

Supplement A:

**ESI(+)/TOF, HPLC/ESI(+)/TOF and ESI(+)/Q-TOF experiments:
Mass spectra and chromatograms**

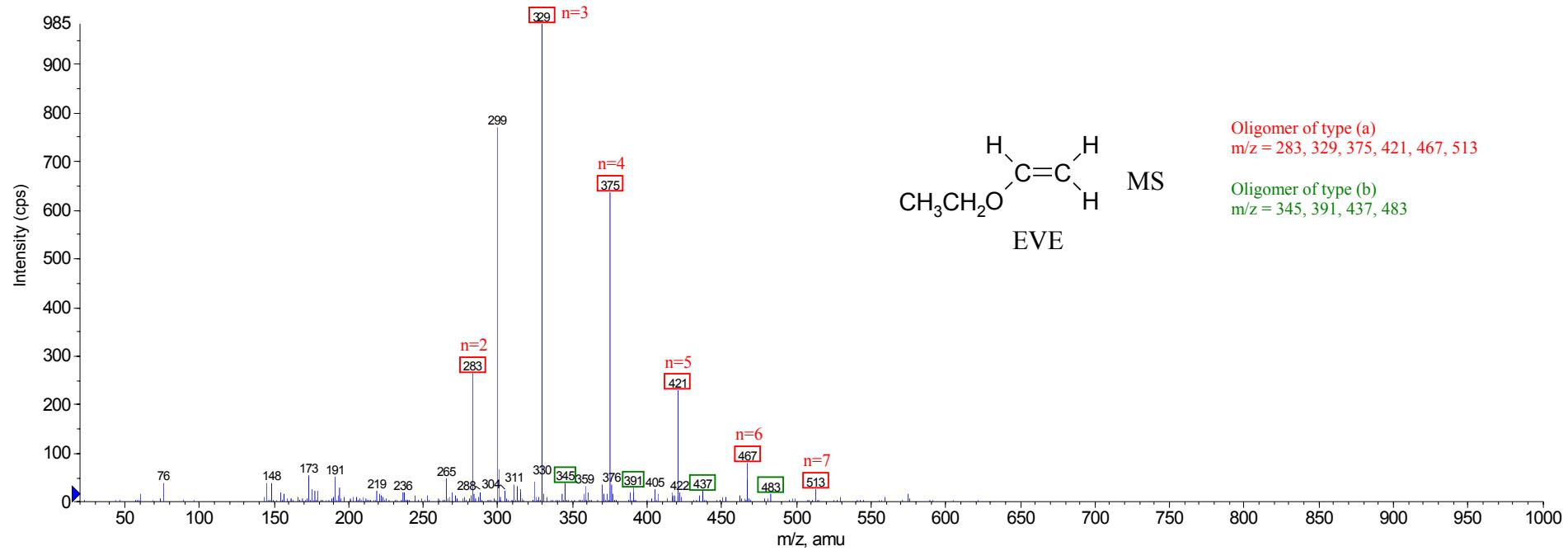


Figure A.1a: ESI(+)MS-TOF mass spectrum of SOA formed during the gas-phase ozonolysis of ethyl vinyl ether (EVE) (initial mixing ratios: 8 ppm ozone, 9 ppm EVE).

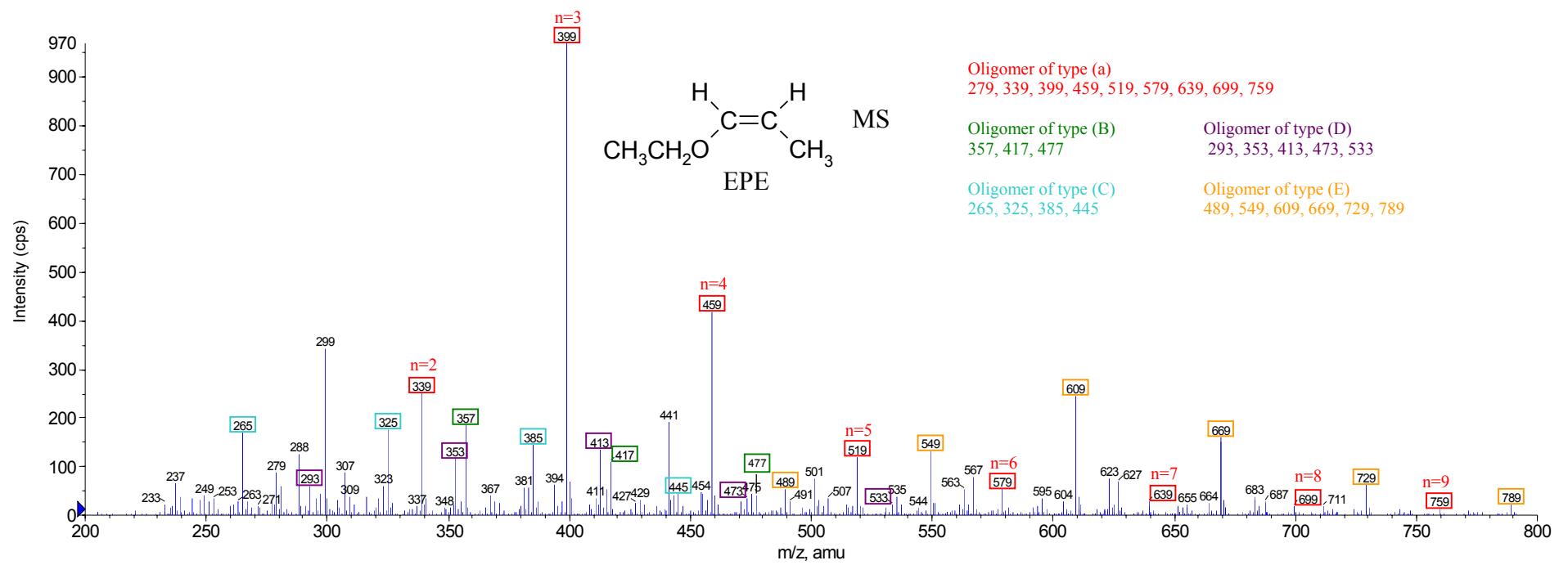


Figure A.1b: ESI(+)/MS-TOF mass spectrum of SOA formed during the gas-phase ozonolysis of ethyl propenyl ether (EPE) (initial mixing ratios: 8 ppm ozone, 9 ppm EPE).

