Experimental and theoretical study of the degradation of malonamide extractant molecules under ionizing radiation

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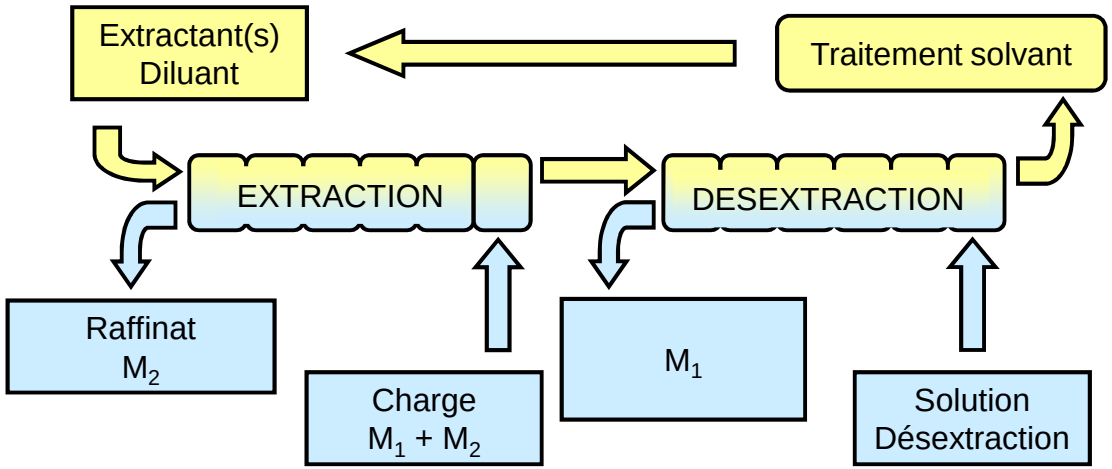
Context

Liquid-liquid extraction in the context of nuclear waste separation.



➡ **Solvent degradation:** chemistry, radiolysis….

- Change of physico-chemical, chemical properties…..

check the robustness of the extractant solution submitted to radiolysis

➡ Effect of the radiolysis on extractant molecules (malonamides) diluted in organic phase (octane).

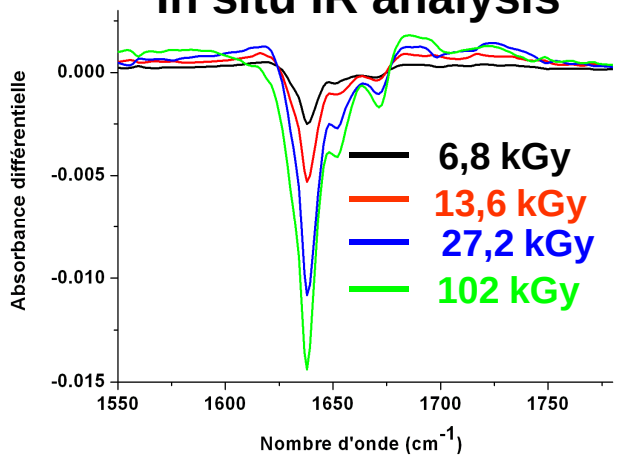
Methodology

Sample irradiation

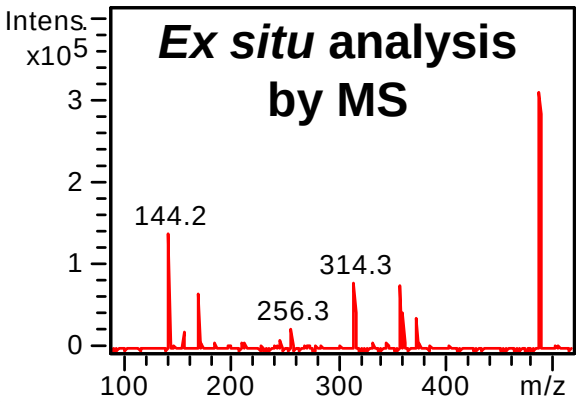
LINAC/FT-IR coupling

Experimental studies

In situ IR analysis

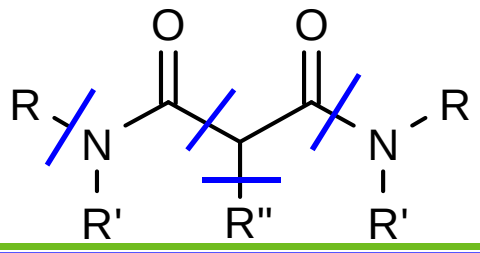


***Ex situ* analysis by MS**



Assignment of the IR bands

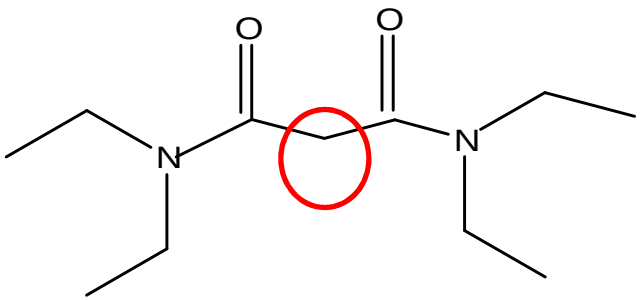
Quantum chemistry calculations



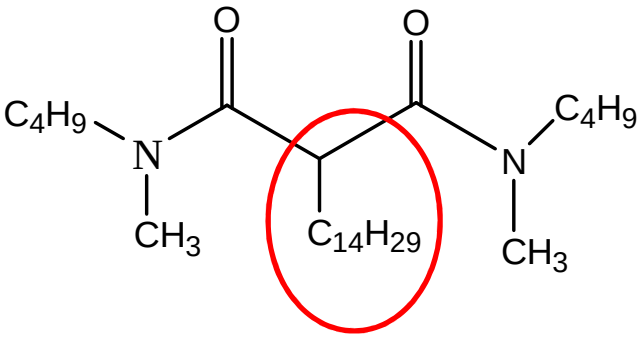
Theoretical studies

Simulation of the IR spectra of the reactant and of the products

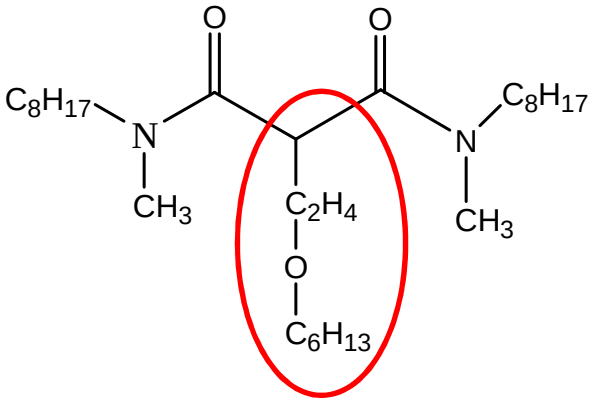
Malonamides under study



Tetraethylmalonamide (TEMA)



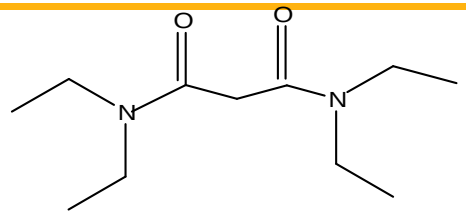
Dimethyldibutyltetradecylmalonamide (DMDBTDMA)

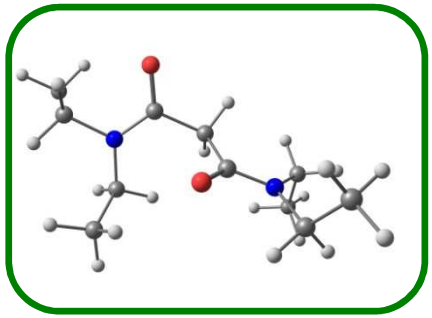


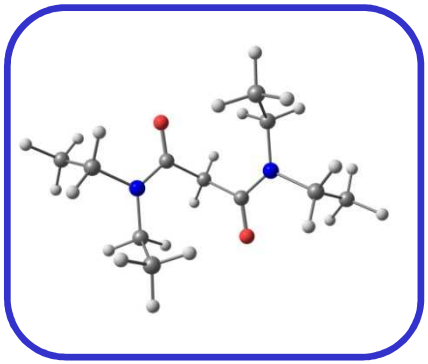
Dimethyldioctylhexyloxyethylmalonamide (DMDOHEMA)

