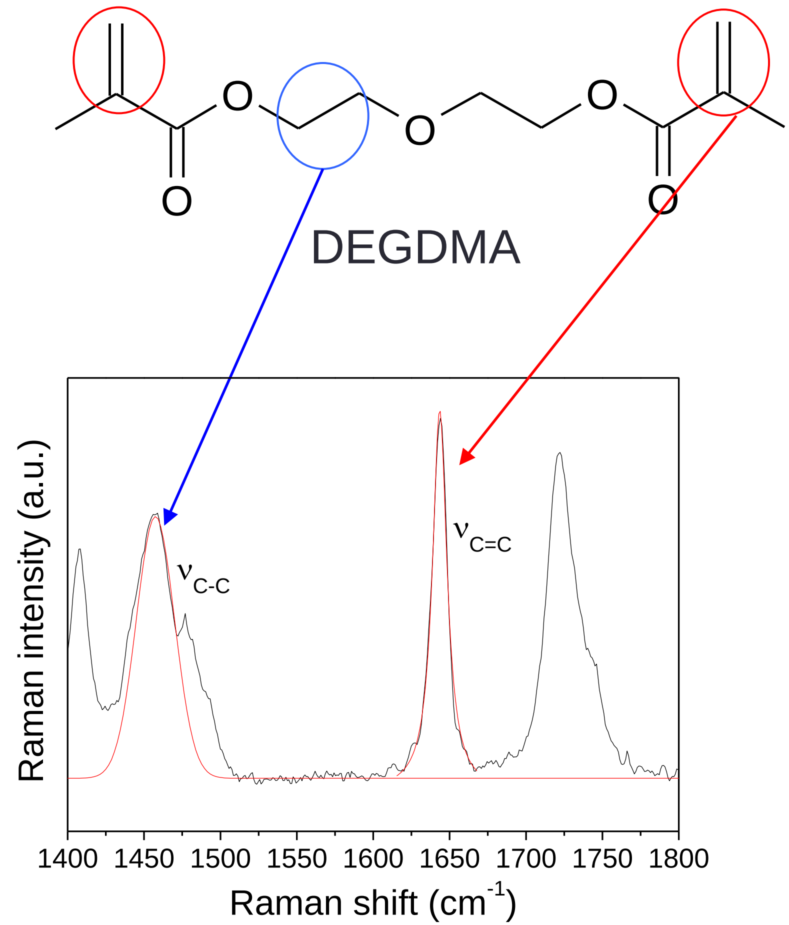


Study of polymerization kinetics

Gamma radiation induced precipitation polymerization of diethylene glycol dimethacrylate (DEGDMA) in different solvents.



Raman spectrum of the monomer mixture polymerized with different doses.



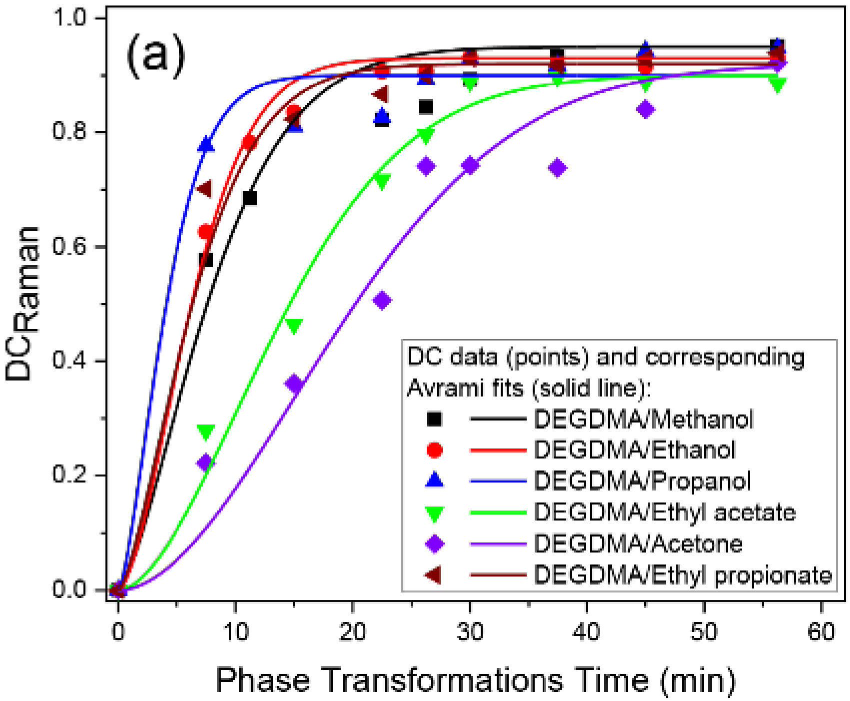
C=C vibration – 1640 cm^{-1}

C–C vibration – 1458 cm^{-1}

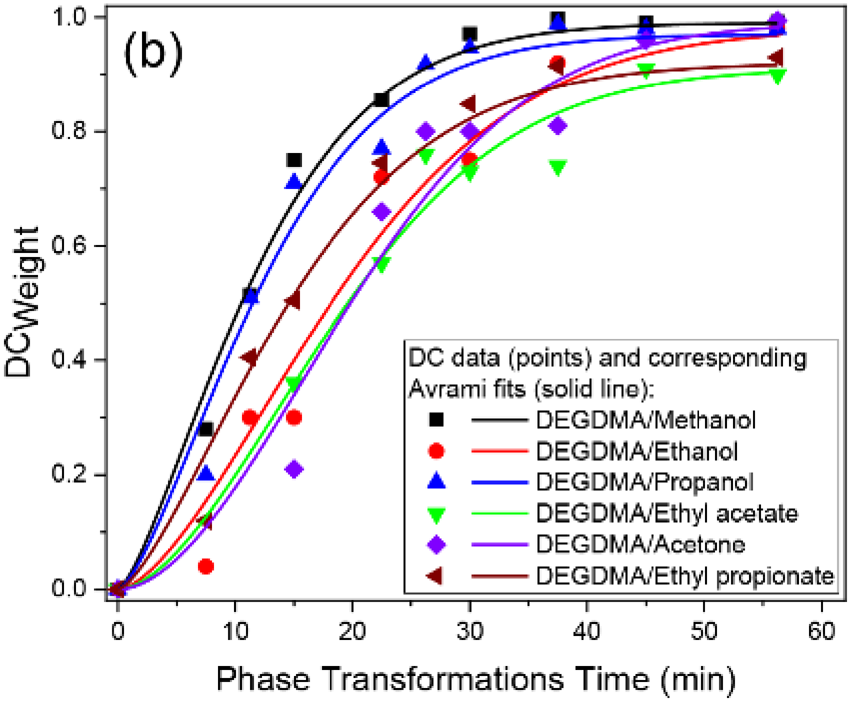
Study of polymerization kinetics

Conversion determined from Raman data and mass difference measurements.