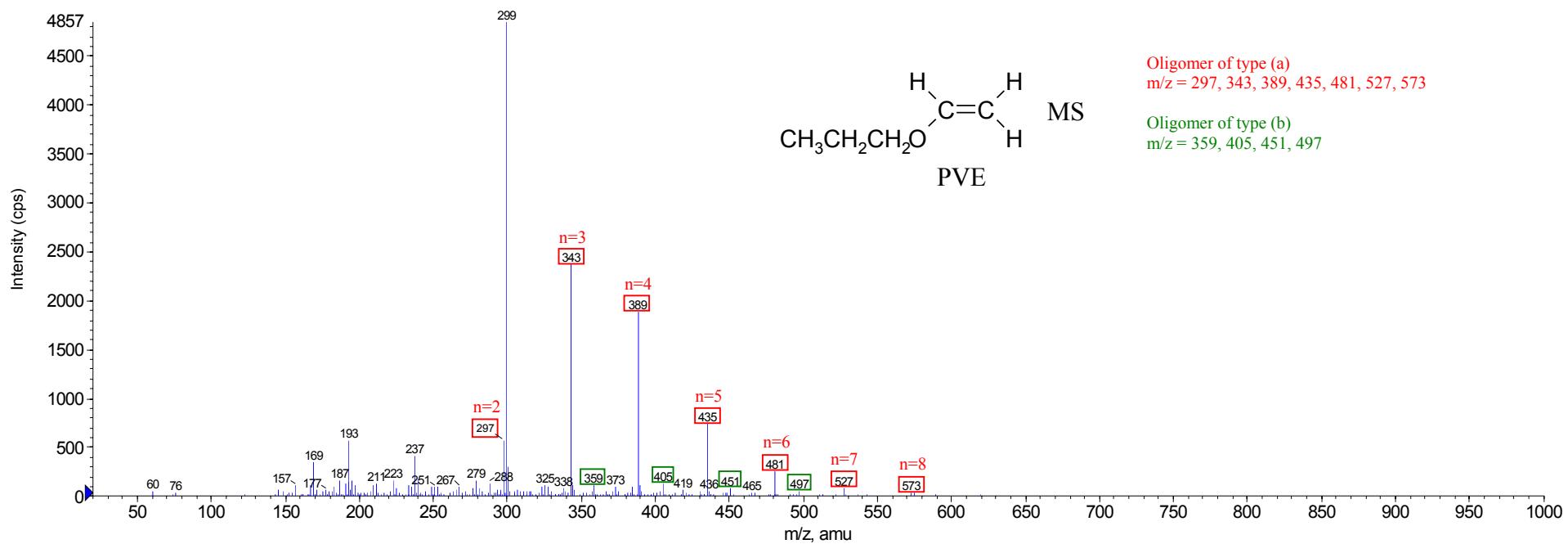


Figure A.1c: ESI(+)MS-TOF mass spectrum of SOA formed during the gas-phase ozonolysis of propyl vinyl ether (PVE) (initial mixing ratios: 8 ppm ozone, 9 ppm PVE).