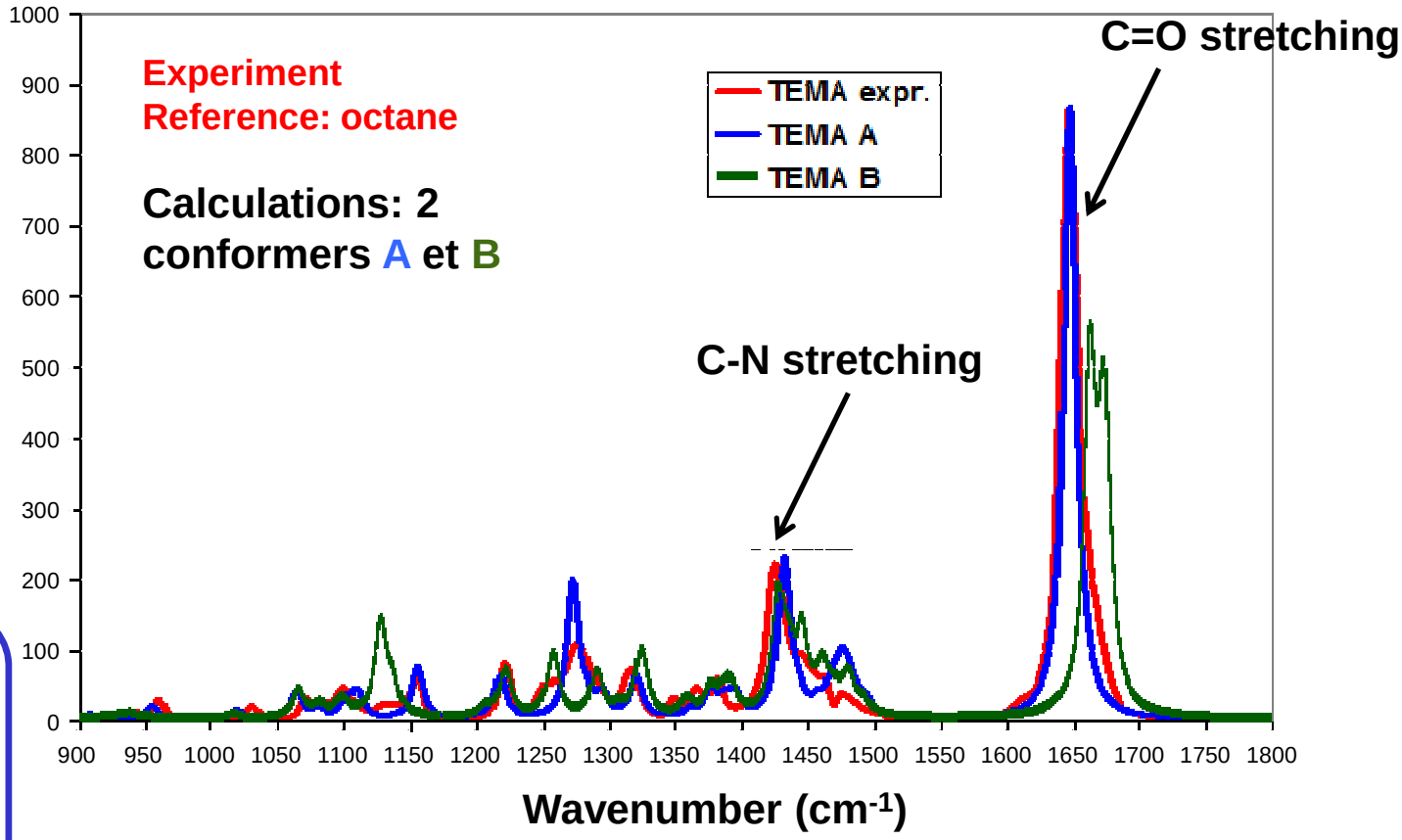
IR spectrum of TEMA: experiment/simulation comparison

DFT calculations
B3LYP/6-311+G(d,p)



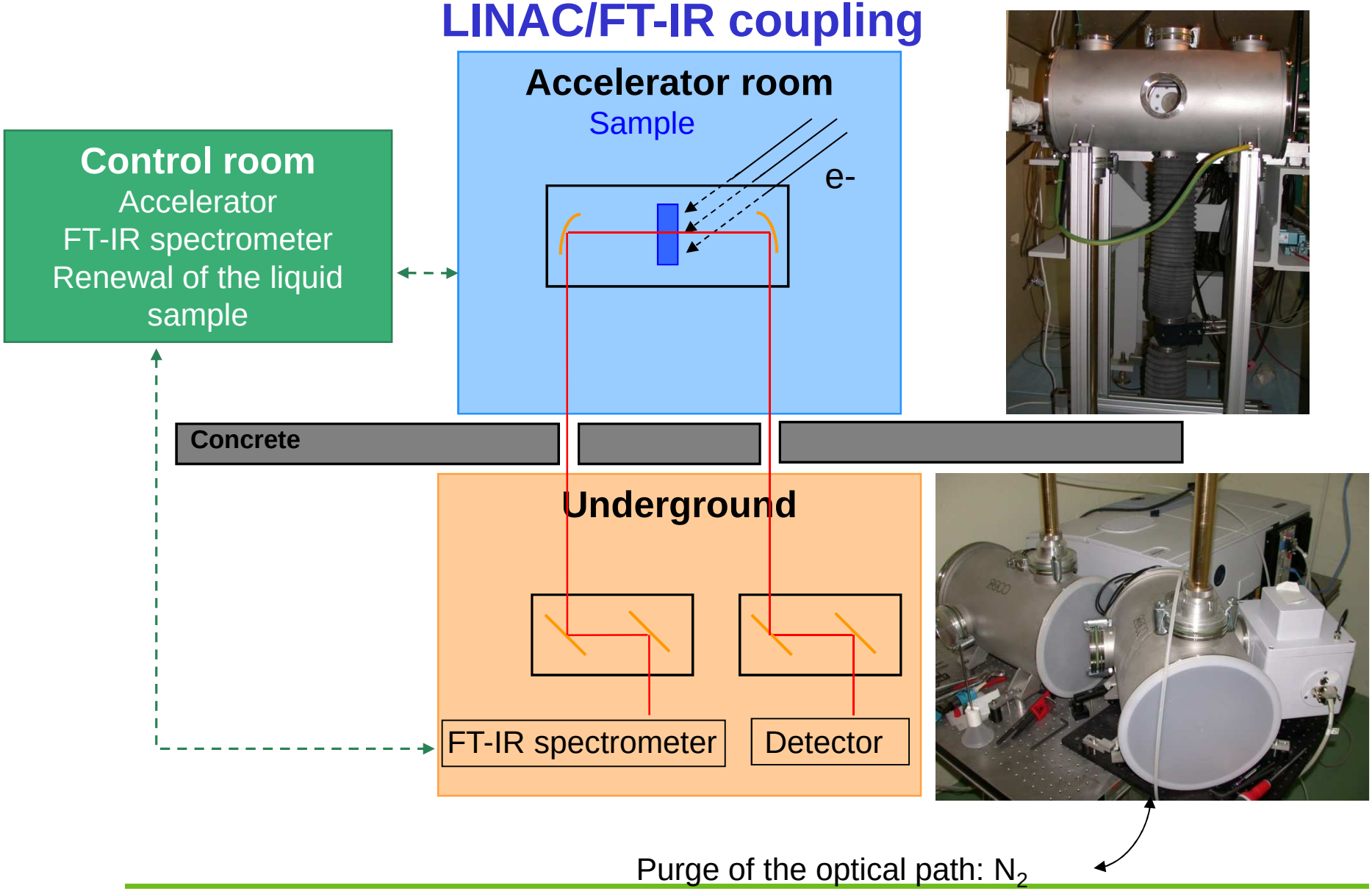






The calculated spectrum for conformation A is in very good agreement with the measured spectrum.