Raman spectroscopy



Mass difference



- The C=C peak intensity >0 even for the maximum degree of conversion indicating that intact C=C bonds remain in the polymer matrix belonging to trapped or „dangling” monomers.

M. Veres et al. IAEA Rad. Tech. Reports (2015)

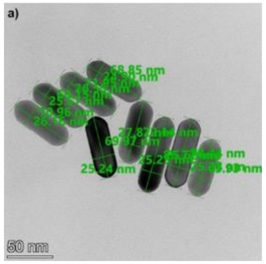
Polymer samples for irradiation experments

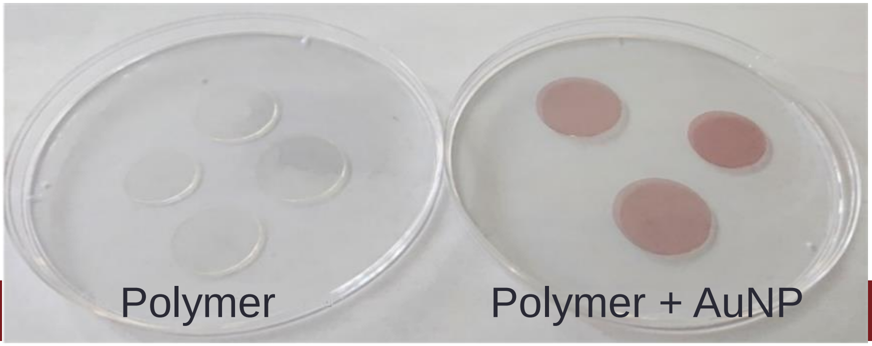
Polymerization mixture

Monomers
- Urethane dimethacrylate (UDMA)
- Triethylene glycol dimethacrylate (TEGDMA)

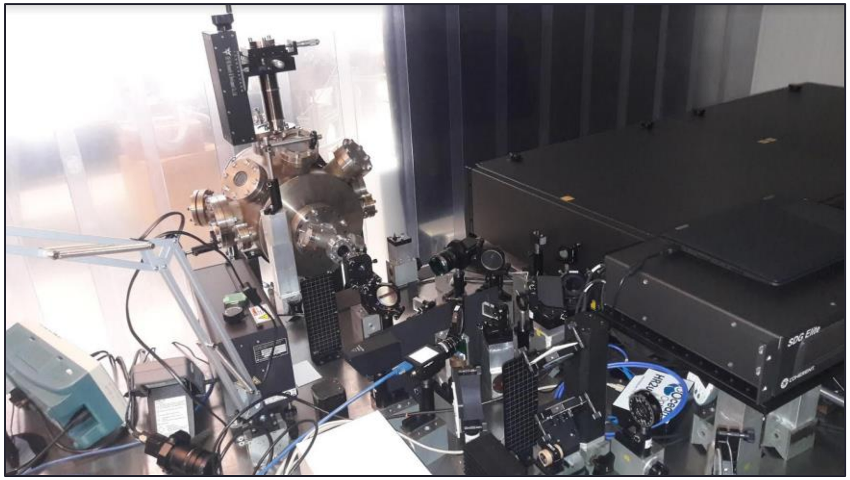
Photoinitiators
- Camphorquinone
- Ethyl 4-dimethylaminobenzoate

+ GOLD NANORODS (AuNP)