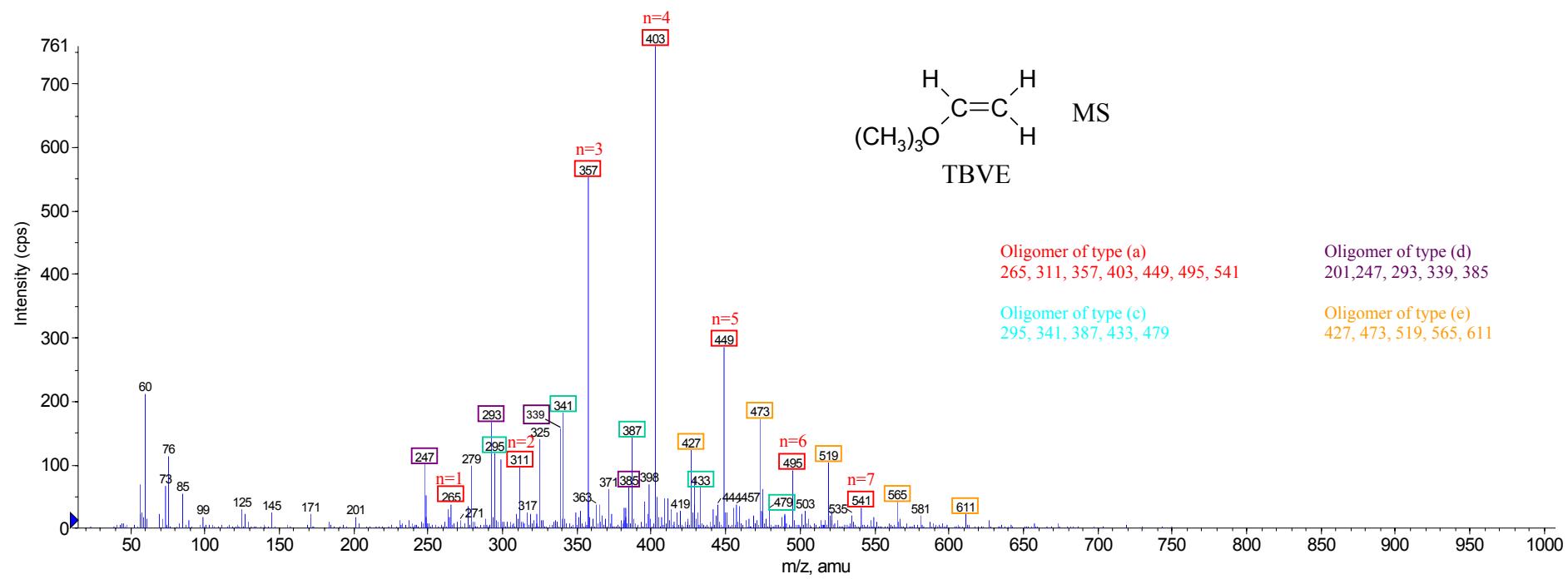


Figure A.1d: ESI(+)MS-TOF mass spectrum of SOA formed during the gas-phase ozonolysis of tertiary butyl vinyl ether (TBVE) (initial mixing ratios: 8 ppm ozone, 9 ppm TBVE).

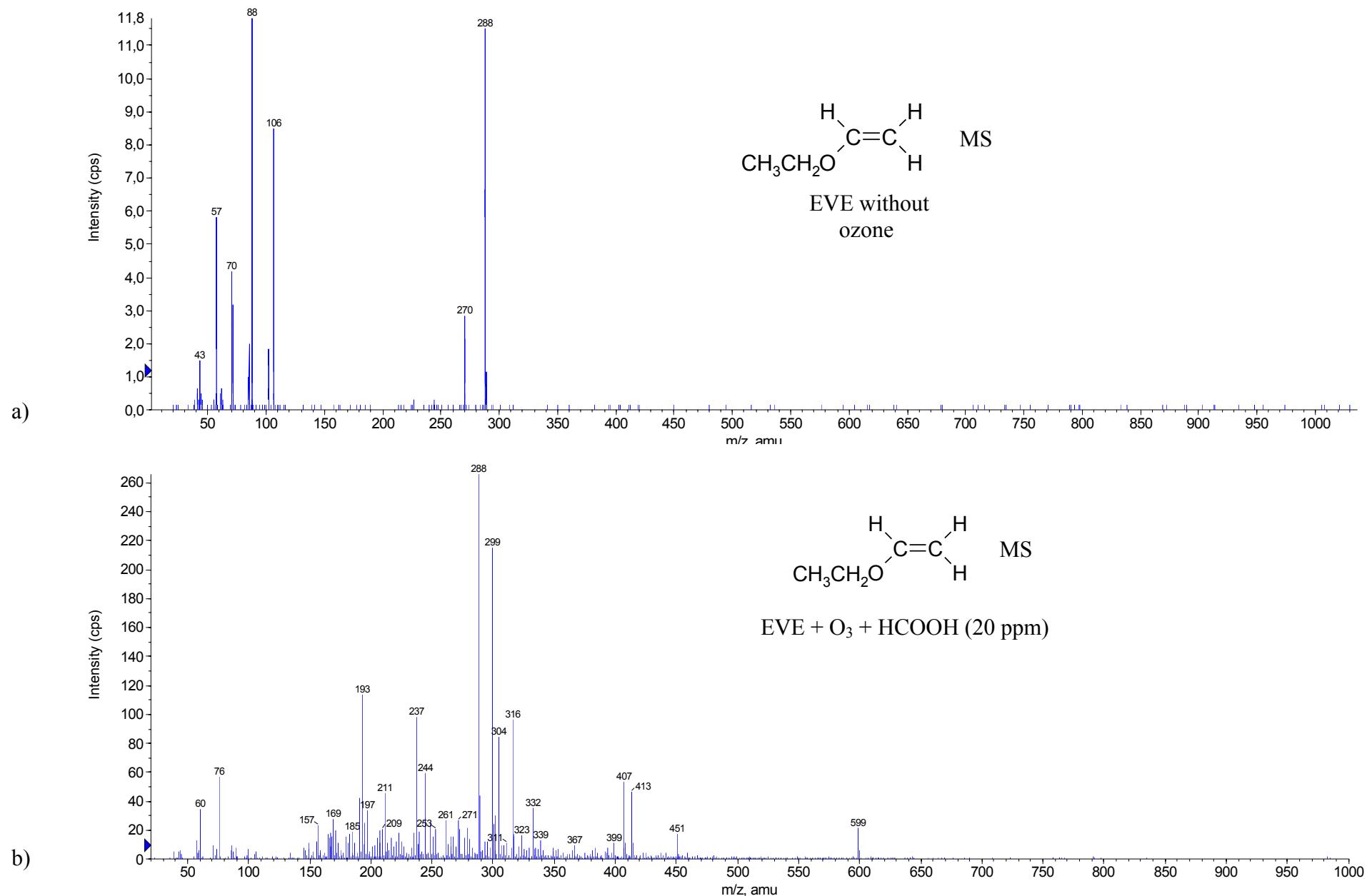


Figure A.2: MS spectra of filter samples from background experiments: a) 9 ppm of EVE introduced in the reactor without ozone b) Reaction of EVE (9 ppm) and O_3 (8 ppm) with addition of a 20 ppm of HCOOH to the mixture (Reduction of the SOA yield to less than $1 \mu\text{g}/\text{m}^3$)

