Electronic Supplementary Material

Analytical and Bioanalytical Chemistry

High-precision frequency measurements: indispensable tools at the core of the molecular-level analysis of complex systems

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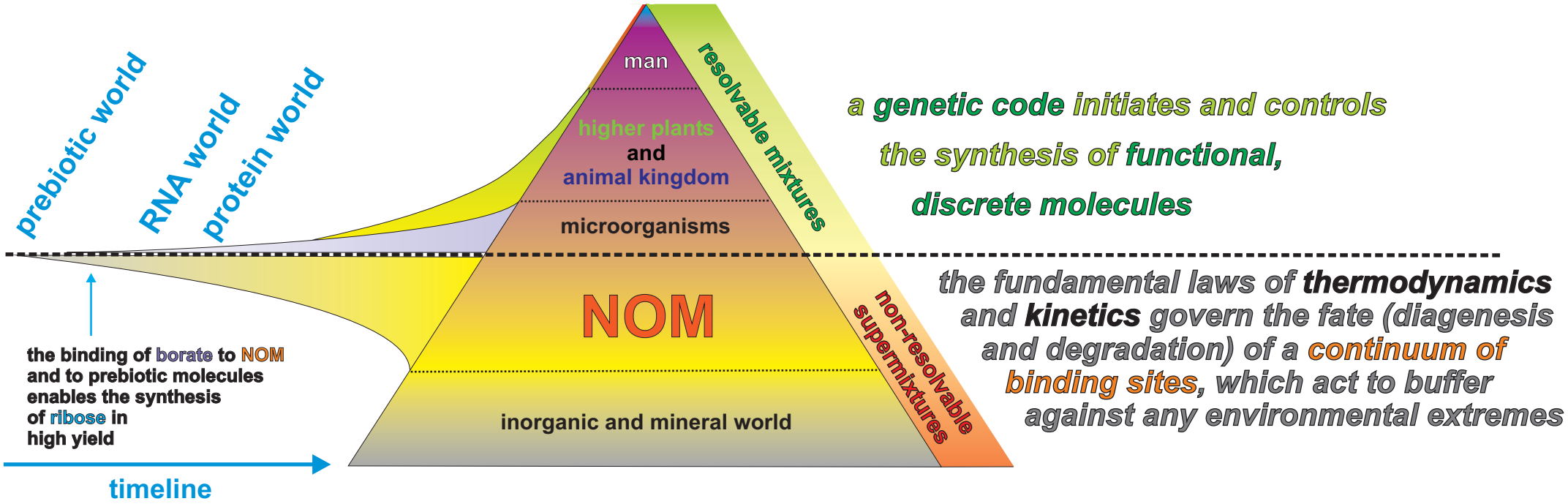