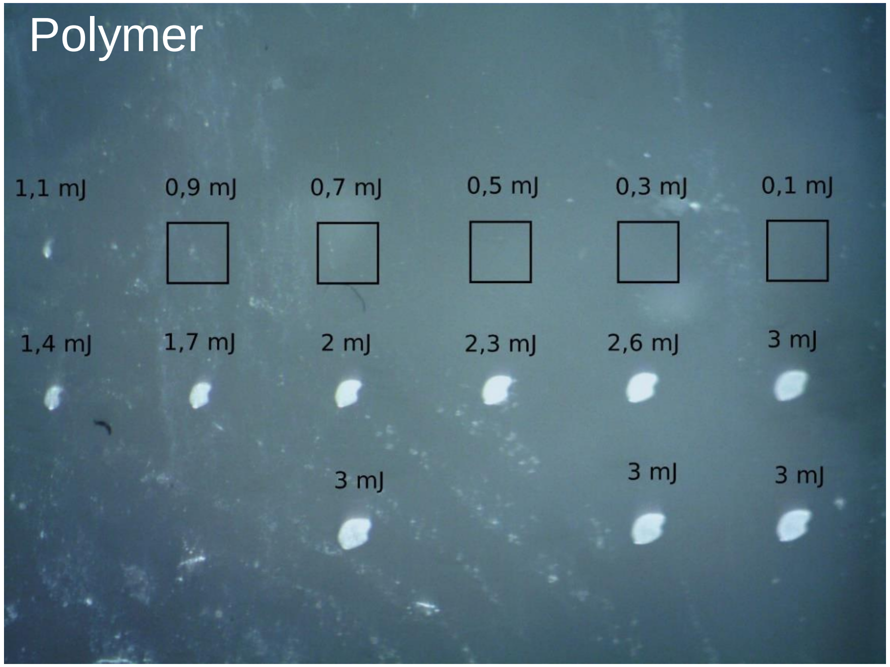


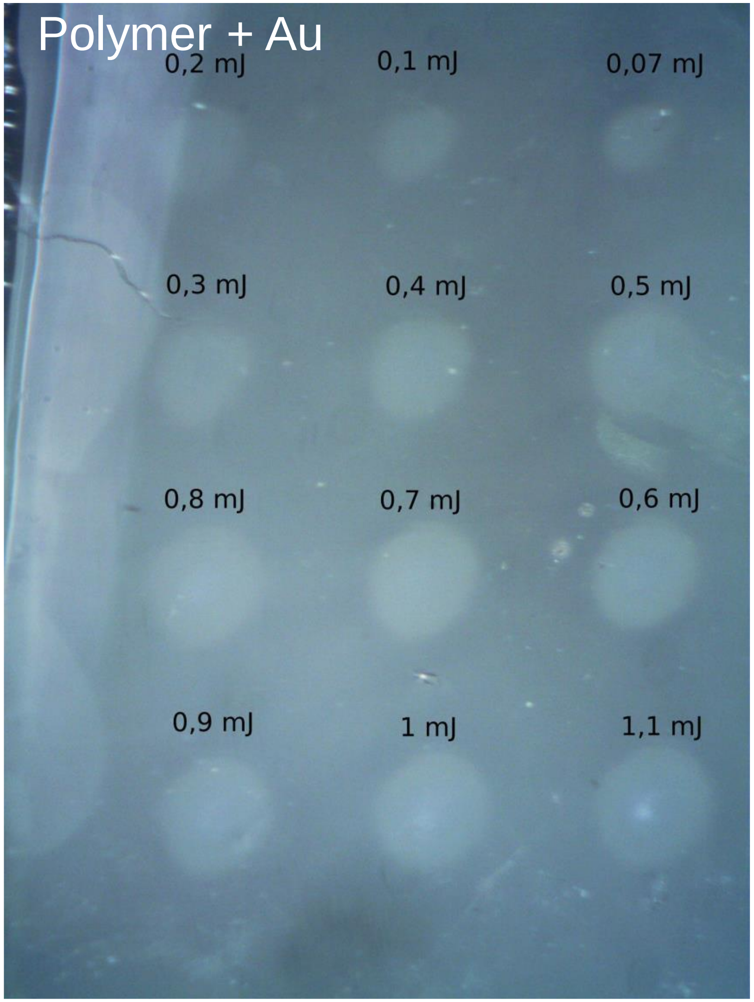
Irradiation



- Ti:Sa based chirped-pulse two-stage amplifier-laser system (Coherent Hydra)
- Smallest impulse length: 40 fs
- Central wavelength: 795 nm
- Repetition rate: 10 Hz
- Max. pulse energy: 30mJ
- Pressure in the vacuum chamber: ~10^{-5} mbar

Low-energy laser pulses

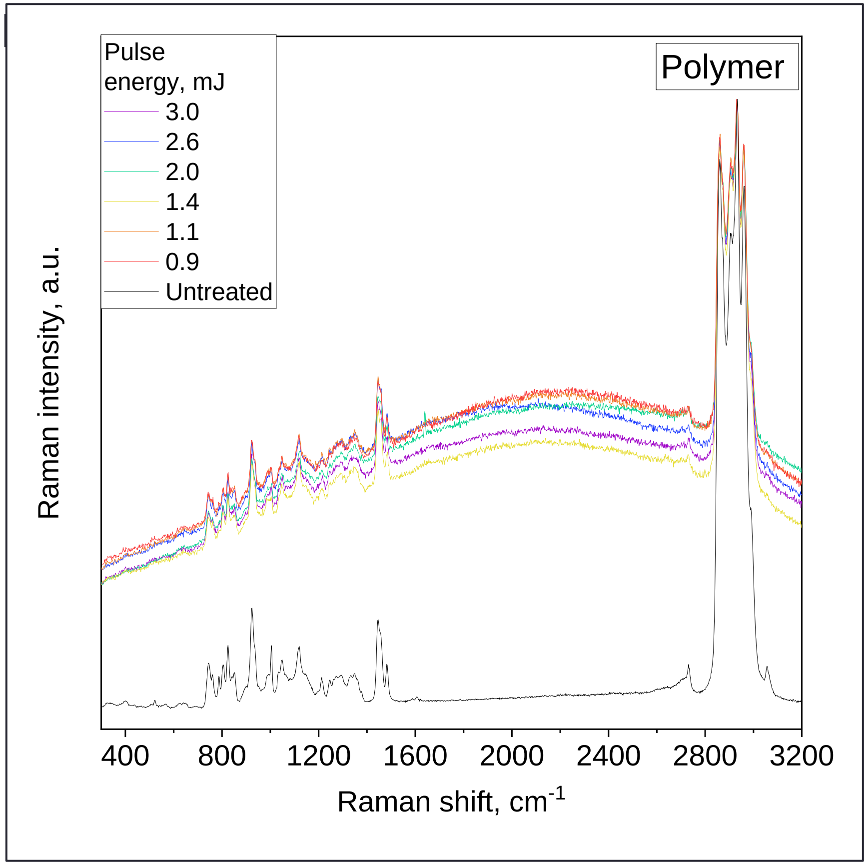


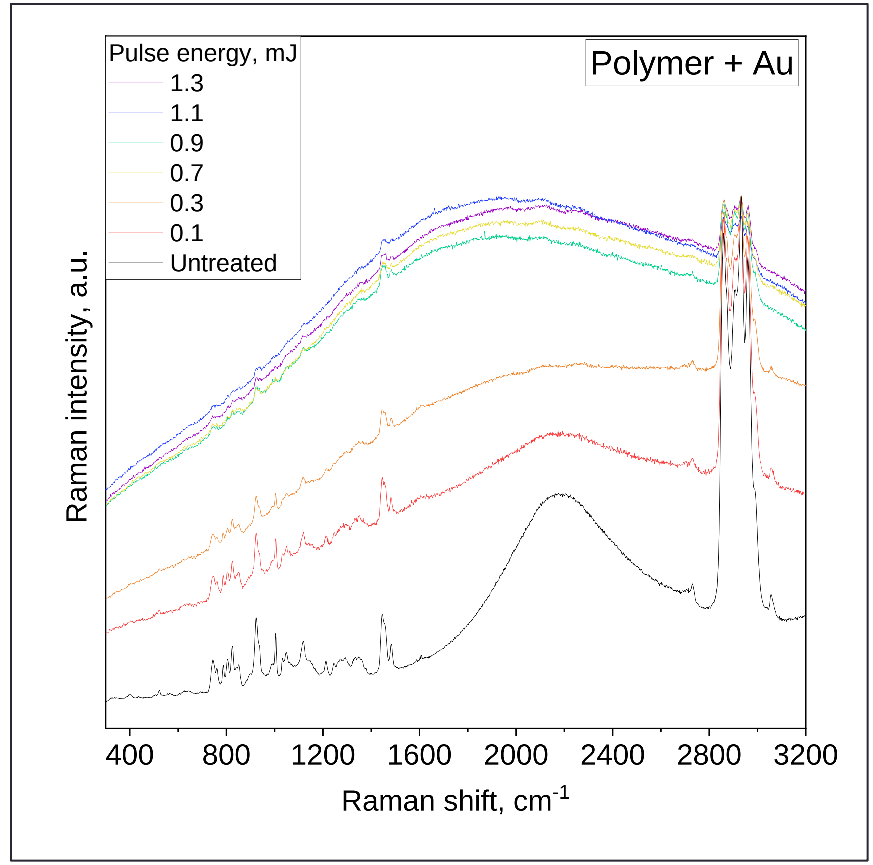


- No crater formation
- The irradiation spot is visible from 1.1 mJ
- The spot size depends on the laser pulse energy

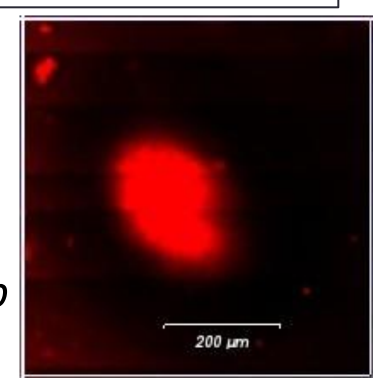
- The doping with gold nanorods affects the structural transformation of the polymer upon laser treatment