In situ study of irradiation effects by means of LINAC/FT-IR coupling

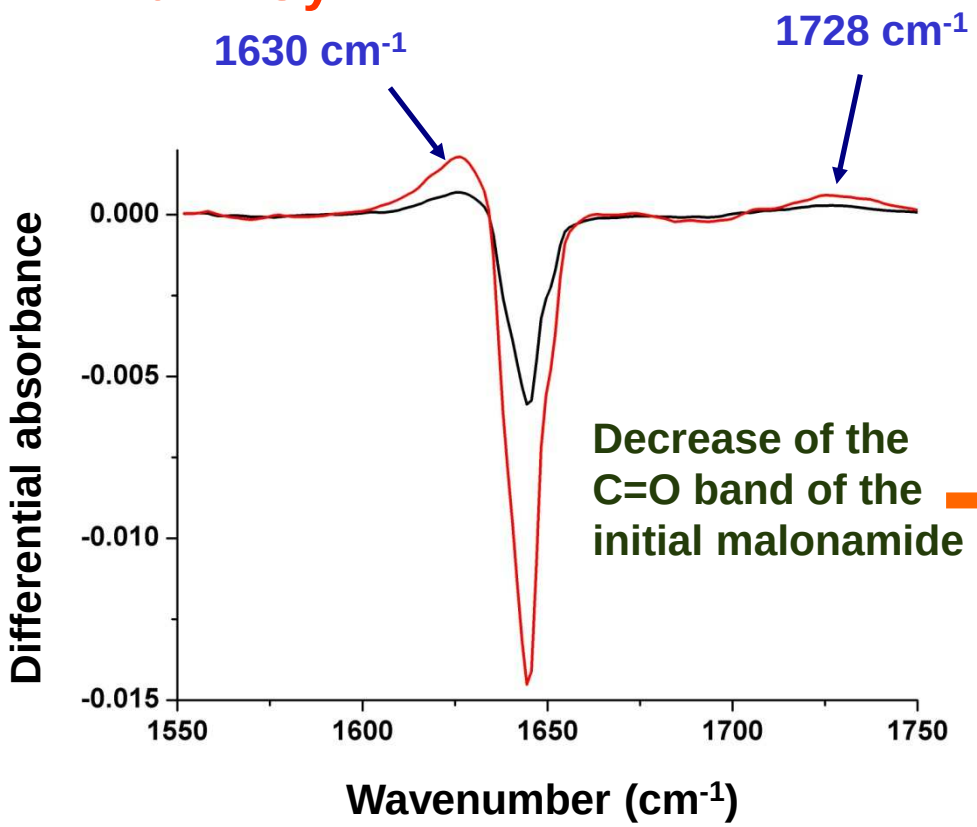


Chem. Phys. Lett., **2006**, 426: 71-76. *Rad. Phys. Chem.*, **2007**, 76: 1280-1284.

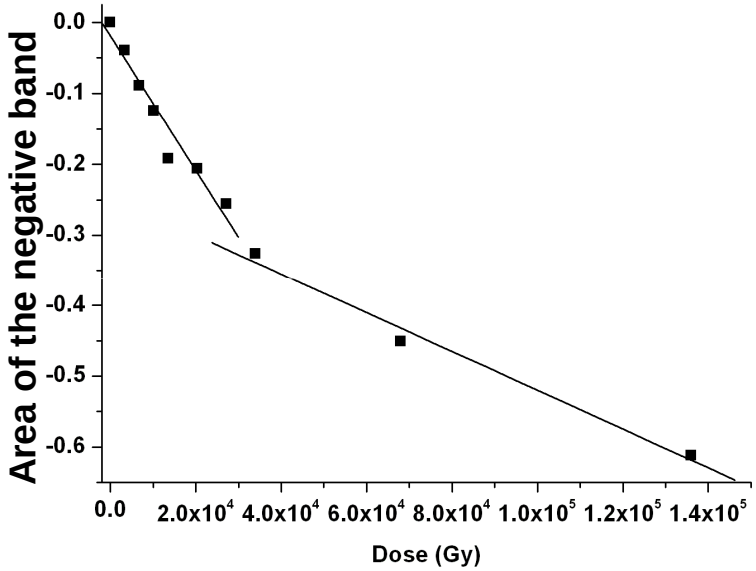
Study by infrared spectroscopy of the behaviour of TEMA under irradiation

6.8 kGy

20.4 kGy

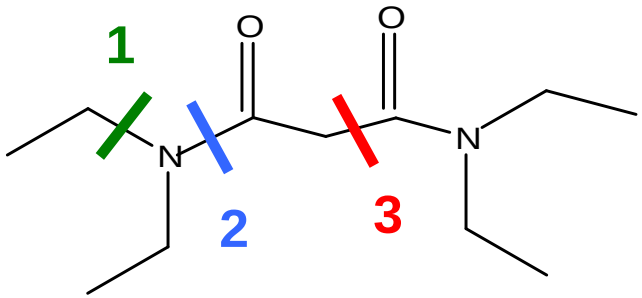


Quantitative measurements:
It is in principle possible to measure radiolytic yields.



The deconvolution of the C=O stretching band is different in the initial malonamide and in the irradiated one, indicating that products absorbing in this spectral region are formed upon irradiation.

Different bond cleavages in TEMA



G3 (MP2) calculations
Gaussian 03

Cleavage of the C-N bond:

$R_2NCOCH_2CONR_2 \rightarrow R\cdot + \cdot RNCOCH_2CONR_2$ (R1)

$R_2NCOCH_2CONR_2 \rightarrow R_2N\cdot + \cdot COCH_2CONR_2$ (R2)

Cleavage of the C-C bond:

$R_2NCOCH_2CONR_2 \rightarrow R_2NCO\cdot + \cdot CH_2CONR_2$ (R3)

Cleavage of the central C-H bond:

$R_2NCOCH_2CONR_2 \rightarrow R_2NCOCHCONR_2 \cdot + \cdot H$ (R4)

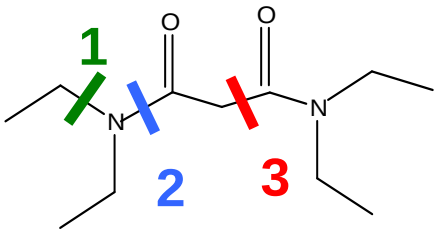
with R = C_2H_5

Bond dissociation energy	Reaction 1 (kJ.mol^{-1})	Reaction 2 (kJ.mol^{-1})	Reaction 3 (kJ.mol^{-1})	Reaction 4 (kJ.mol^{-1})
C_2H_5 (TEMA)	**388**	**416**	**362**	**408**

The **cleavage of the C-C bond** is thermodynamically more favorable than the other bond cleavages.

Assignment of the observed IR bands

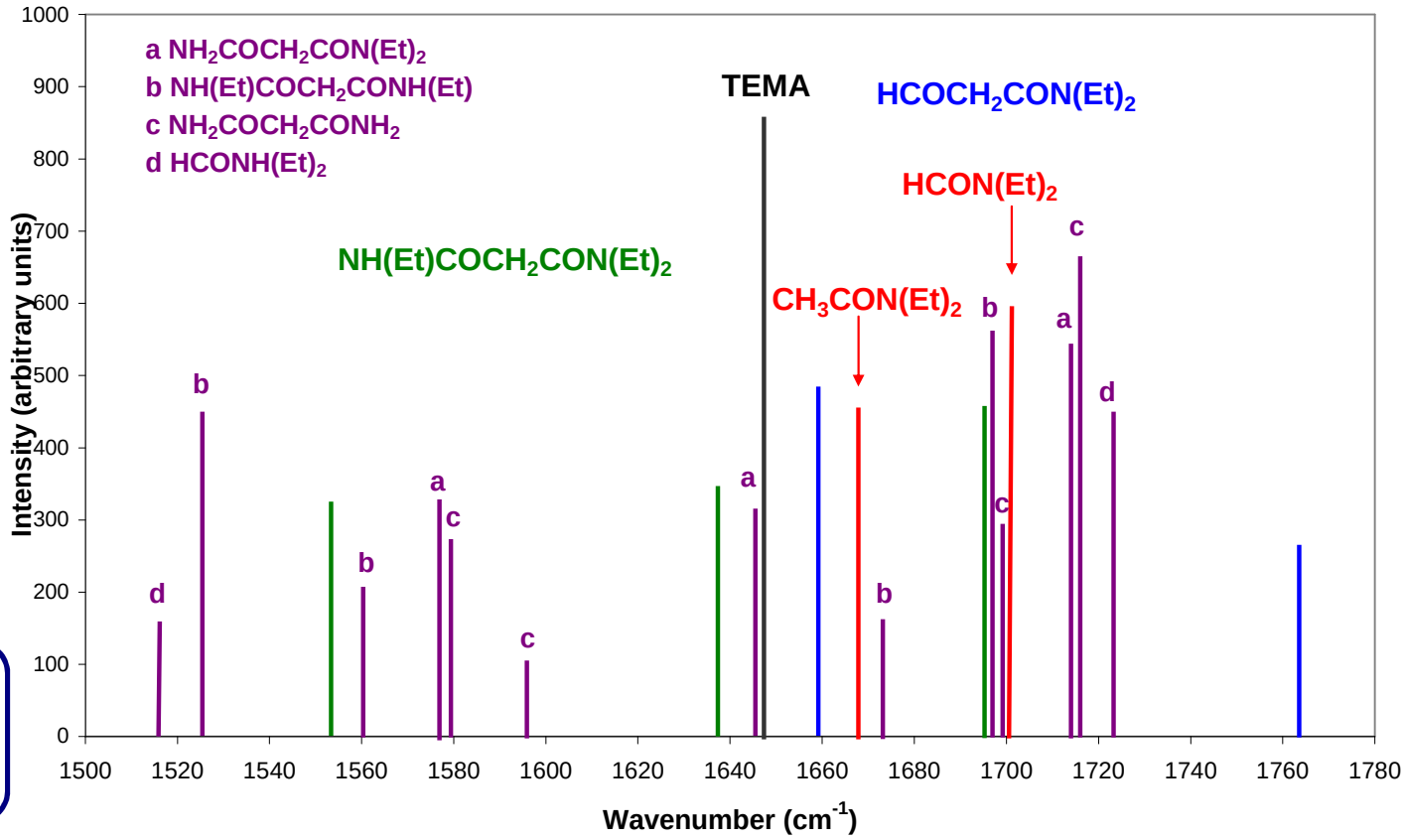
Experimentally, after irradiation, two positive bands are detected at 1630 and 1728 cm^{-1} in the 1500-1800 cm^{-1} spectral region.