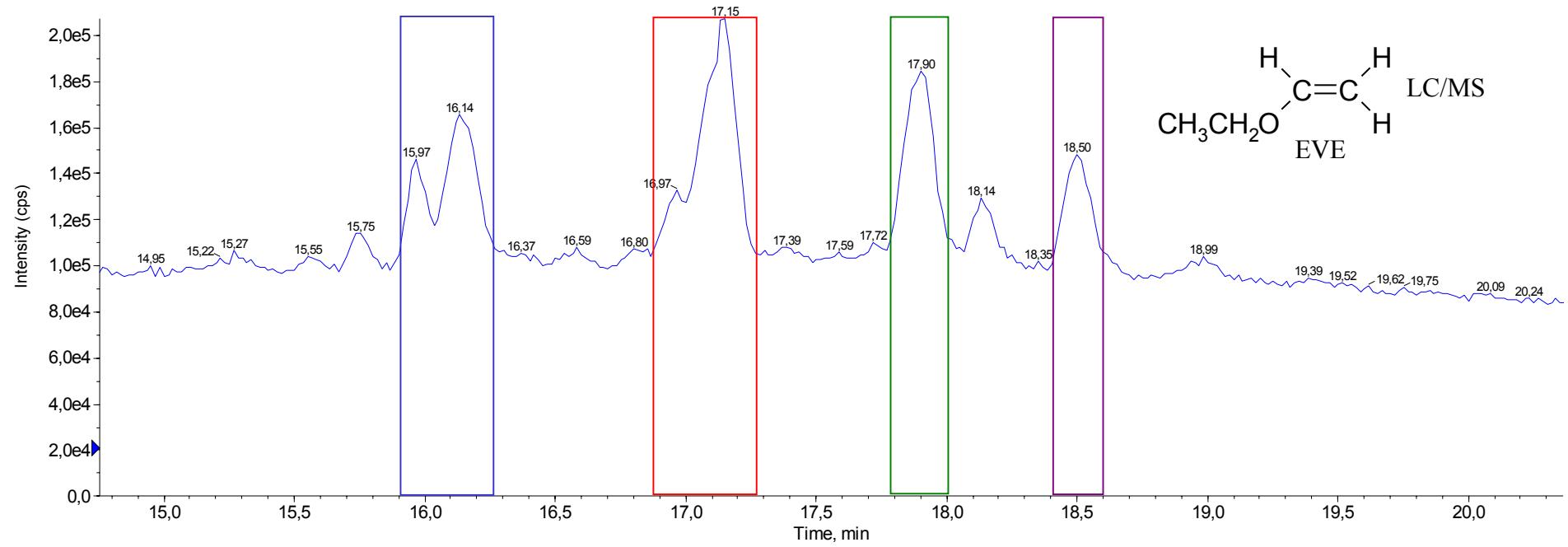


Figure A.3a: TIC (total ion current) chromatogram of SOA formed during ozonolysis of EVE (initial mixing ratios: 8 ppm ozone, 9 ppm EVE): Chromatographic peaks in different retention time (RT) zones surrounded with different colours contain an intense pseudomolecular ion signal of oligomer (a) with $m/z = 329$ (blue-marked zone, RT = 16 min), 375 (red-marked zone, RT = 17 min), 421 (green-marked zone, RT = 17.9 min) and 467 (violet-marked zone, RT = 18.5 min), respectively, and a less intense pseudomolecular ion of oligomer (b) with $m/z = 345$ (blue-marked zone, RT = 16 min), 391 (red-marked zone, RT = 17 min), 437 (green-marked zone, RT = 17.9 min) and 483 (violet-marked zone, RT = 18.5 min), respectively, as shown in Figure S.3b.

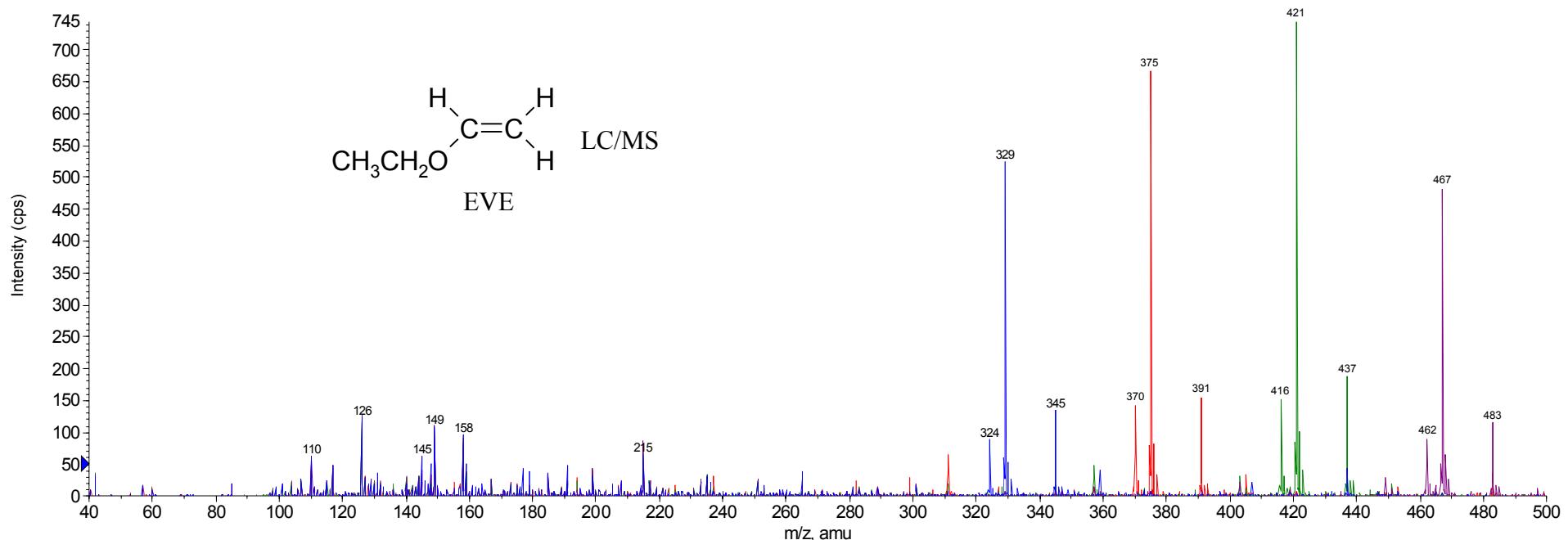


Figure A.3b: SOA formed during ozonolysis of EVE (initial mixing ratios: 8 ppm ozone, 9 ppm EVE):