Low-energy laser pulses



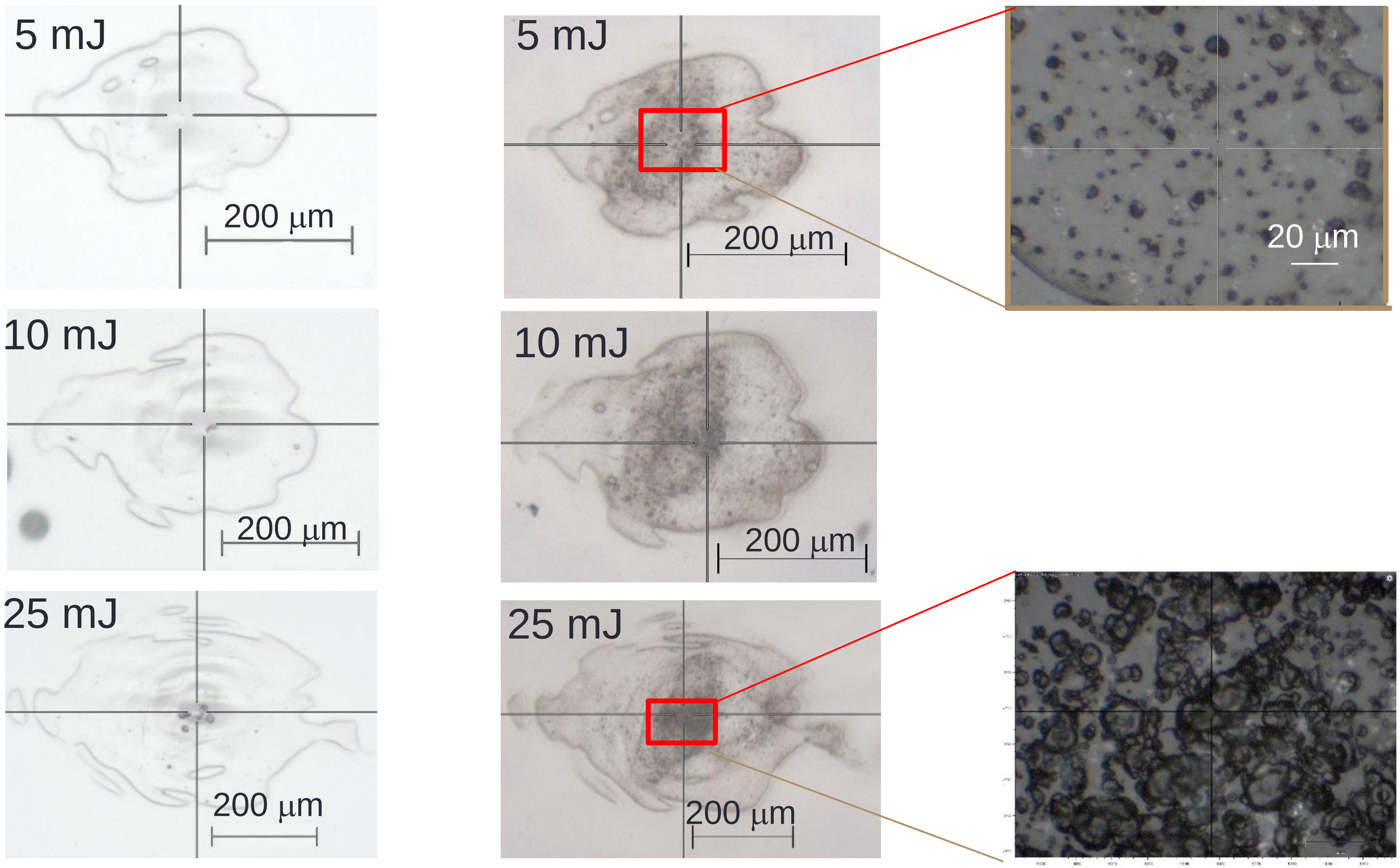


- The increase of the photoluminescence background is an indication of changes in the bonding configuration
- The Raman spectra of the non-doped polymer are very similar
- Gradual structural transformations occur in the polymer doped with gold nanorods



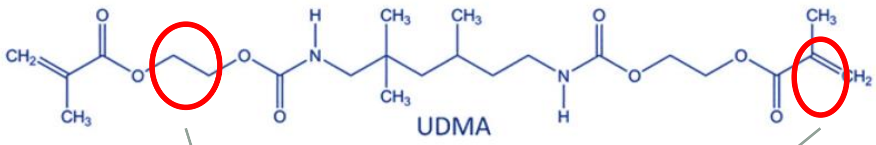
Intensity map at 1440 cm^{-1}

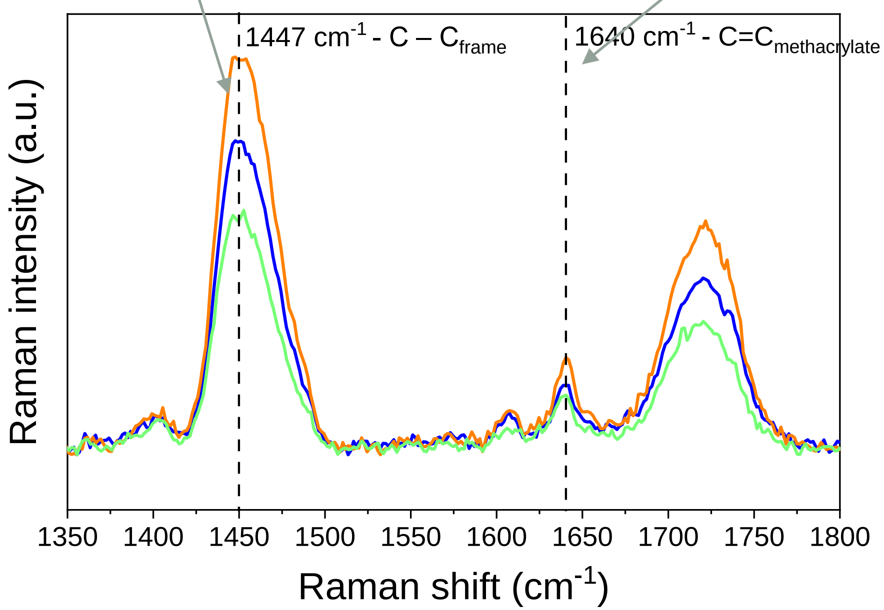
Higher pulse energies - Crater formation