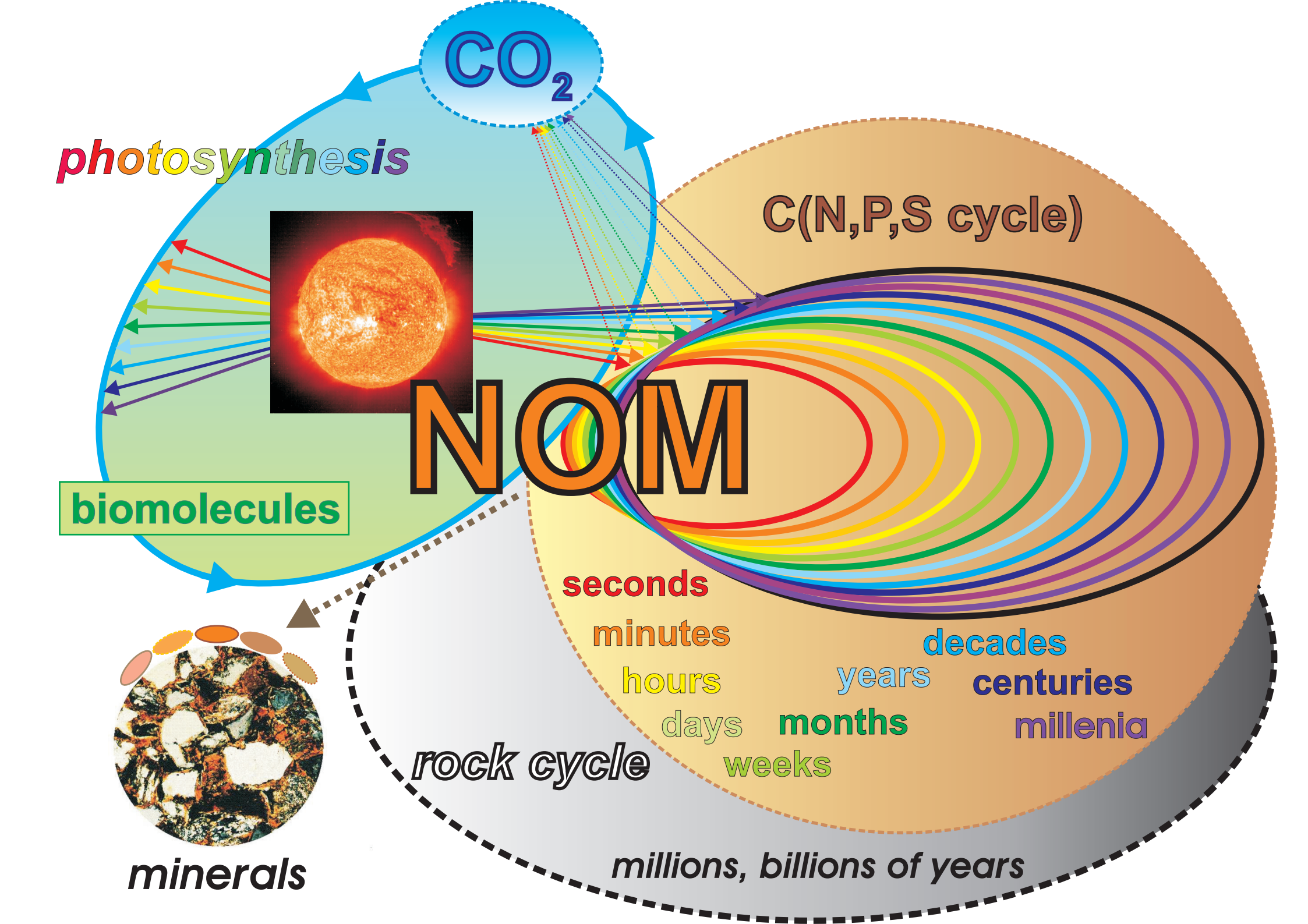
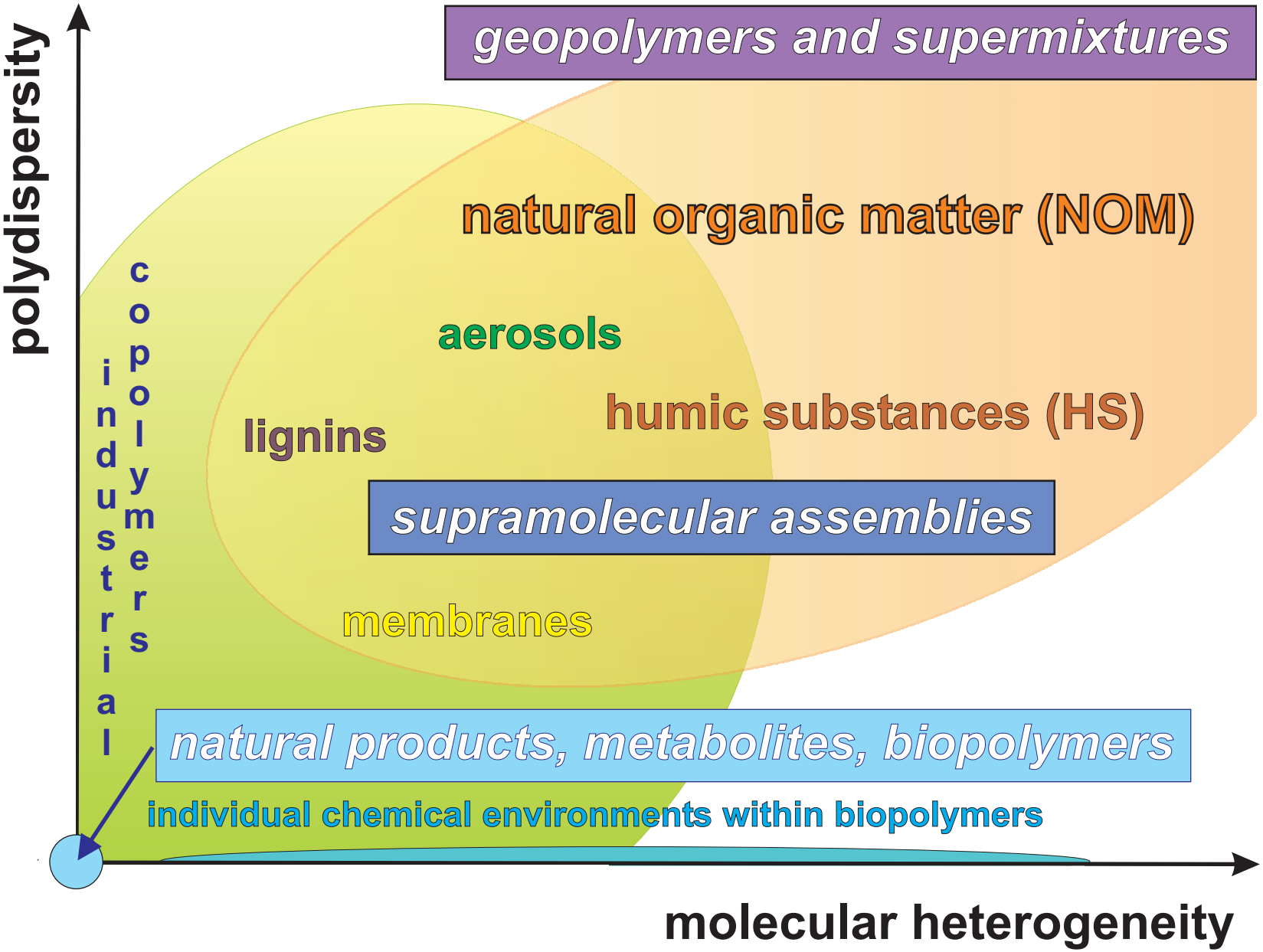
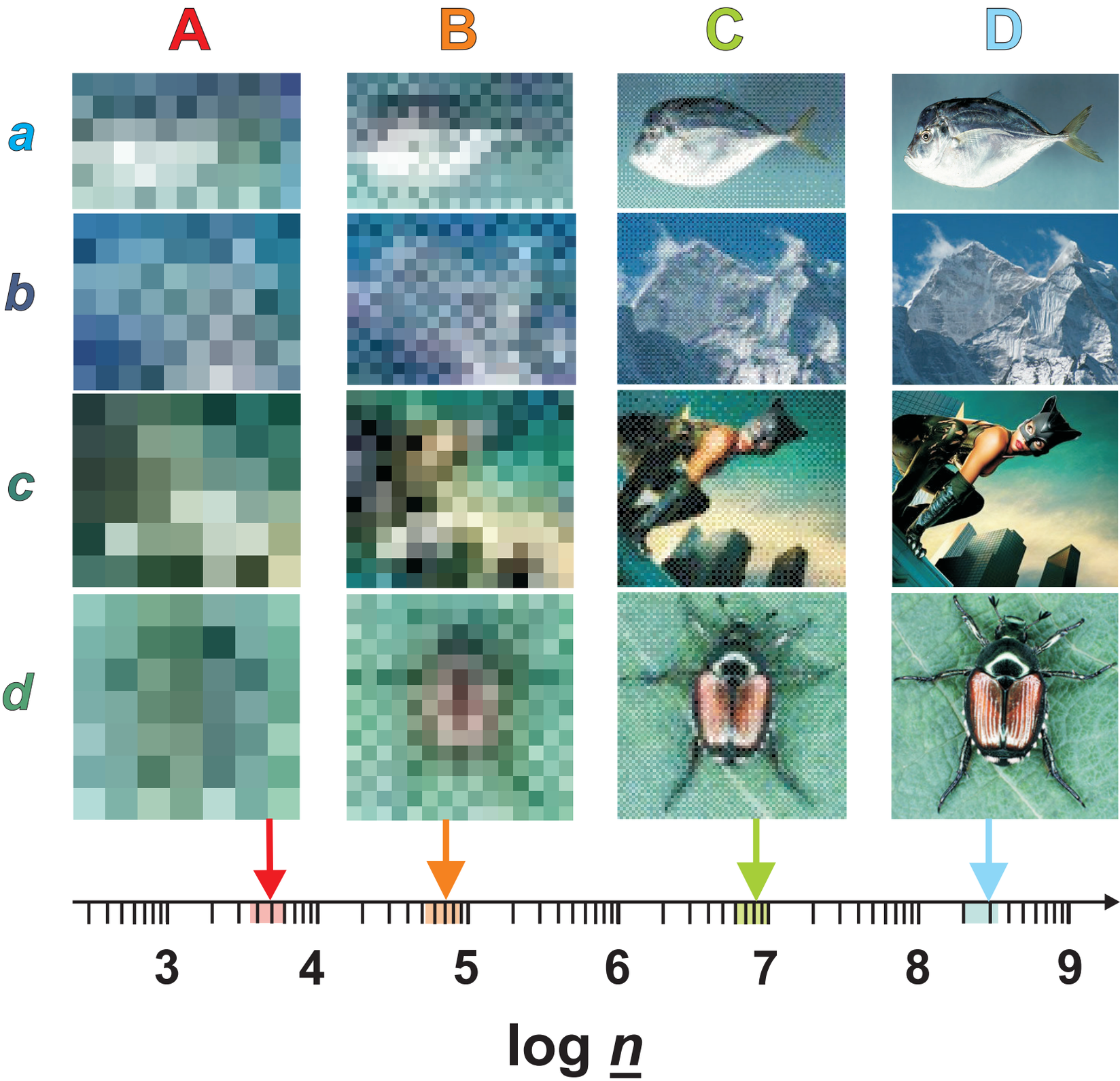
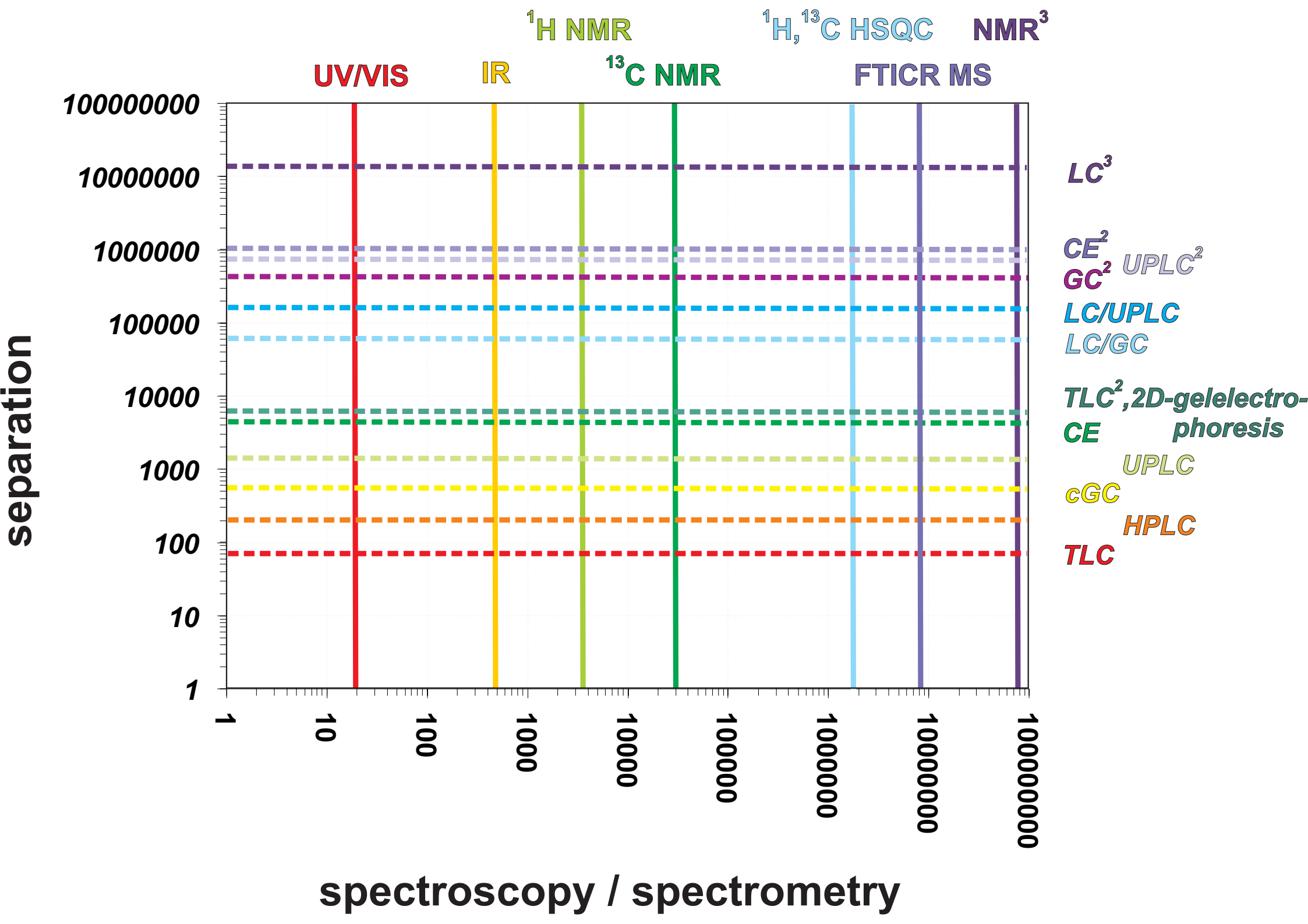
The authors have provided high resolution images of the figures of this article. They are available as supplementary material to authorized users.