Overlaid MS spectra of the retention time (RT) zones visible in the TIC chromatogram in figure S.3a marked with the corresponding colours. The strong ion peaks with $m/z = 329$ (blue-marked zone, RT = 16 min), 375 (red-marked zone, RT = 17 min), 421 (green-marked zone, RT = 17.9 min) and 467 (violet-marked zone, RT = 18.5 min) represent each a molecule of the oligomer of type (a), and the weaker ion peaks with $m/z = 345$ (blue-marked zone, RT = 16 min), 391 (red-marked zone, RT = 17 min), 437 (green-marked zone, RT = 17.9 min) and 483 (violet-marked zone, RT = 18.5 min) represent each an oligomer molecule of type (b).

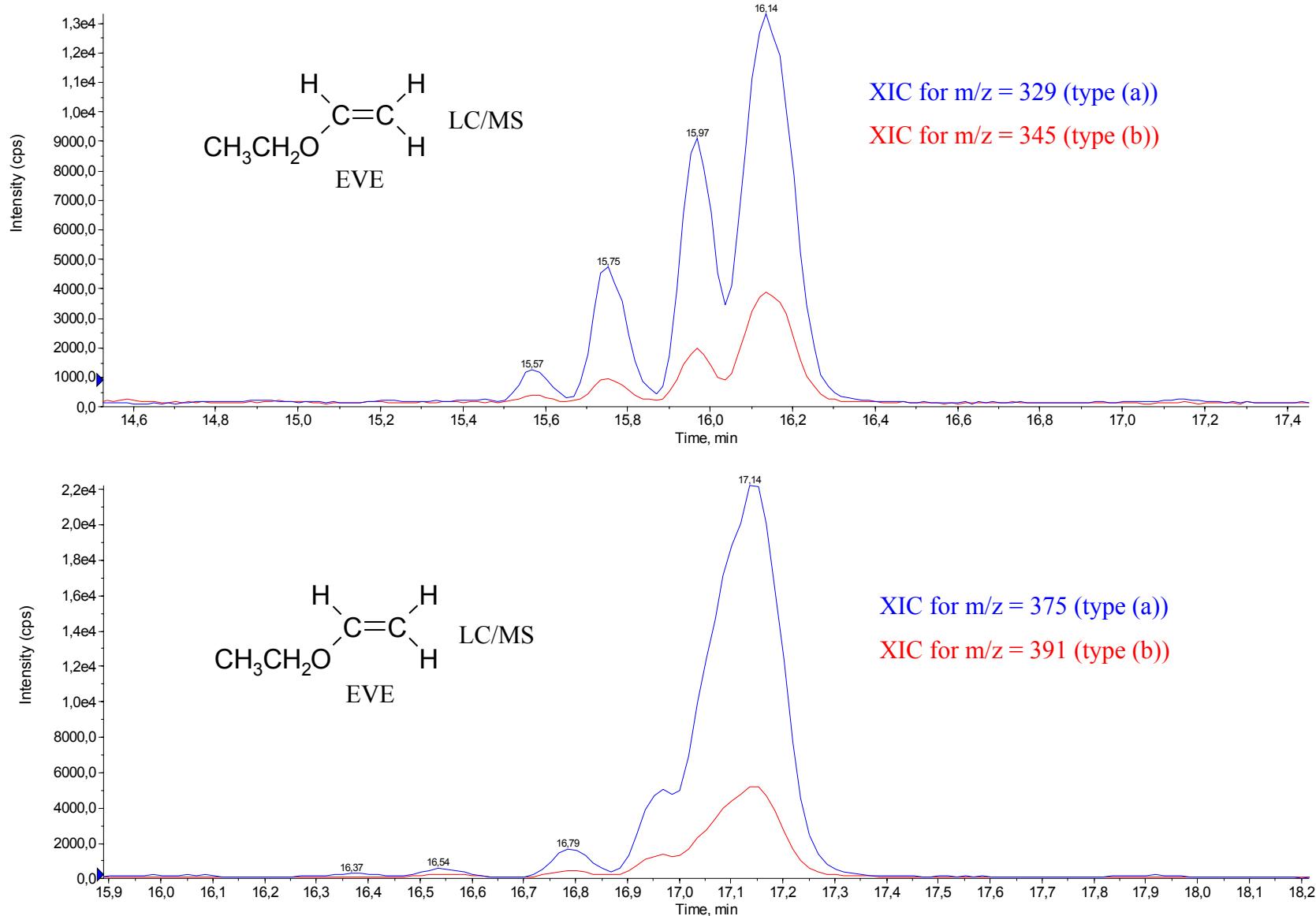


Figure A.3c: SOA formed during ozonolysis of EVE (initial mixing ratios: 8 ppm ozone, 9 ppm EVE): XIC (eXtracted Ion Current) chromatogram from the TIC chromatogram shown in Figure S.3a for the pseudomolecular ions 329 and 375 (type (a)) as well as 345 and 391 (type(b)).