Different bond cleavages

No bond cleavage is observed here.

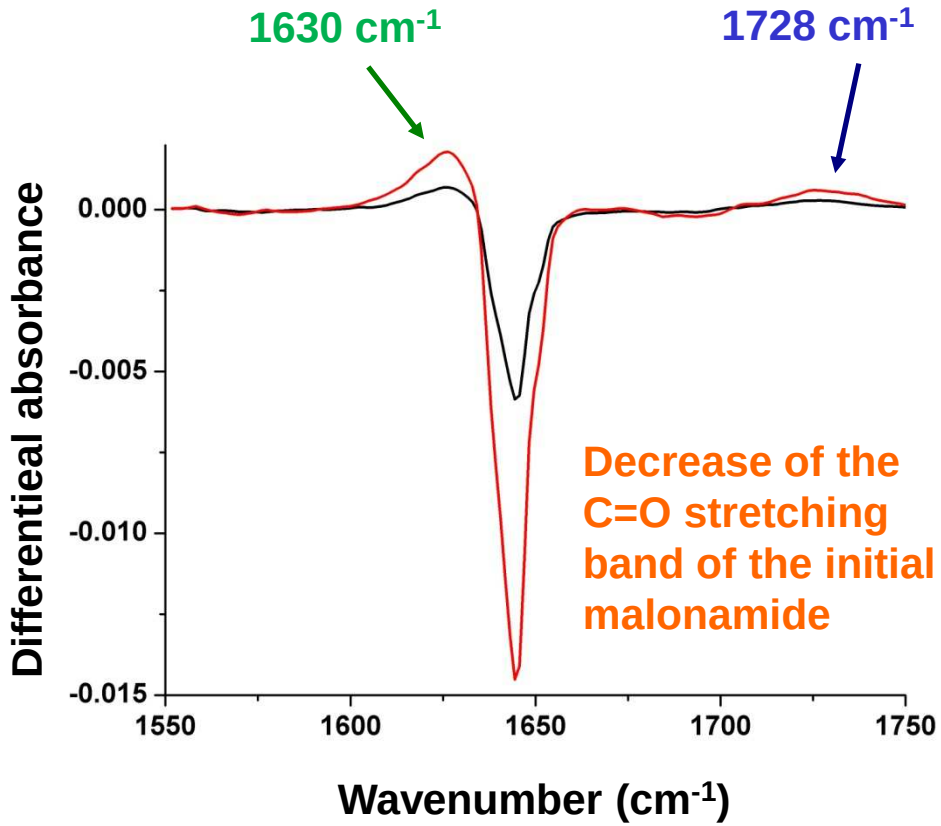
Calculated infrared frequencies and intensities for TEMA and some of its derivatives