prebiotic world
RNA world
protein world
man
higher plants
and
animal kingdom
microorganisms
NOM
inorganic and mineral world
resolvable mixtures
non-resolvable
supermixtures
a genetic code initiates and controls
the synthesis of functional,
discrete molecules
the fundamental laws of thermodynamics
and kinetics govern the fate (diagenesis
and degradation) of a continuum of
binding sites, which act to buffer
against any environmental extremes
the binding of borate to NOM
and to prebiotic molecules
enables the synthesis
of ribose in
high yield
timeline

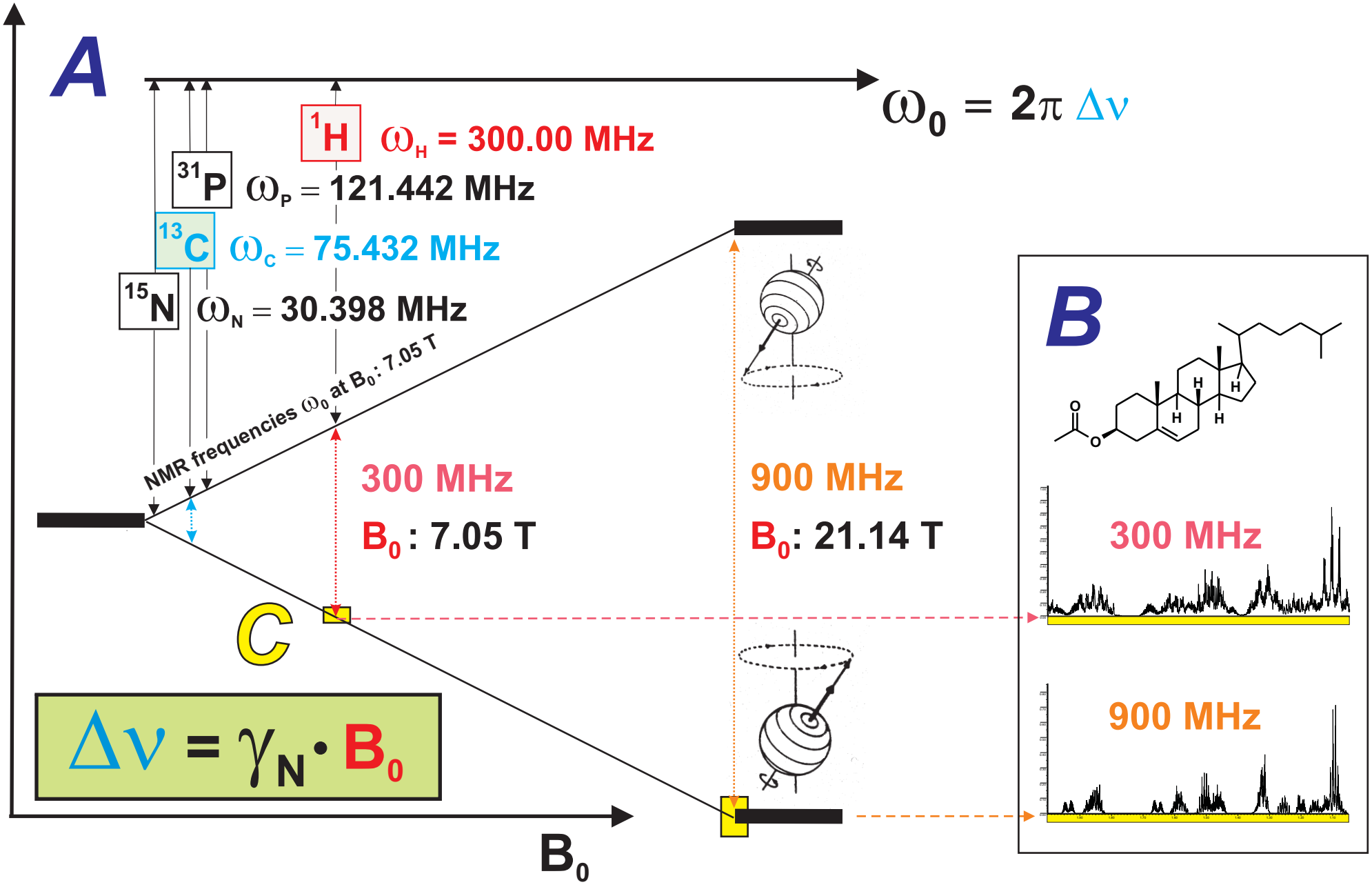

CO_2
photosynthesis
C(N,P,S cycle)
NOM
biomolecules
seconds
minutes
hours
days
weeks
months
years
decades
centuries
millenia
rock cycle
minerals
millions, billions of years

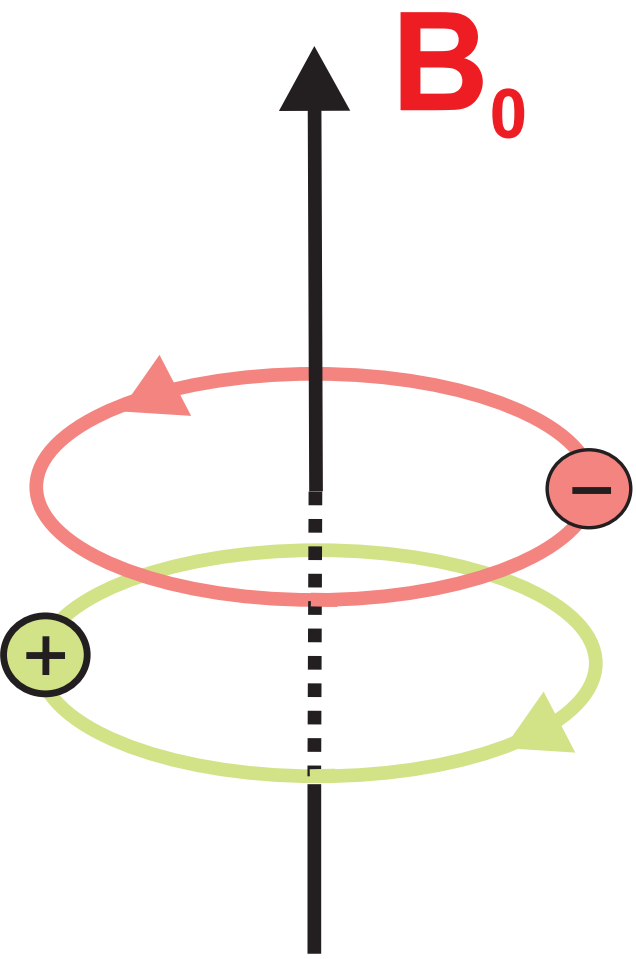

polydispersity
geopolymers and supermixtures
natural organic matter (NOM)
aerosols
humic substances (HS)
lignins
supramolecular assemblies
membranes
industrial copolymers
natural products, metabolites, biopolymers
individual chemical environments within biopolymers
molecular heterogeneity