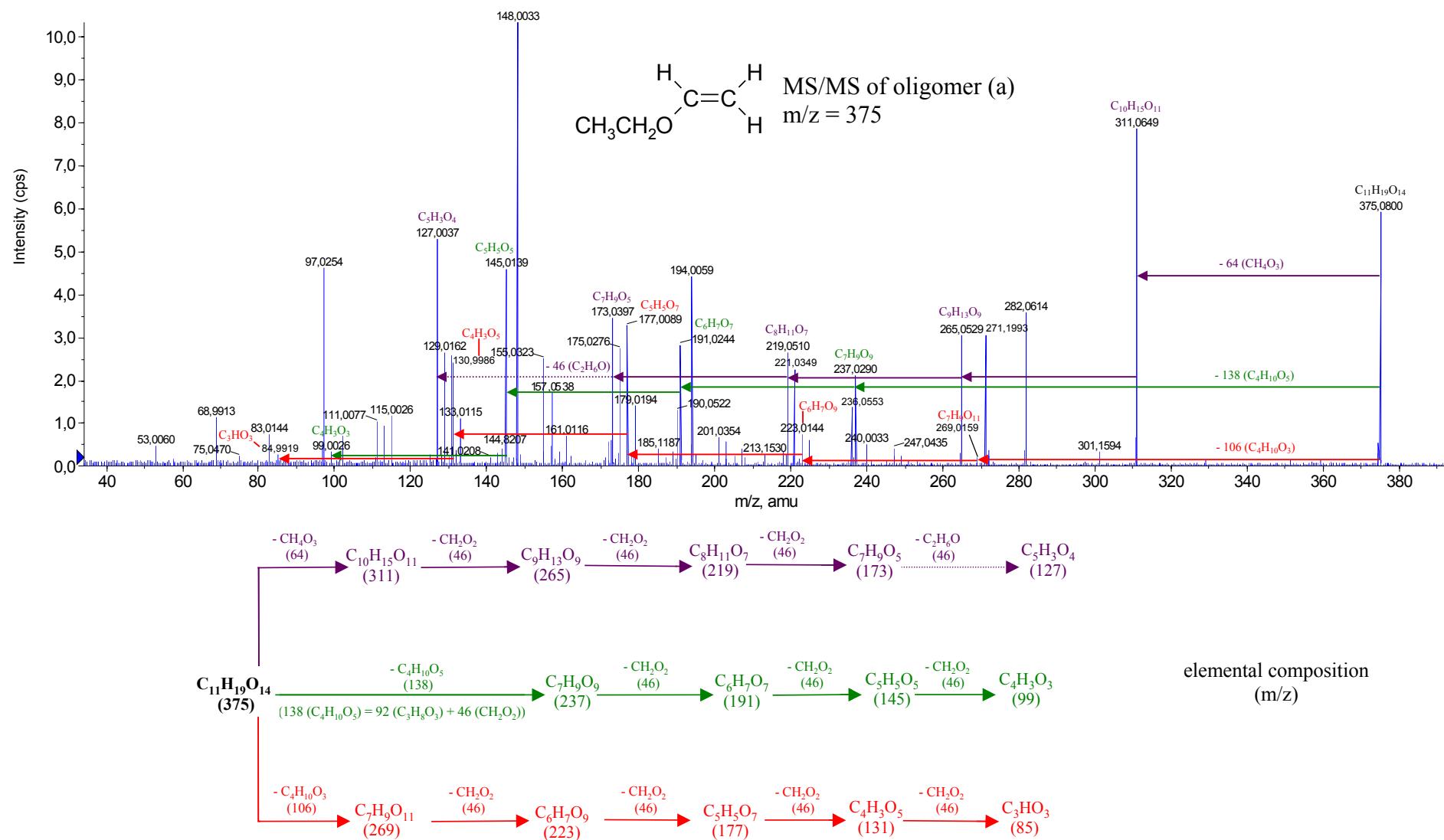


Figure A.4a: SOA formed from ozonolysis of ethyl vinyl ether EVE (initial mixing ratios: 8 ppm ozone, 9 ppm EVE): MS/MS spectrum of the parent ion $m/z = 375$ of oligomer (a). Three fragmentation pathways consisting of successive losses of the chain unit as neutral mass 46 are marked in violet, red and green colours in the MS/MS spectrum and are schematically represented in the bottom section of this figure.