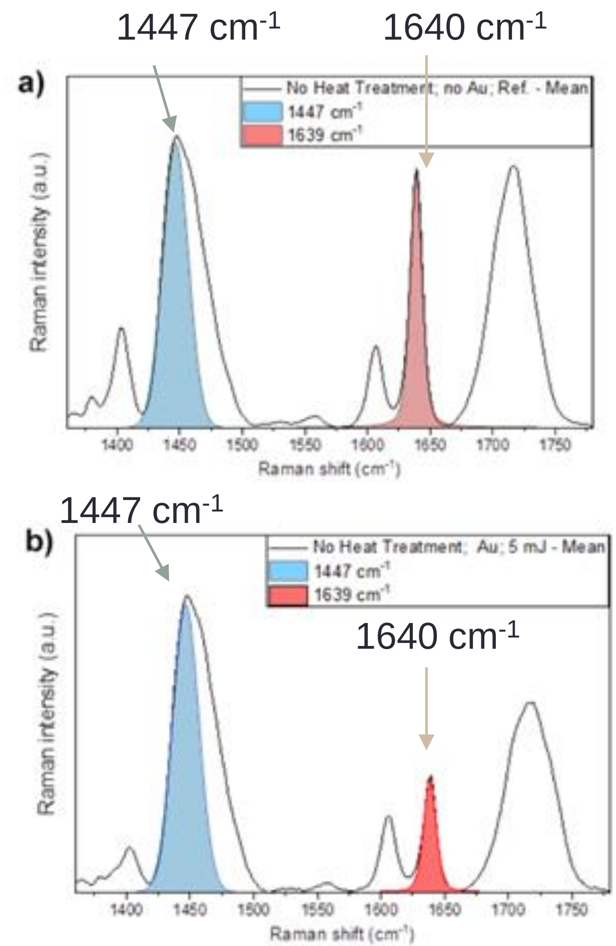
Raman characterization of the polymer

Structure of the urethane dimethacrylate (UDMA) monomer





Typical Raman spectra of the UDMA polymer

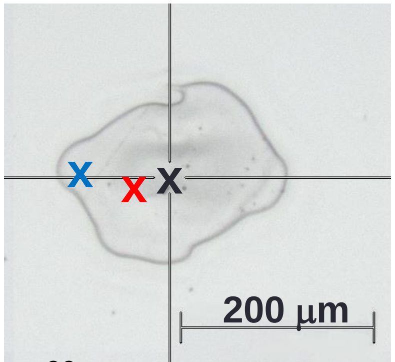


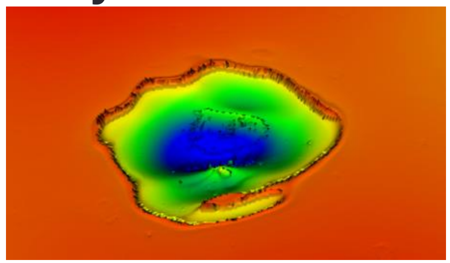
During the polymerization, the ratio of the two peaks characterizes the degree of conversion.

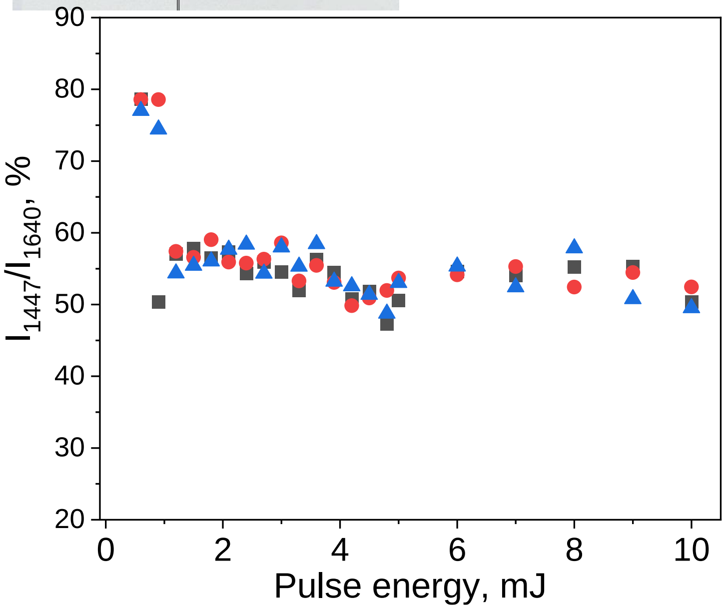
For the craters it shows the level of structural transformation – breaking of C-C bonds.