A
B
C
D
a
b
c
d
3
4
5
6
7
8
9
log n


^{1}H NMR
^{1}H, ^{13}C HSQC
NMR^{3}
UV/VIS
IR
^{13}C NMR
FTICR MS
100000000
10000000
1000000
100000
10000
1000
100
10
1
separation
LC^{3}
CE^{2}
GC^{2}
UPLC^{2}
LC/UPLC
LC/GC
TLC^{2},2D-gelelectro-
CE
phoresis
UPLC
cGC
HPLC
TLC
1
10
100
1000
10000
100000
1000000
10000000
spectroscopy / spectrometry

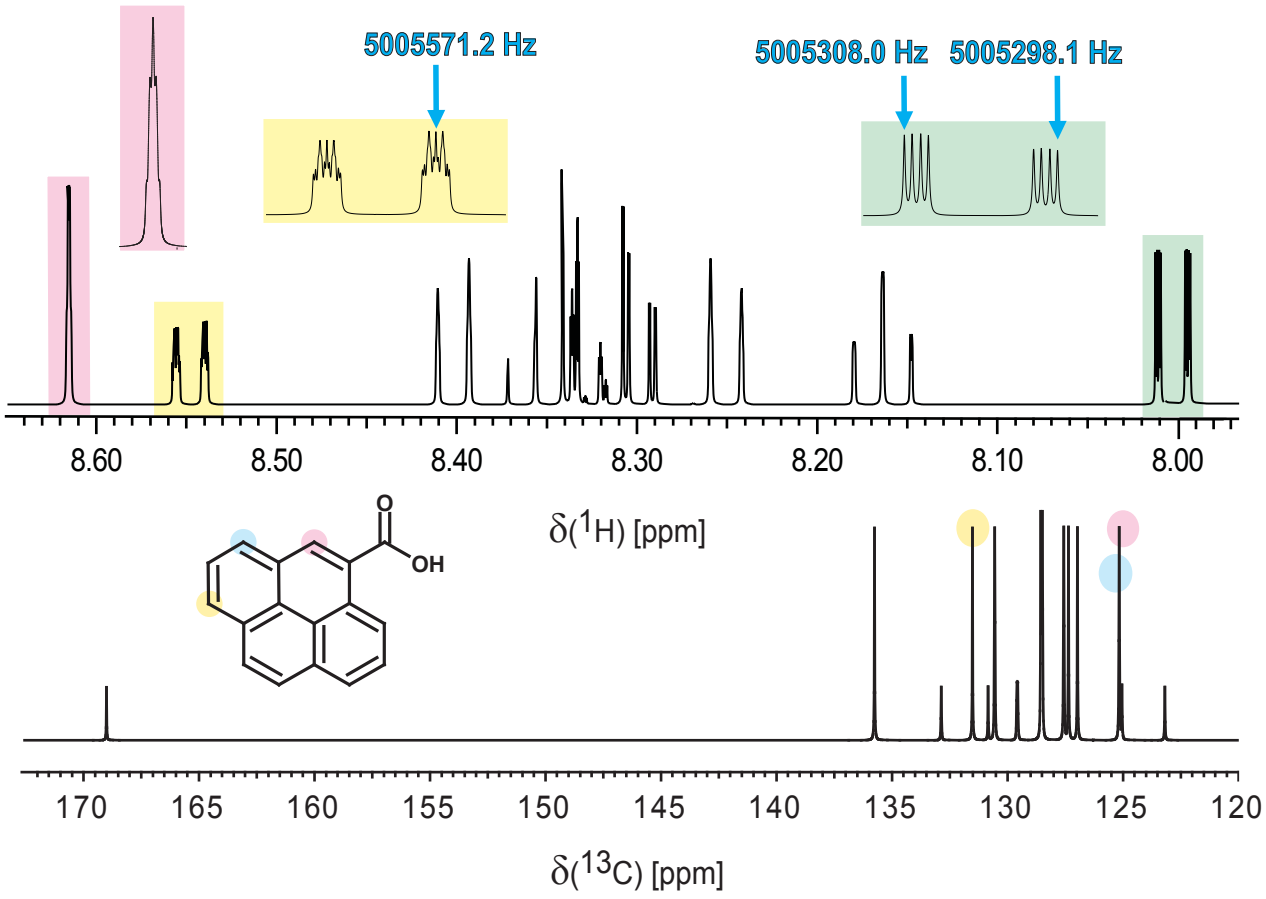
$\Delta E = h\,\Delta\nu$

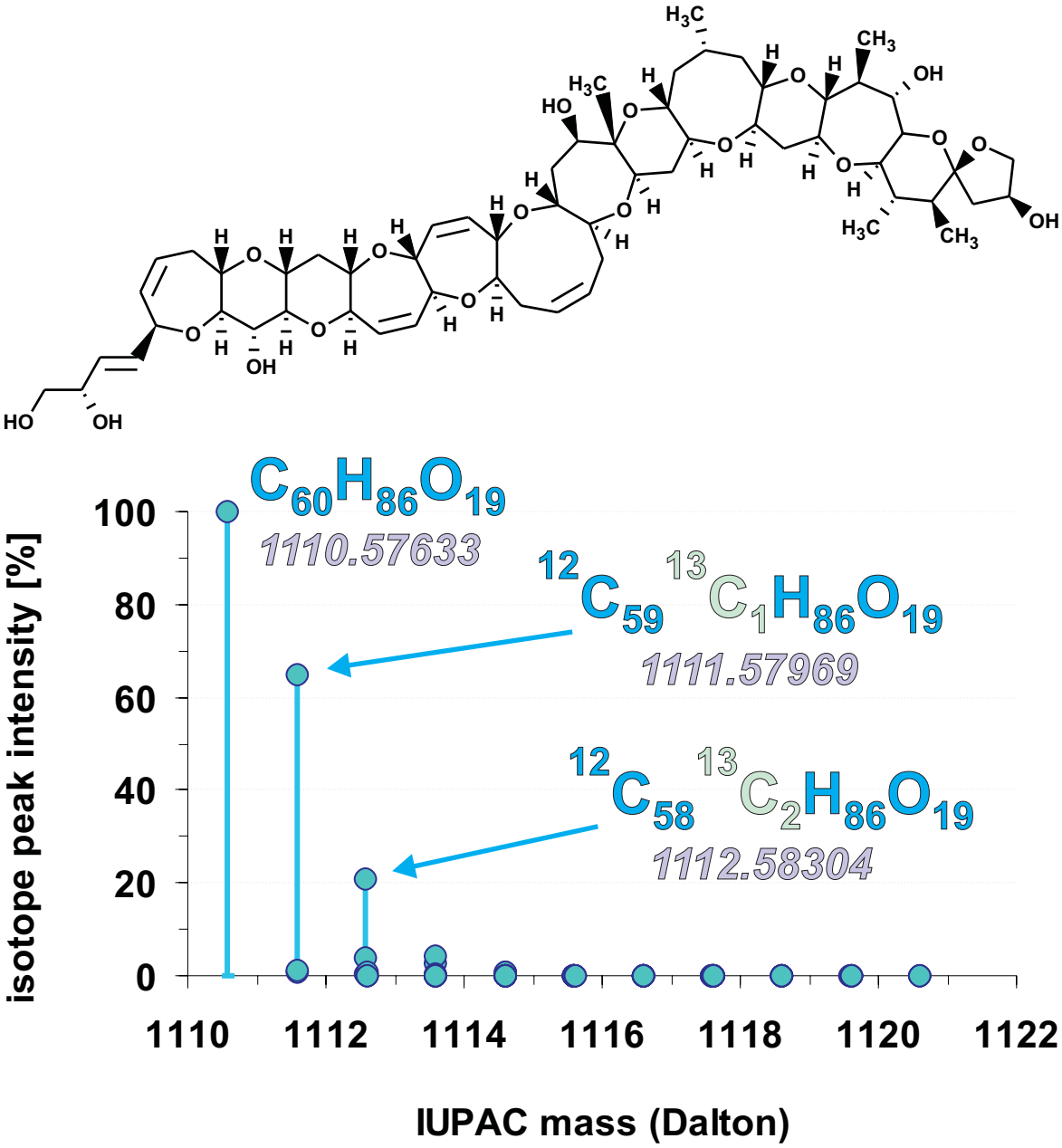


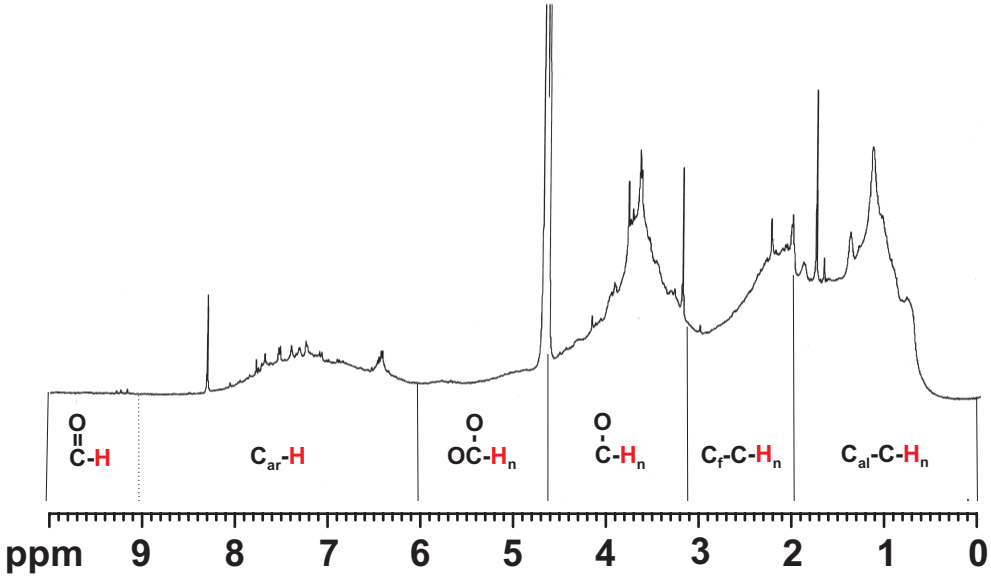


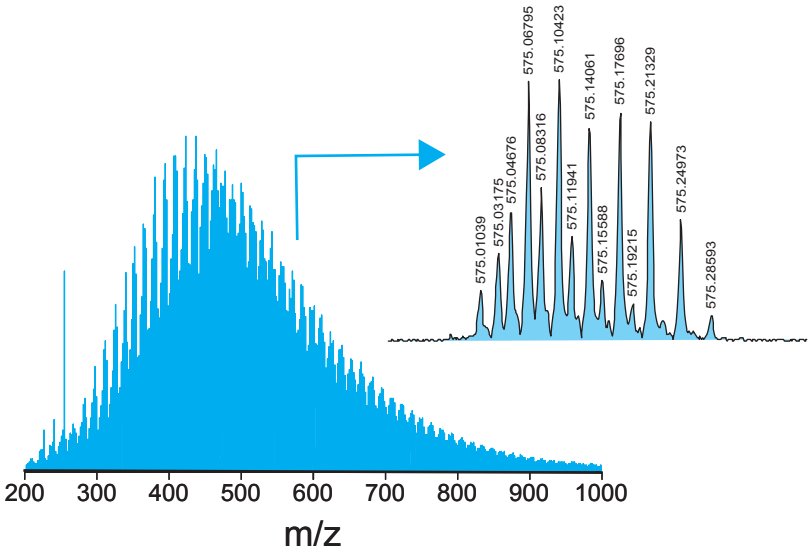
$$\omega_c = q \cdot B_0 / m$$

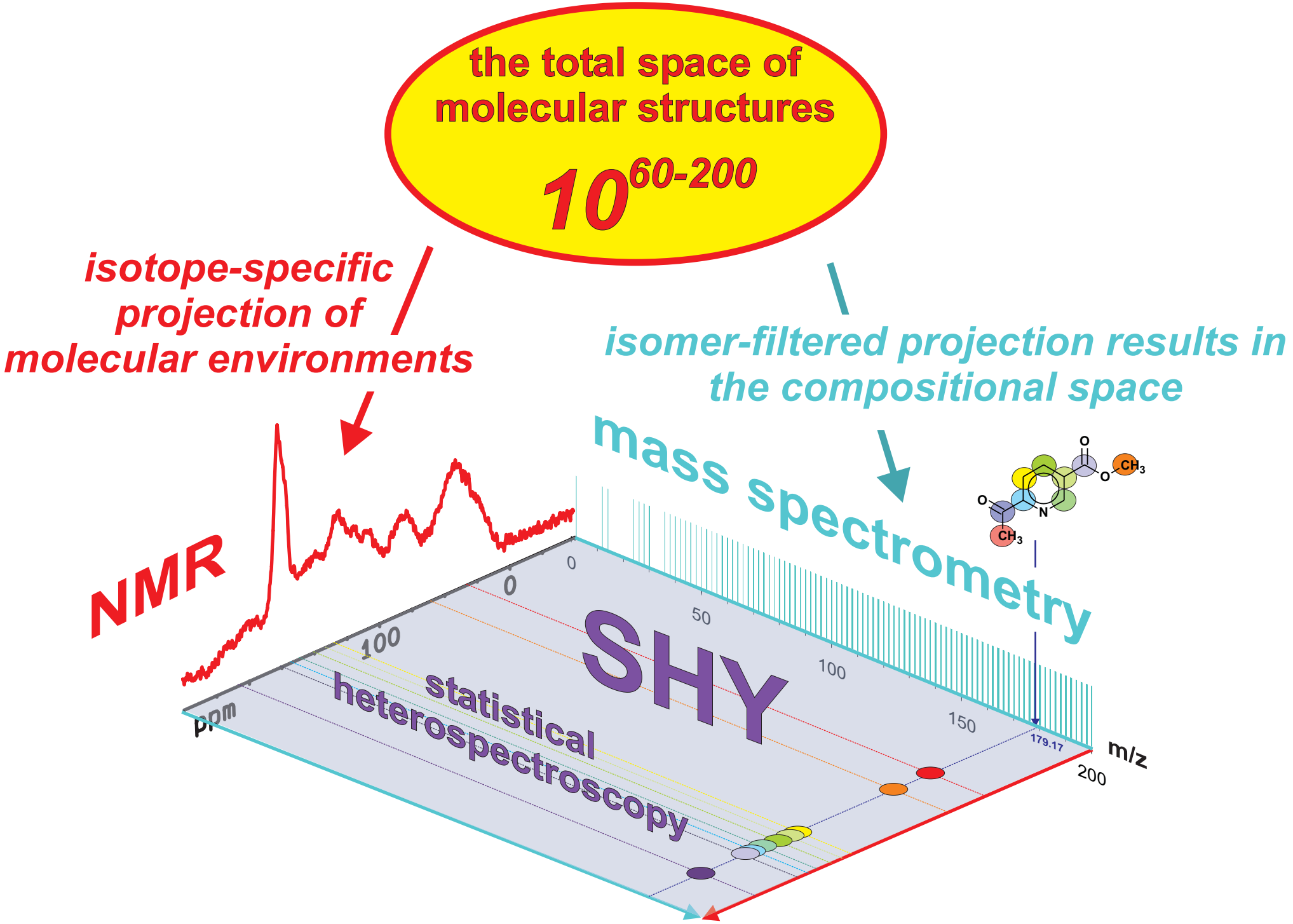
$$\omega_c = \frac{\nu_c}{2\pi} = \frac{1.535611\ B_0 \cdot q}{m}$$