Behaviour of TEMA under irradiation

6.8 kGy

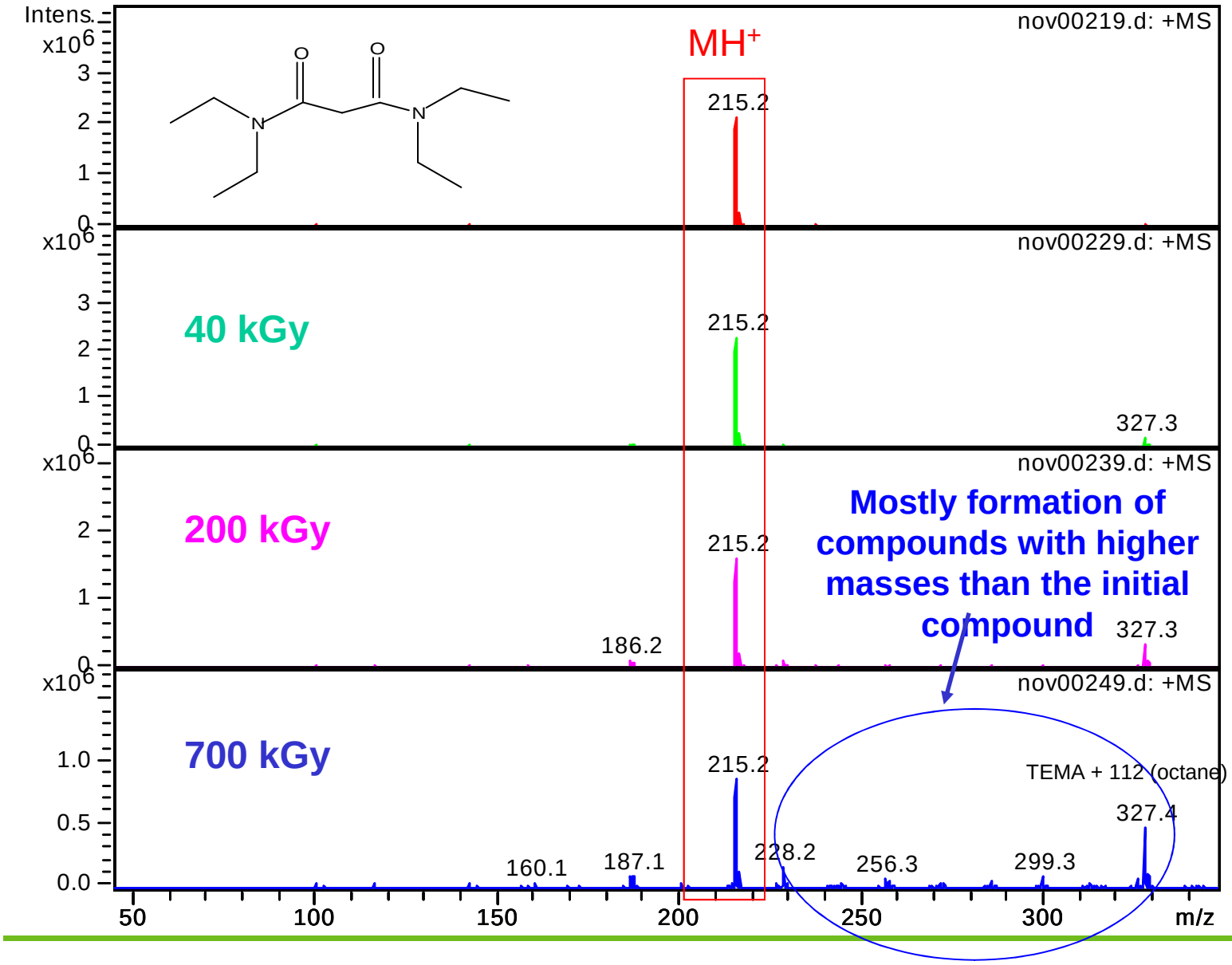
20.4 kGy



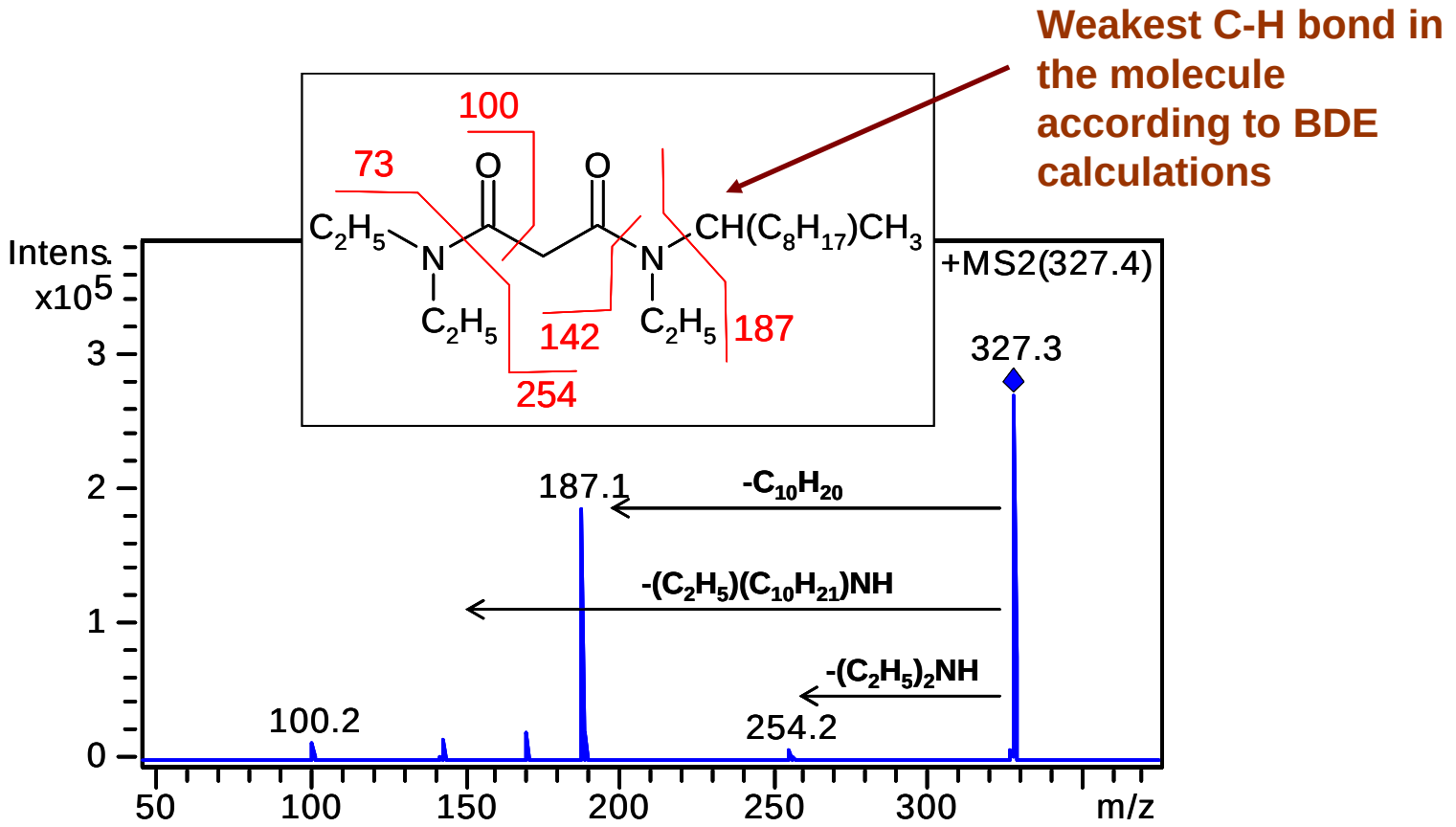
The positive band measured at ~ 1630 cm^{-1} may correspond to a displacement of the C=O stretching vibration which overlaps partly with the main band of the initial product.

Acid formation resulting from reaction with trace water molecules.

ESI-MS spectra of TEMA after 10 MeV electrons irradiation

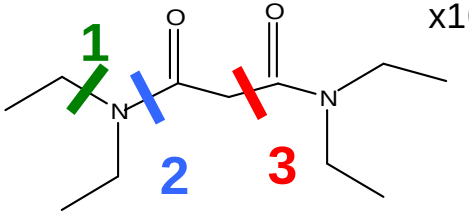


The addition of the octyl group takes place on the carbon in the ethyl group in alpha position of the nitrogen atom

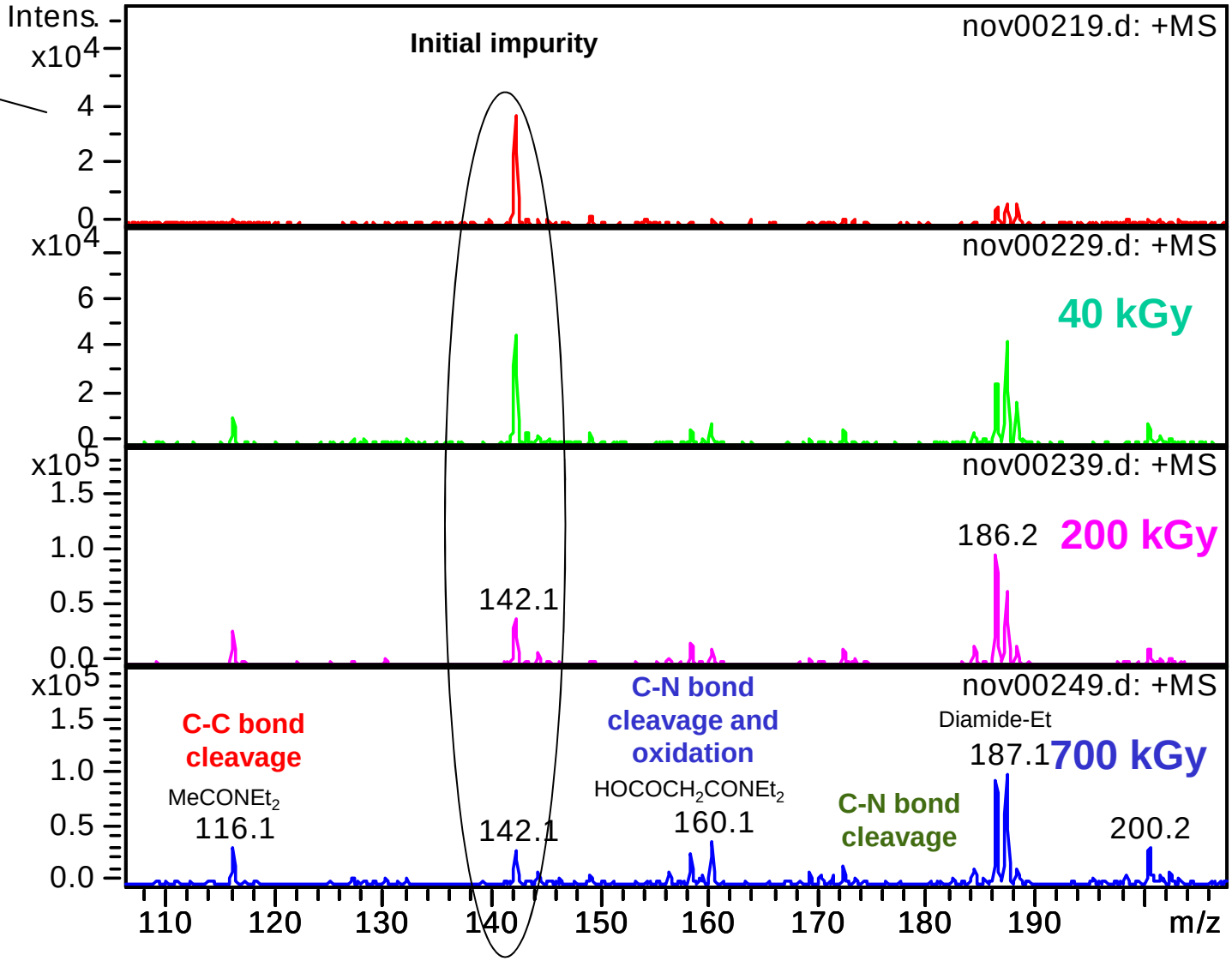


ESI-MS^2 spectrum of a TEMA solution in octane after radiolysis.