Higher pulse energies - Crater formation

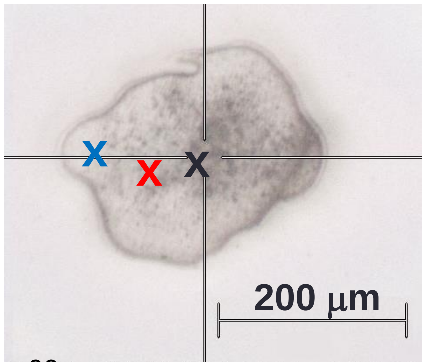
Polymer

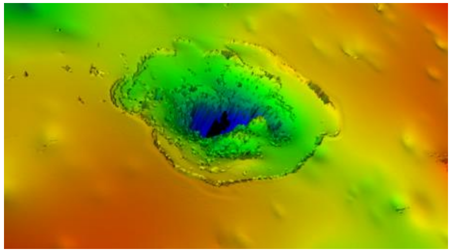


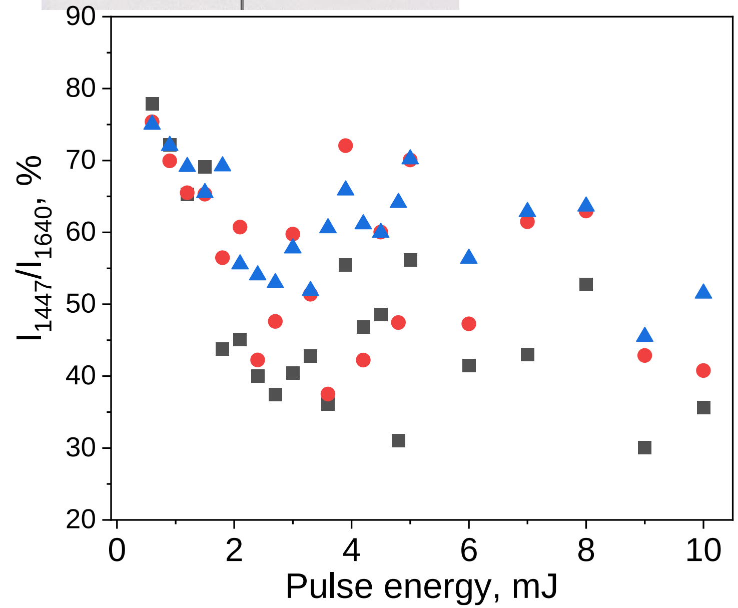




Polymer + Au

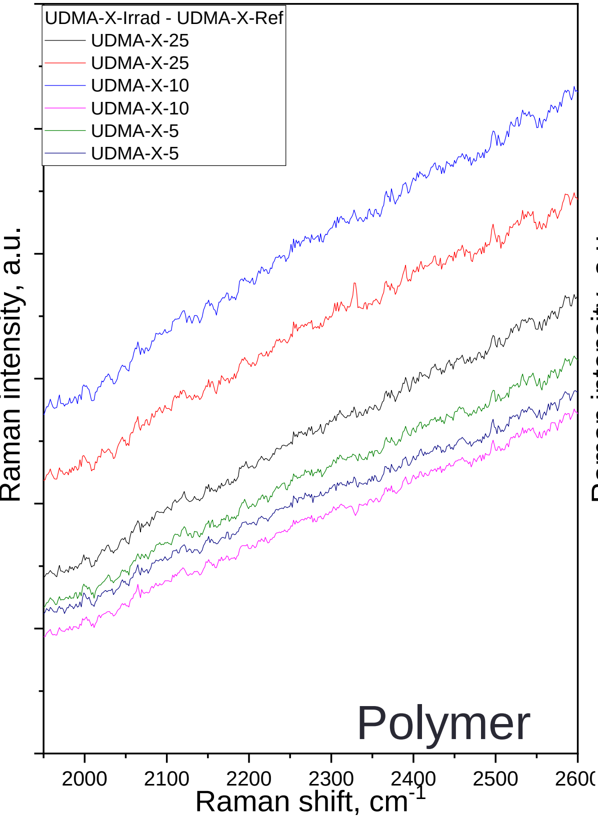


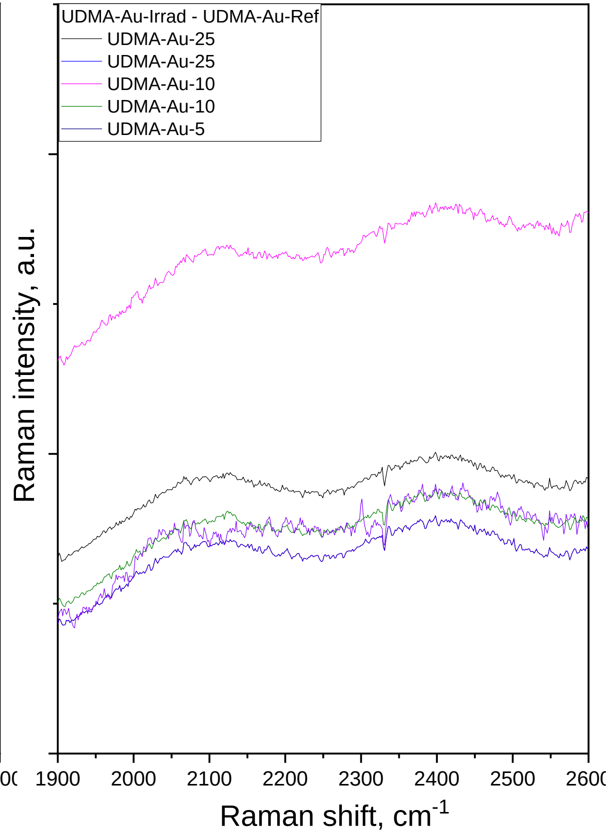




- The surface of the craters in non-doped polymer changes similarly, and that only slightly depends on the pulse energy.
- With gold nanorods the matrix is altered in a stochastic way, affected by the distribution of the nanorods. The change in the center is more remarkable.

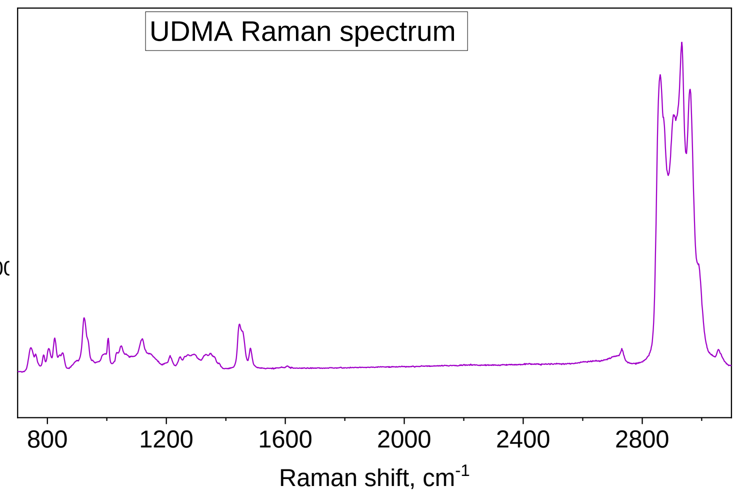
Higher pulse energies - Crater formation





Possible origin:

- Photoluminescence
- Contamination
- Structural transformation



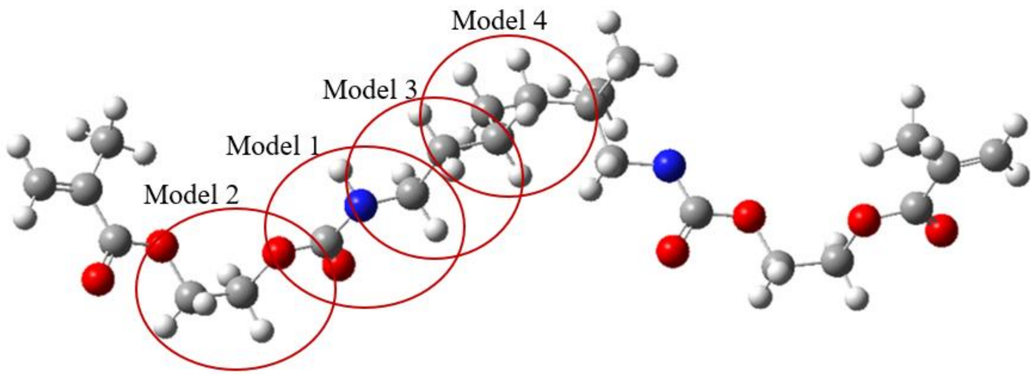
The Raman intensity of the polymer doped with gold increase remarkably in the 2000-2500 cm^{-1} region.