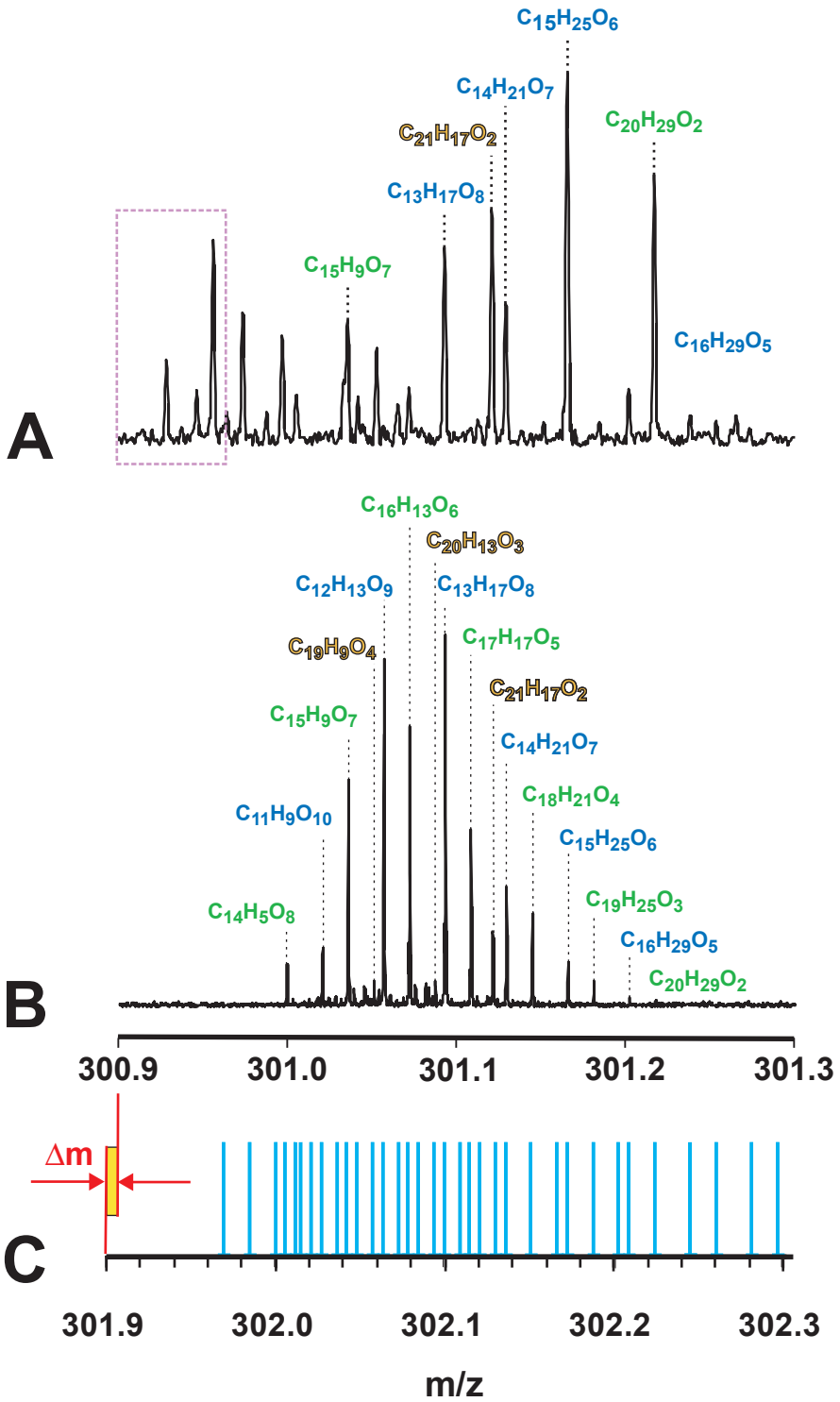

5005571.2 Hz
5005308.0 Hz
5005298.1 Hz
8.60
8.50
8.40
8.30
8.20
8.10
8.00
δ(1H) [ppm]
O
OH
170
165
160
155
150
145
140
135
130
125
120
δ(13C) [ppm]

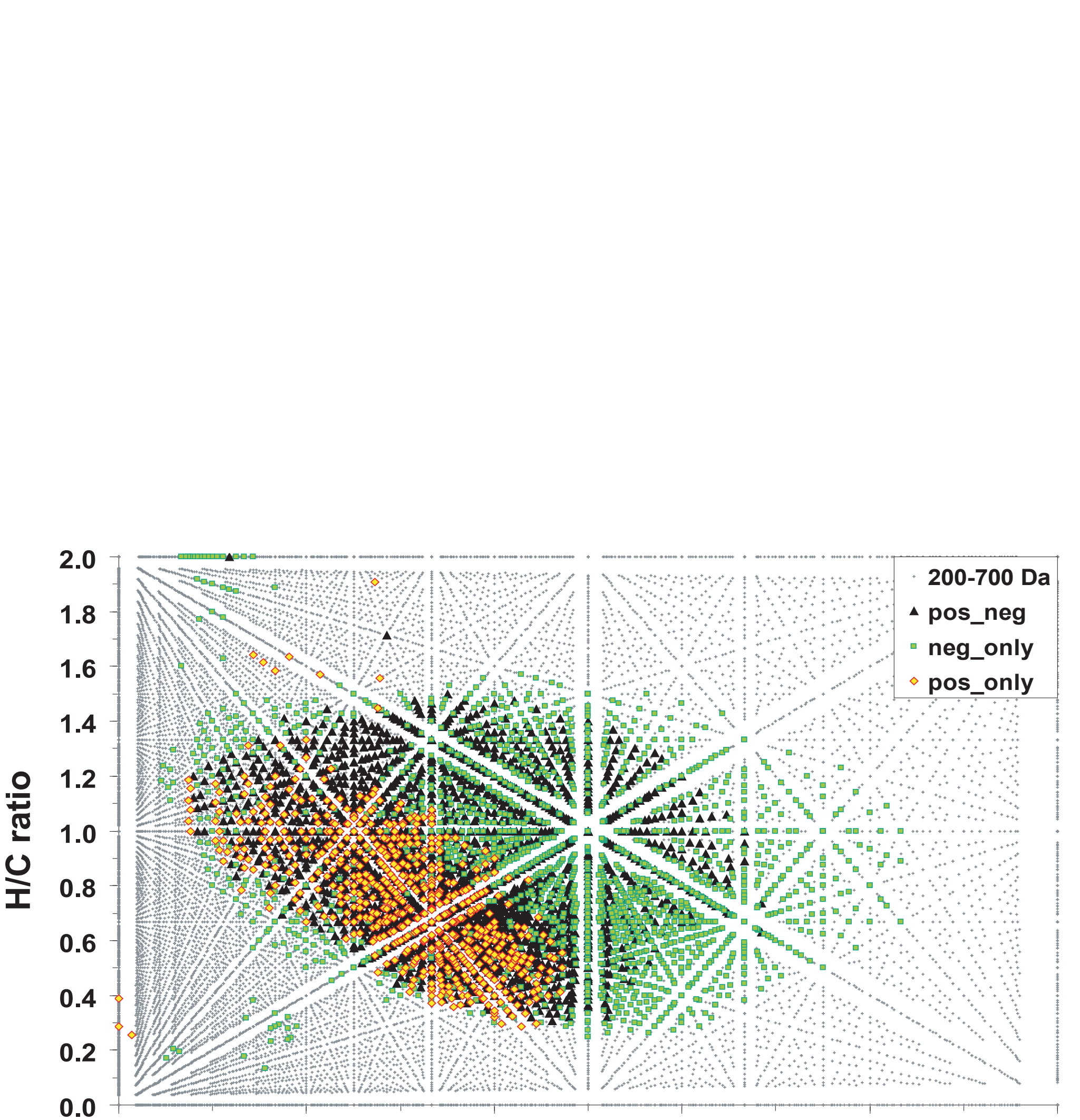

$C_{60}H_{86}O_{19}$
1110.57633
$^{12}C_{59}\,^{13}C_1H_{86}O_{19}$
1111.57969
$^{12}C_{58}\,^{13}C_2H_{86}O_{19}$
1112.58304
isotope peak intensity [%]
100
80
60
40
20
0
1110
1112
1114
1116
1118
1120
1122
IUPAC mass (Dalton)