ESI-MS of TEMA after 10 MeV electrons irradiation



Focus on 110 < *m/z* < 220

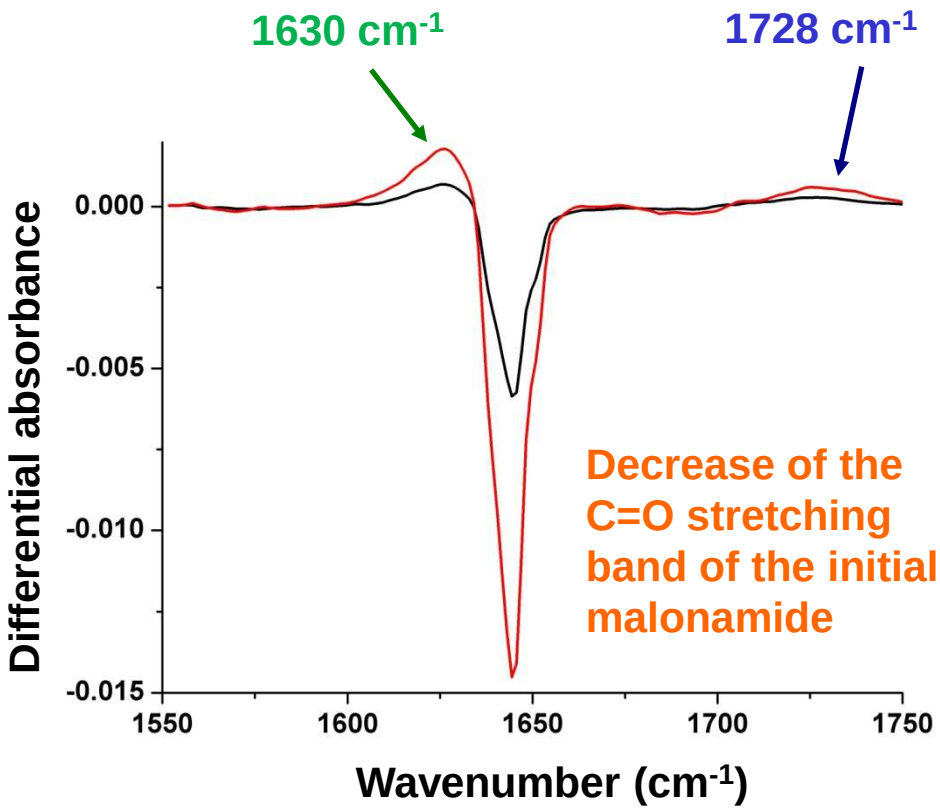


<u>…but also minor lighter compounds</u> resulting from the fragmentation of the initial malonamide

Behaviour of TEMA under irradiation

— 6.8 kGy
— 20.4 kGy

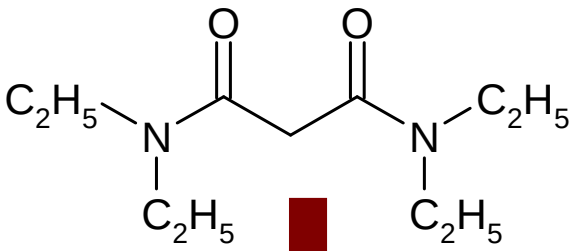
The positive band measured at ~ 1630 cm^{-1} may correspond to a displacement of the C=O stretching vibration which overlaps partly with the main band of the initial product.



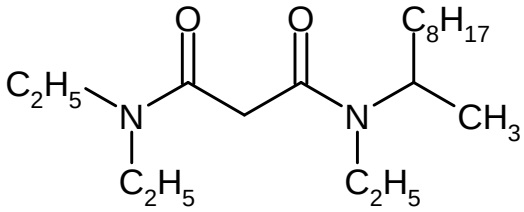
Acid formation resulting from reaction with trace water molecules.

The major processes are recombination reactions. ESI-MS experiments evidence the addition of an octyl group (arising from the solvent).
A band is detected in the spectral region of malonamide which is consistent with the formation of a new malonamide.

Irradiation of TEMA



Major products

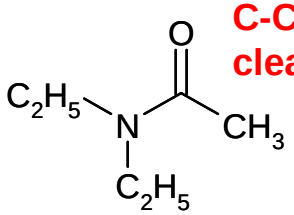


C-H bond cleavage and C_8H_{17} addition

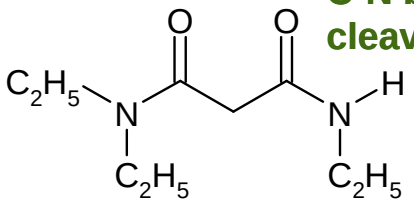
Mostly heavier compounds than the initial malonamide.

Lighter compounds (fragmentation of the molecule)

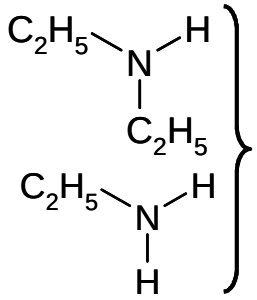
C-C bond cleavage



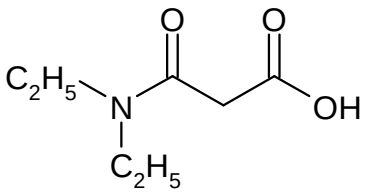
C-N bond cleavage



C-N bond cleavage

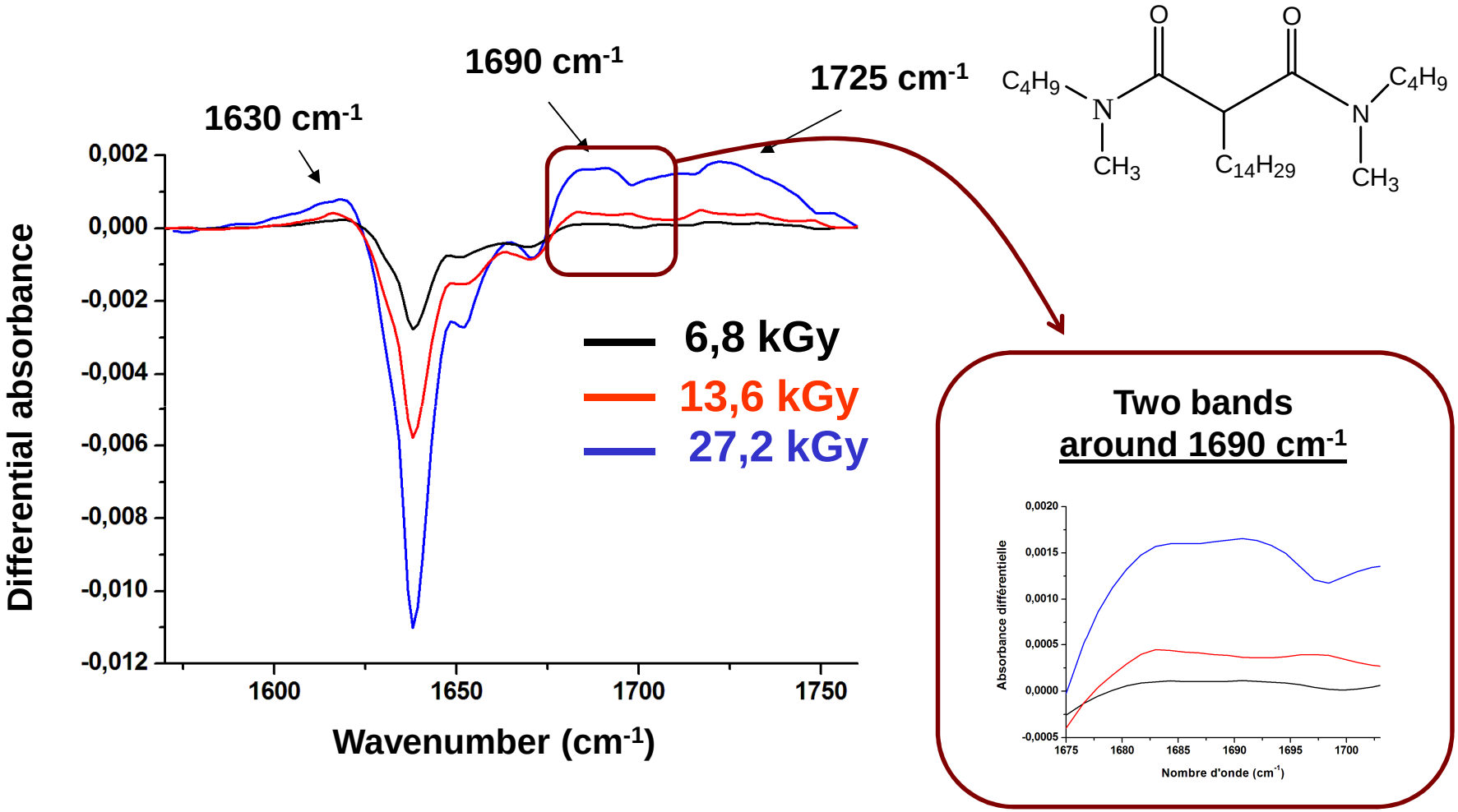


+ C_8H_{16}



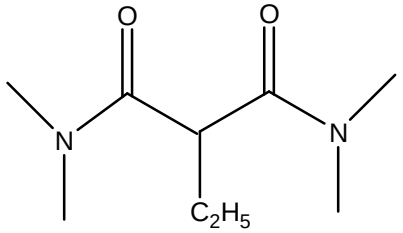
Minor compounds observed by ESI-MS at the higher doses