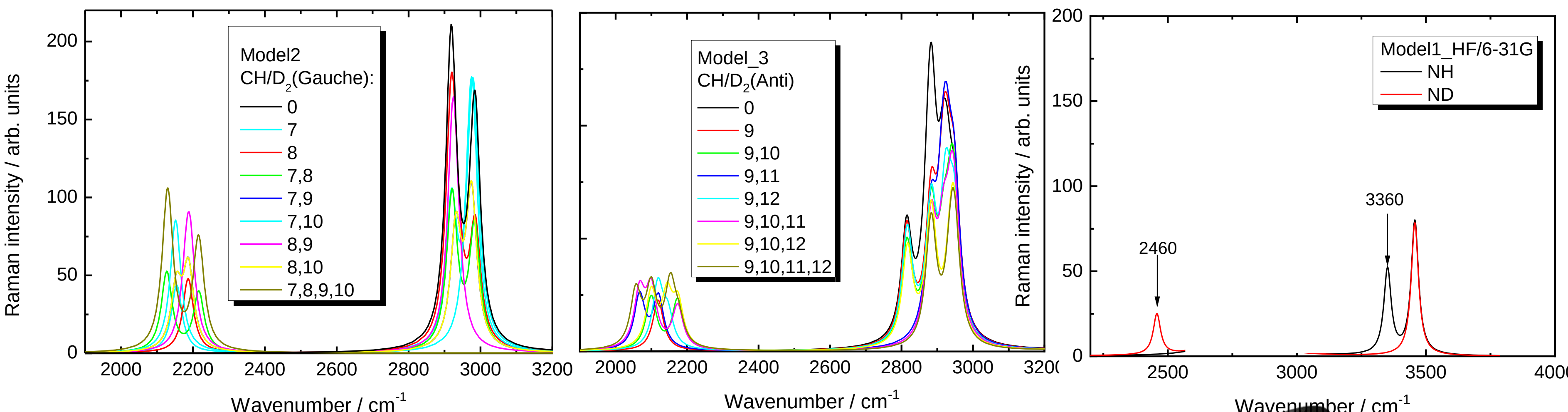
Preliminary results

Origin of the new Raman peaks

Possible assigment – C-D vibrations

DFT calculations of Raman active vibrations of deuterized UDMA



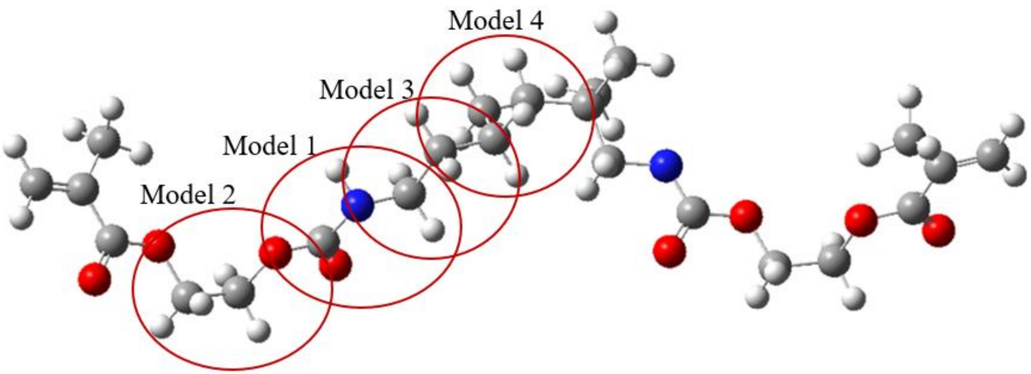


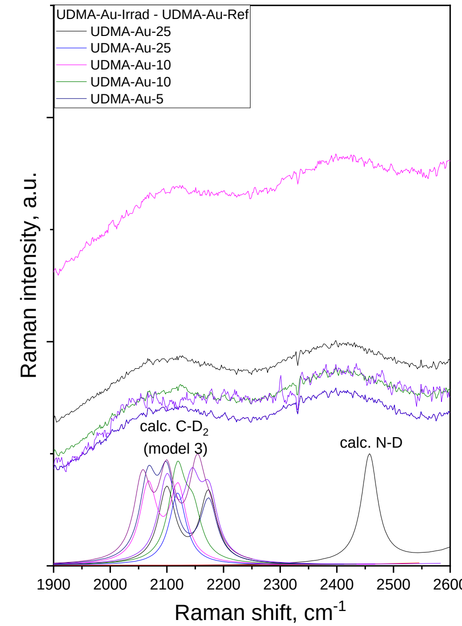
Preliminary results

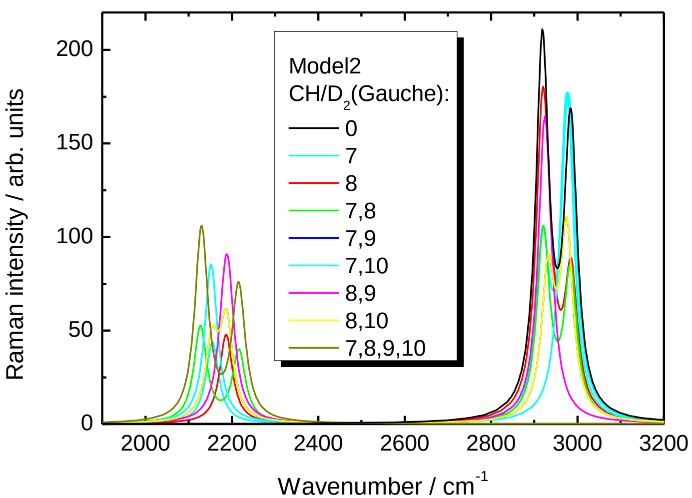
Origin of the new Raman peaks

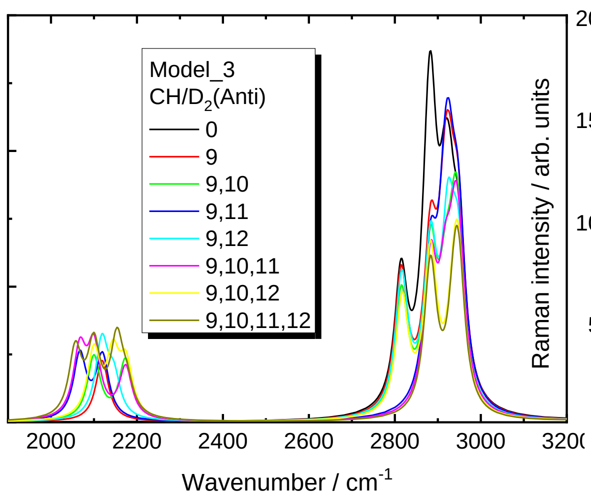
Possible assigment – C-D vibrations

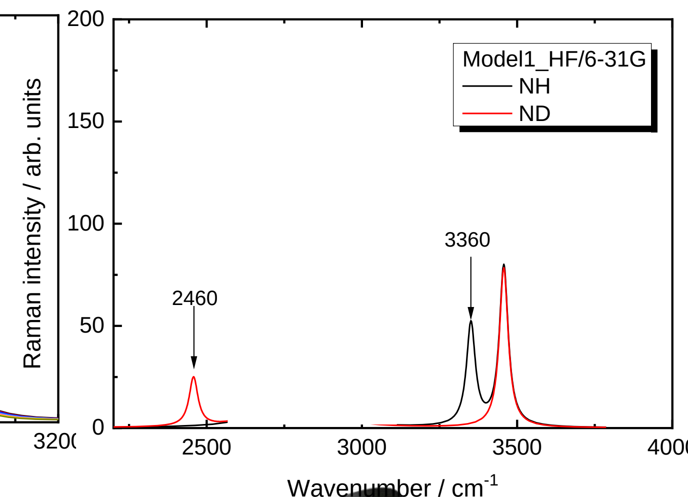
DFT calculations of Raman active vibrations of deuterized UDMA