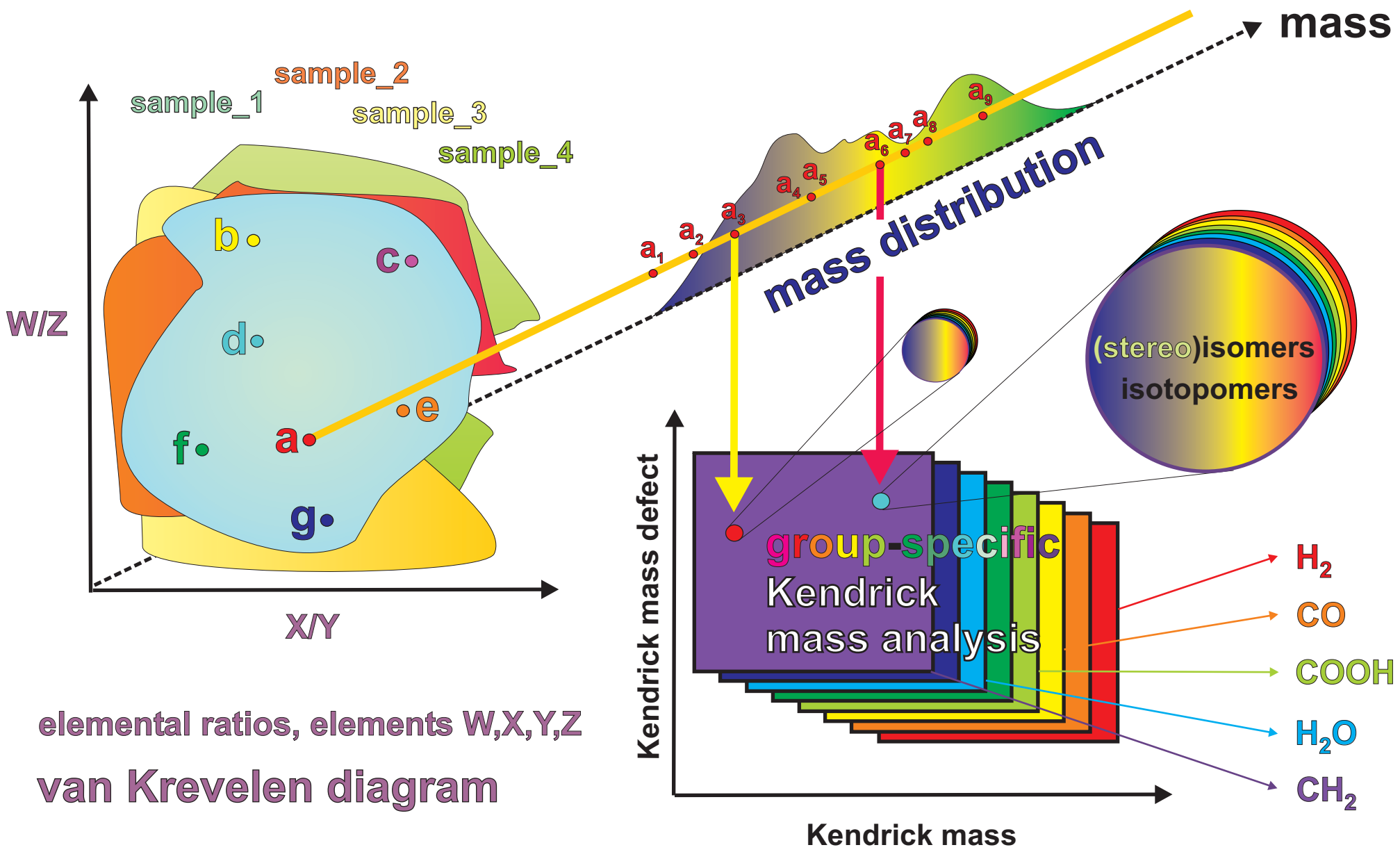

O
C-H
C$_{ar}$-H
O
OC-H$_n$
O
C-H$_n$
C$_f$-C-H$_n$
C$_{al}$-C-H$_n$
ppm 9 8 7 6 5 4 3 2 1 0

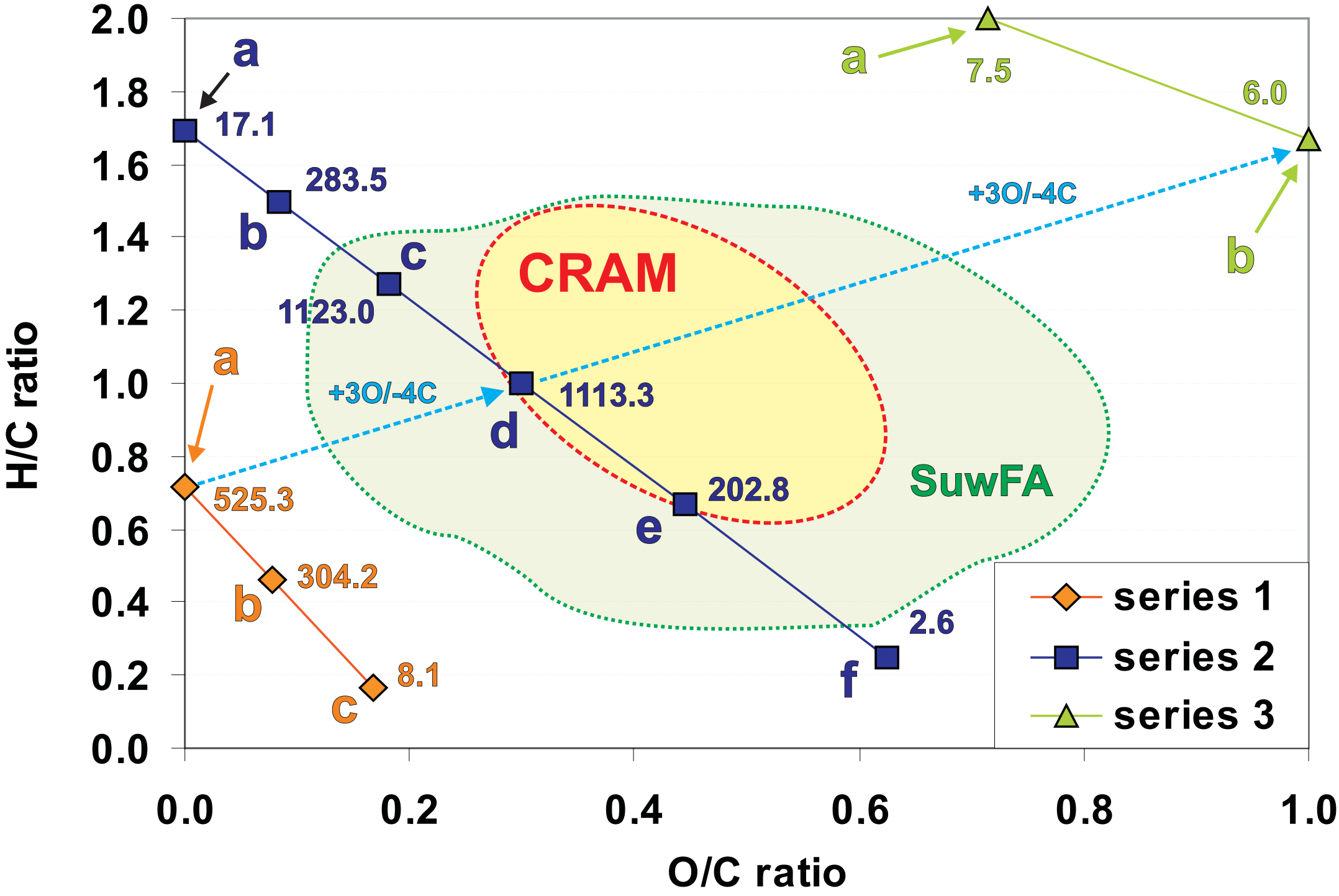

575.01039
575.03175
575.04676
575.06795
575.08316
575.10423
575.11941
575.14061
575.15588
575.17696
575.19215
575.21329
575.24973
575.28593
200
300
400
500
600
700
800
900
1000
m/z