Behaviour of DMDBTDMA under irradiation: *In situ* detection by infrared spectroscopy

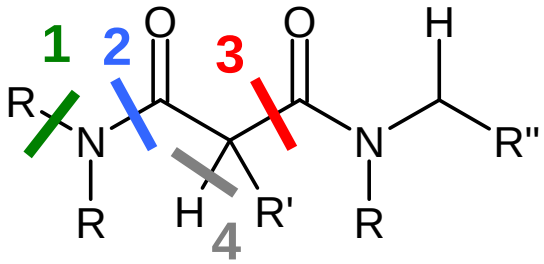


Differential spectra obtained in the case of the radiolysis of DMDBTDMA diluted in octane

Different bond cleavages in a compound similar to DMDBTDMA



G3 (MP2) calculations
Gaussian 03



C-N bond cleavage:

$R_2NCOCHR'CONR_2 \rightarrow R\cdot + \cdot RNCOCHR'CONR_2$ (R1)

$R_2NCOCHR'CONR_2 \rightarrow R_2N\cdot + \cdot COCHR'CONR_2$ (R2)

C-C bond cleavage:

$R_2NCOCHR'CONR_2 \rightarrow R_2NCO\cdot + \cdot CHR'CONR_2$ (R3)

C-C (on the lateral chain) bond cleavage:

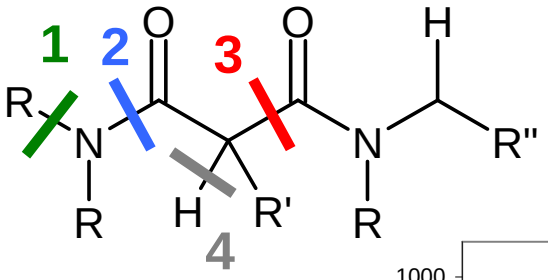
$R_2NCOCHR'CONR_2 \rightarrow R'\cdot + R_2NCOCH\cdot CONR_2$ (R4)

with R = CH_3
R' = C_2H_5

Bond dissociation energy	Reaction 1 ($kJ.mol^{-1}$)	Reaction 2 ($kJ.mol^{-1}$)	Reaction 3 ($kJ.mol^{-1}$)	Reaction 4 ($kJ.mol^{-1}$)
	373	**385**	**339**	**354**

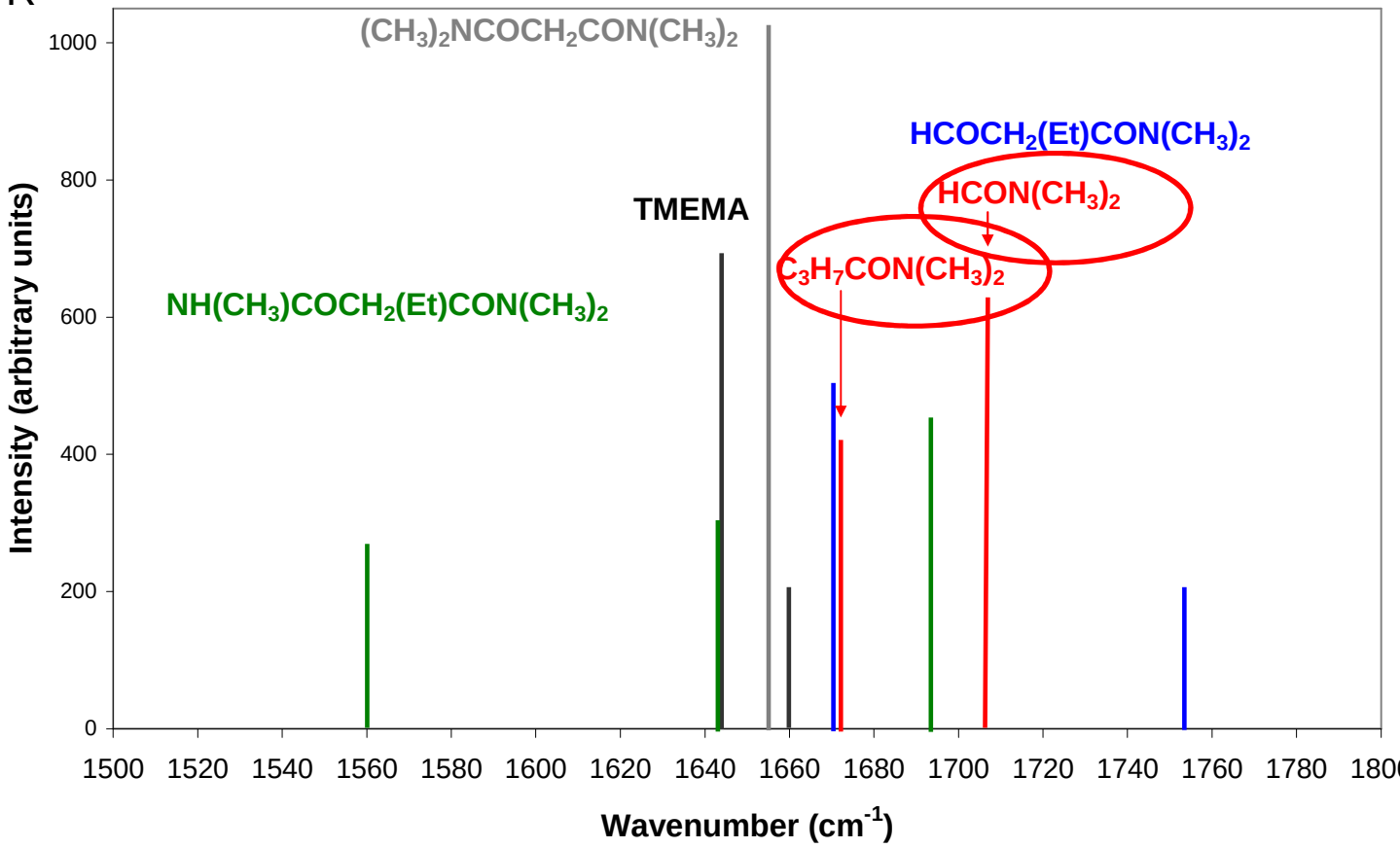
The cleavage of the C-C bond is thermodynamically more favorable than the other bond cleavages. The C-C bond is weakened as compared to the TEMA case (362 $kJ.mol^{-1}$).