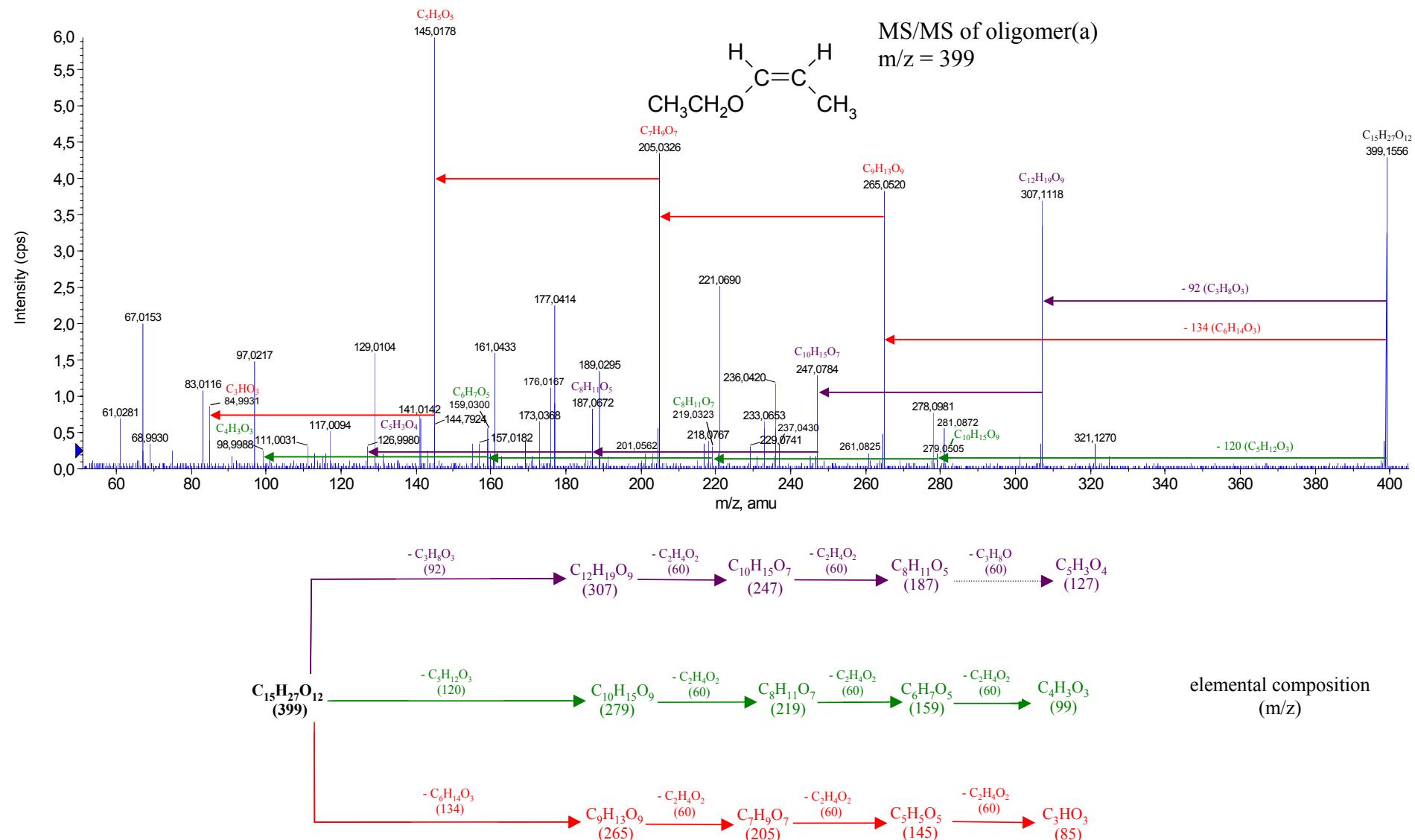


Figure A.4b: SOA formed from ozonolysis of ethyl propenyl ether EPE (initial mixing ratios: 8 ppm ozone, 9 ppm EPE): MS/MS spectrum of the parent ion m/z = 399 of oligomer (a). Three fragmentation pathways consisting of successive losses of the chain unit as neutral mass 60 are marked in violet, red and green colours in the MS/MS spectrum and are schematically represented in the bottom section of this figure.