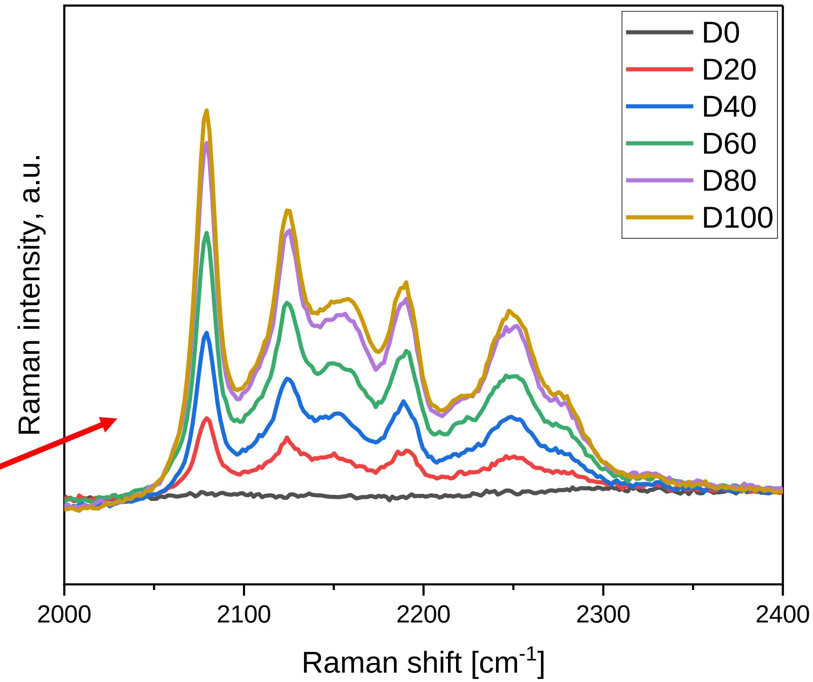
Preliminary results

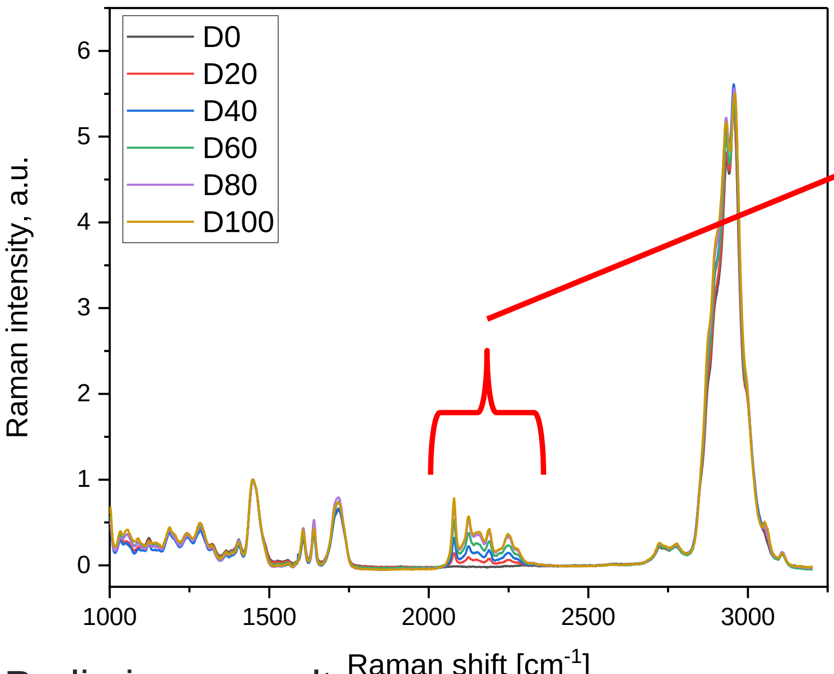
Origin of the new Raman peaks

Possible assigment – C-D vibrations

Raman experiments with deuterized methyl methacrylate polymer of different deuterium content

Composition						
Sample ID	MMA-D [g]	MMA [g]	UDMA [g]	Au [ml]	CQ [mg]	EDAB [mg]
D0	0	0,1	0,3	34,8	0,8	1,6
D20	0,02	0,08	0,3	34,8	0,8	1,6
D40	0,04	0,06	0,3	34,8	0,8	1,6
D60	0,06	0,04	0,3	34,8	0,8	1,6
D80	0,08	0,02	0,3	34,8	0,8	1,6
D100	0,1	0	0,3	34,8	0,8	1,6





The C-D vibrations give contribution in the 2050-2300 cm^{-1} region of the Raman spectrum.

Preliminary results

Summary

- Raman spectroscopy is an optical spectroscopic technique allowing to study characteristic vibrations of the sample. It can be used to characterize the polymerization kinetics, the degree of conversion and structural transformations in polymers.

- The Raman spectroscopic study of polymer targets doped with gold nanorods and irradiated with ultrashort laser pulses showed that the presence of plasmonic gold nanoparticles has a remarkable effect on the structural transformations occurring due to light-matter interactions

- New Raman peaks were observed in the 2000-2500 cm^{-1} region of the Raman spectrum upon irradiation with high-energy laser pulses. The presumed origin of these features is the formation of C-D and N-D bonds in the structure.

Acknowledgements

- Members of the NAPLIFE Structural Characterization Group

  Gábor Galbács

  Roman Holomb

  Judit Kámán

  Ágnes Nagyné Szokol

  István Rigó

- The NAPLIFE collaboration
- NKFIH and ELKH for financial support

WIGNER

ELKH
Eötvös Loránd
Kutatási Hálózat

NEMZETI KUTATÁSI, FEJLESZTÉSI
ÉS INNOVÁCIÓS HIVATAL

THANKS FOR THE ATTENTION!