Assignment of the observed IR bands



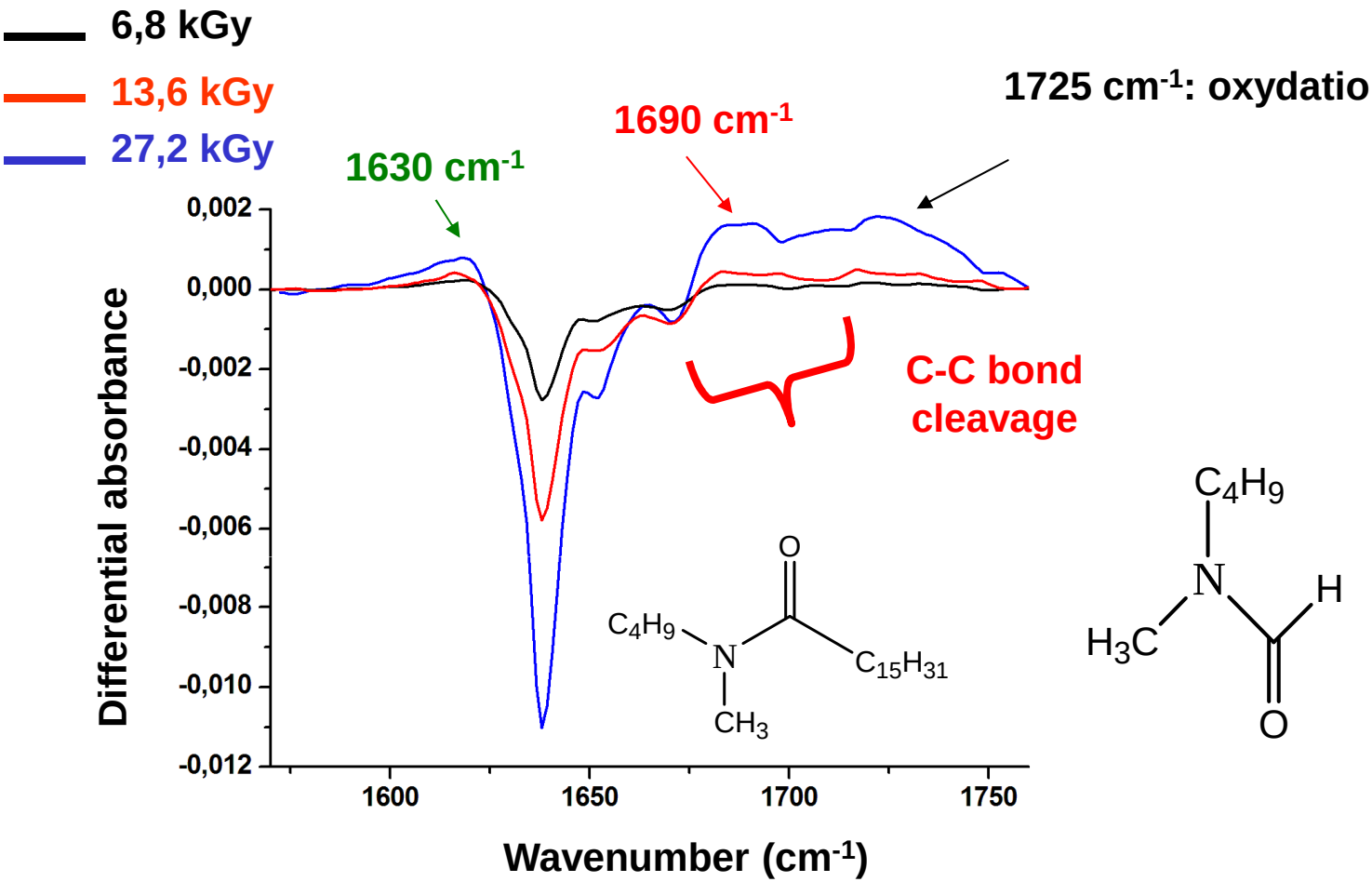
The experimental bands are observed at 1630, 1690 and 1725 cm^{-1} in the 1500-1800 cm^{-1} spectral range.

Simulating the IR bands by quantum chemistry calculations:



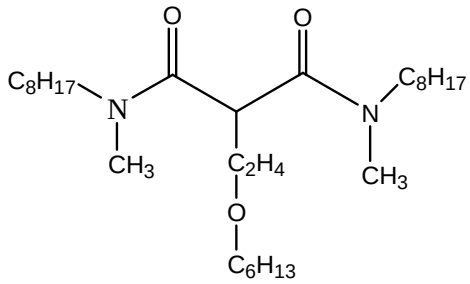
The C-C bond cleavage enables to describe the experimental IR spectra around 1690 cm^{-1}.

Behaviour of DMDBTDMA under irradiation



The 1630 cm^{-1} band can result in the overlap between malonamides formed upon irradiation and the disappearance of the initial DMDBTDMA.

Behaviour of DMDOHEMA under irradiation

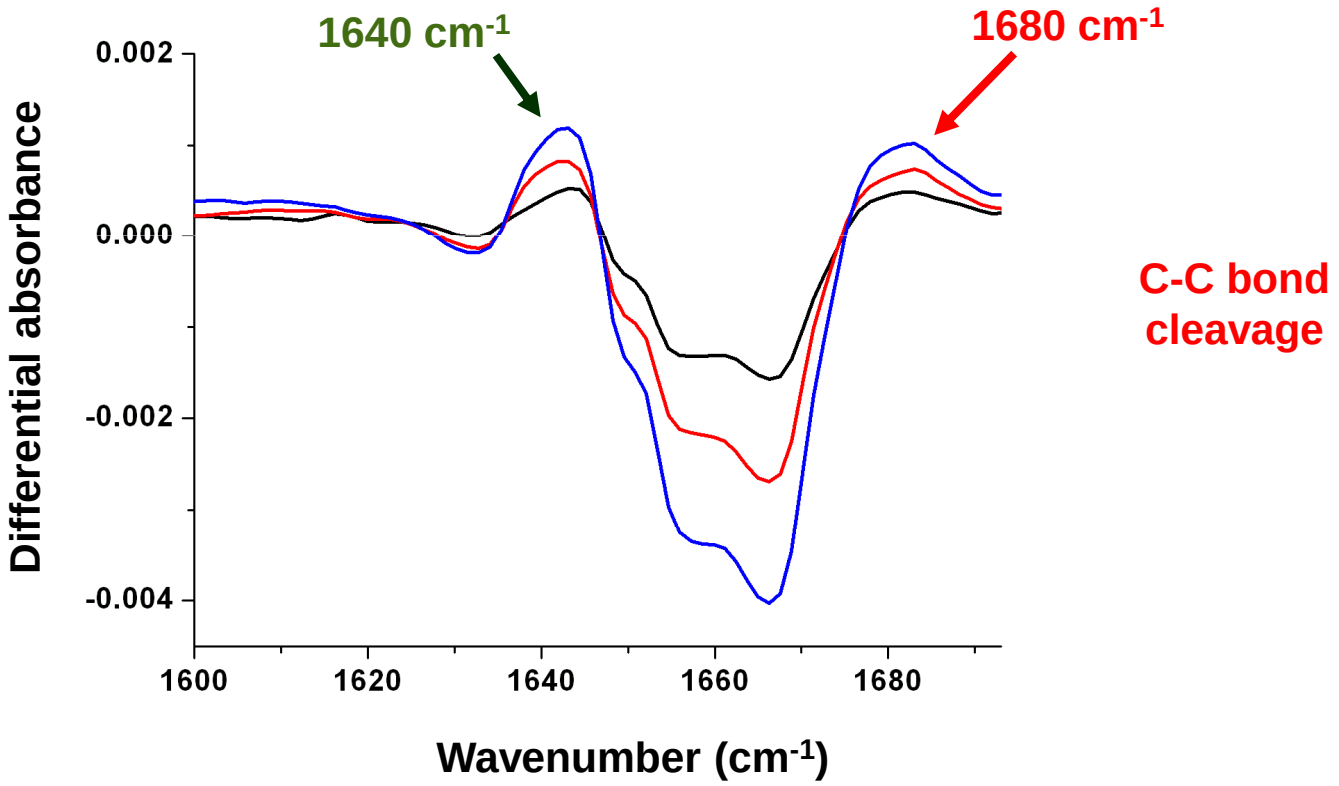


Band resulting from the overlap between malonamides formed upon irradiation and the disappearance of the initial DMDBTDMA.

13,6 kGy

20,4 kGy

34 kGy



C-C bond cleavage

Also ether bond cleavage

Conclusions

● **In situ infrared experiments have enabled to track the reactivity of malonamides under irradiation.** The spectral modifications observed have been explained by means of quantum chemistry calculations and also with the help of ESI-MS experiments.

● Even if the behaviour of malonamides under irradiation is complex, it is possible to evidence a different behaviour according to the structure of the malonamide:

► in the case of TEMA, the major channel is a recombination reaction.

► in the other cases, we observe the preferential cleavage of the central C-C bond, which is consistent with the smallest bond energy calculated: the central C-C bond is weakened as compared to TEMA.

Outlook: to go into the study of reaction mechanisms **with *in situ* time-resolved experiments.**

See poster by Manjusha Shirdonkhar