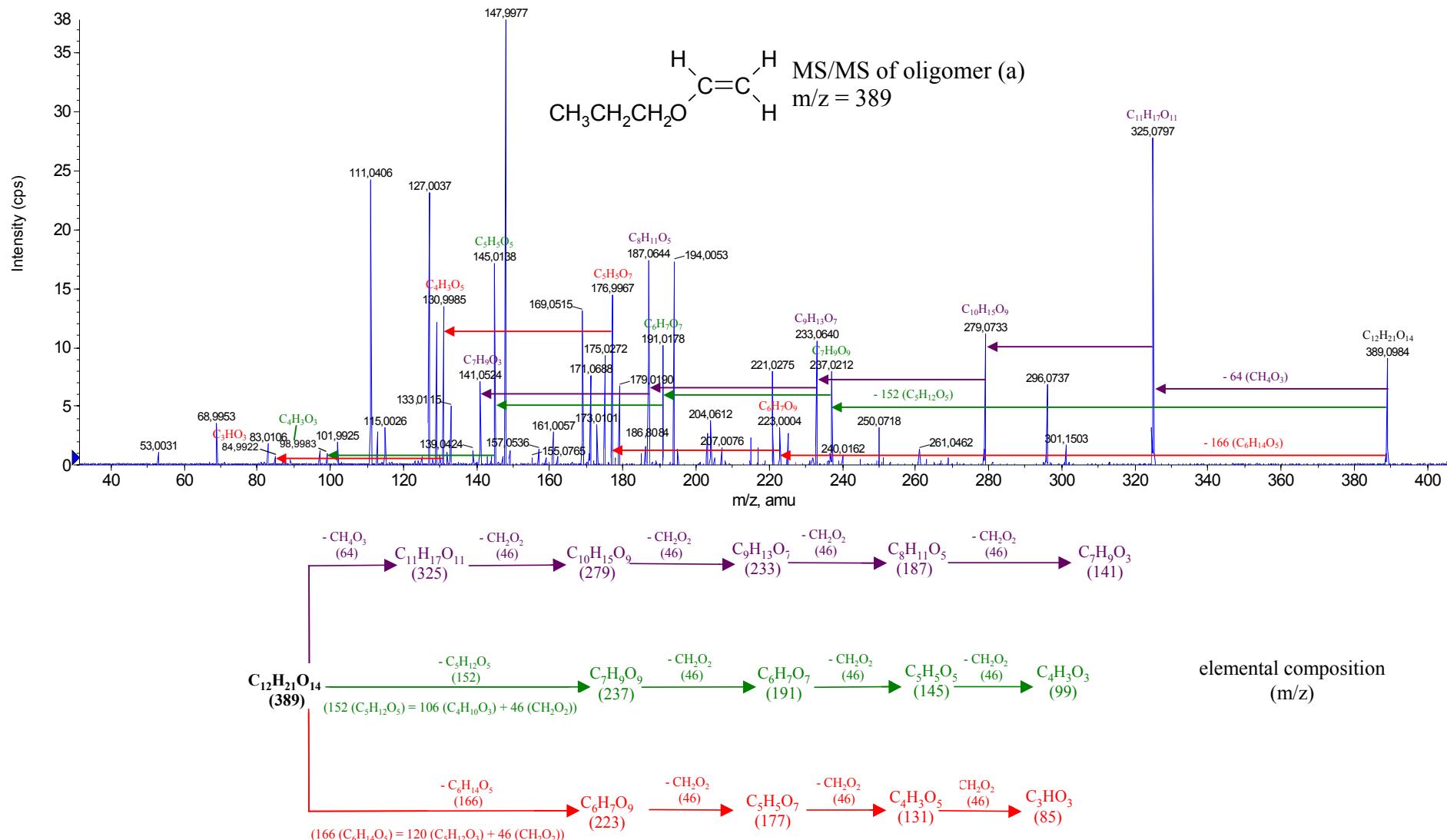


Figure A.4c: SOA formed from ozonolysis of propyl vinyl ether PVE (initial mixing ratios: 8 ppm ozone, 9 ppm PVE): MS/MS spectrum of the parent ion m/z = 389 of oligomer (a). Three fragmentation pathways consisting of successive losses of the chain unit as neutral mass 46 are marked in violet, red and green colours in the MS/MS spectrum and are schematically represented in the bottom section of this figure.

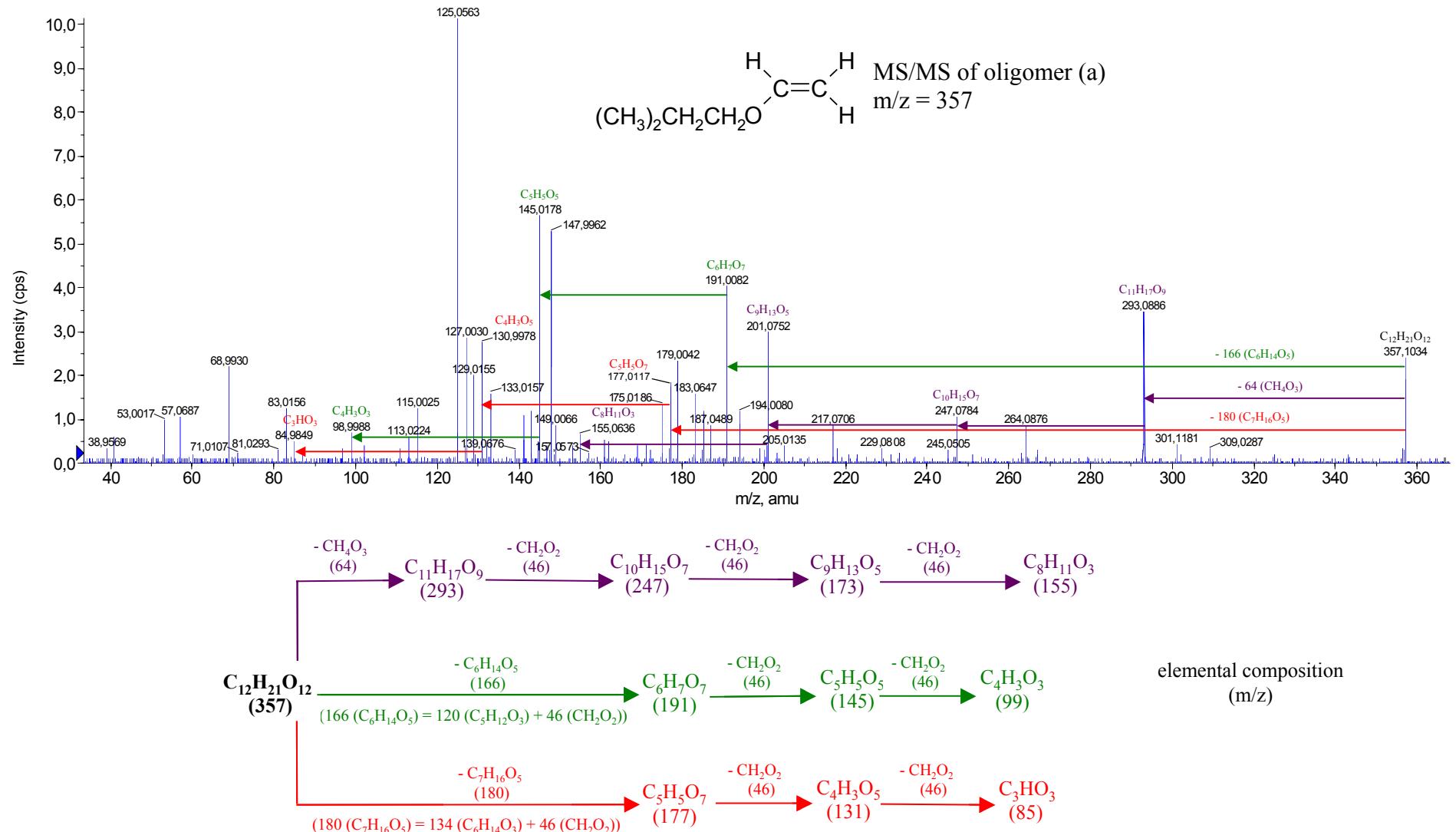


Figure A.4d: SOA formed from ozonolysis of isobutyl vinyl ether IBVE (initial mixing ratios: 8 ppm ozone, 9 ppm IBVE): MS/MS spectrum of the parent ion $m/z = 357$ of oligomer (a). Three fragmentation pathways consisting of successive losses of the chain unit as neutral mass 46 are marked in violet, red and green colours in the MS/MS spectrum and are schematically represented in the bottom section of this figure.