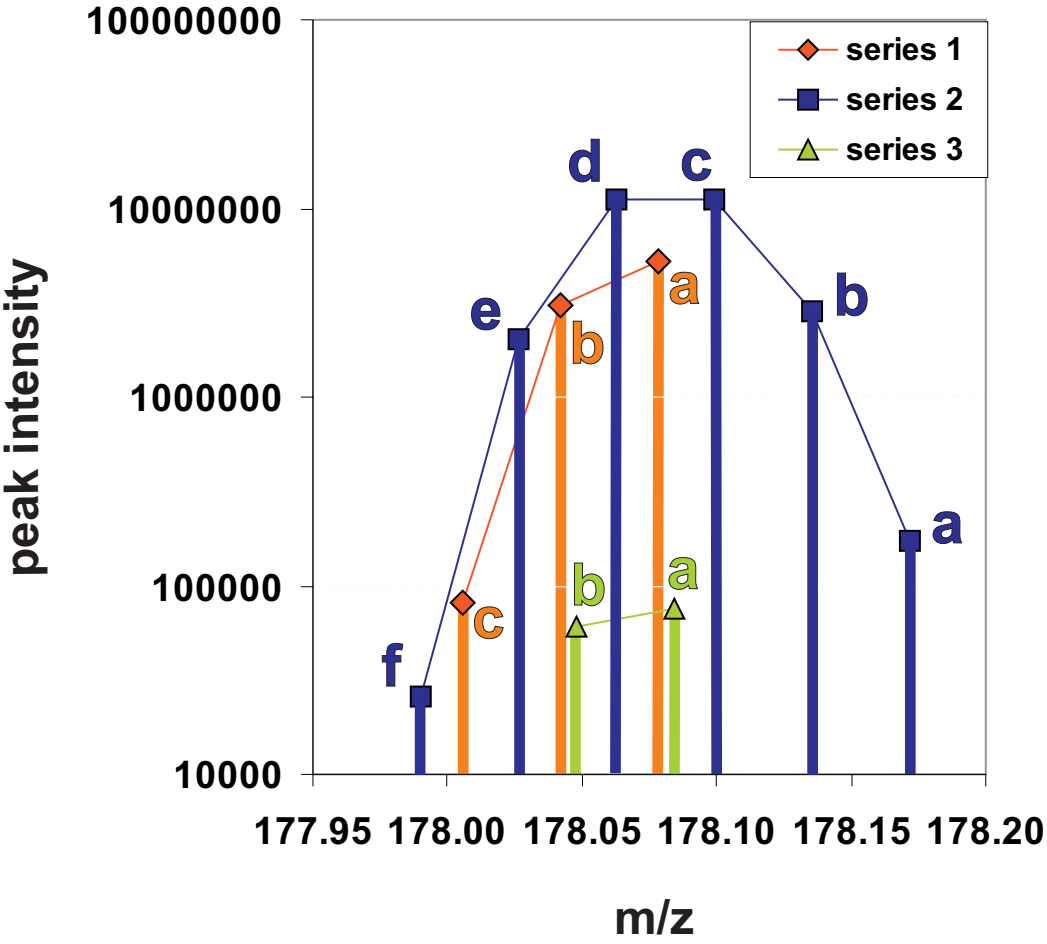

the total space of
molecular structures
$10^{60\text{-}200}$
isotope-specific
projection of
molecular environments
isomer-filtered projection results in
the compositional space
NMR
mass spectrometry
SHY
statistical
heterospectroscopy
ppm
0
100
0
50
100
150
179.17
200
m/z
O
O
CH3
O
N
CH3


A
$C_{15}H_{25}O_6$
$C_{14}H_{21}O_7$
$C_{20}H_{29}O_2$
$C_{21}H_{17}O_2$
$C_{13}H_{17}O_8$
$C_{15}H_9O_7$
$C_{16}H_{29}O_5$
B
$C_{16}H_{13}O_6$
$C_{20}H_{13}O_3$
$C_{12}H_{13}O_9$
$C_{13}H_{17}O_8$
$C_{19}H_9O_4$
$C_{17}H_{17}O_5$
$C_{21}H_{17}O_2$
$C_{15}H_9O_7$
$C_{14}H_{21}O_7$
$C_{18}H_{21}O_4$
$C_{11}H_9O_{10}$
$C_{15}H_{25}O_6$
$C_{14}H_5O_8$
$C_{19}H_{25}O_3$
$C_{16}H_{29}O_5$
$C_{20}H_{29}O_2$
300.9
301.0
301.1
301.2
301.3
Δm
C
301.9
302.0
302.1
302.2
302.3
m/z
D
H/C ratio
O/C ratio
2.5
2
1.5
1
0.5
0
0
0.5
1
1.5
2
16/30/5
15/26/6
14/22/7
13/18/8
12/14/9
11/10/10
20/30/2
19/26/3
18/22/4
17/18/5
16/14/6
15/10/7
14/6/8
21/18/2
20/14/3
19/10/4
$C_XH_YO_Z$ ⟷ X/Y/Z


200-700 Da
pos_neg
neg_only
pos_only
H/C ratio
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0.0
0.2
0.4
0.6
0.8
1.0
O/C ratio

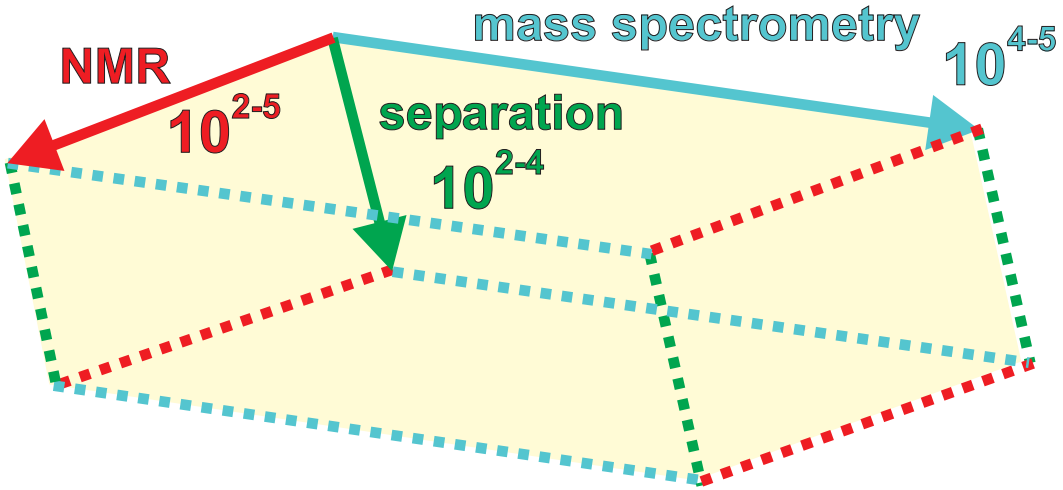

mass
sample_1
sample_2
sample_3
sample_4
W/Z
X/Y
a
b
c
d
e
f
g
a1
a2
a3
a4
a5
a6
a7
a8
a9
mass distribution
(stereo)isomers
isotopomers
group-specific
Kendrick
mass analysis
Kendrick mass defect
Kendrick mass
H2
CO
COOH
H2O
CH2
elemental ratios, elements W,X,Y,Z
van Krevelen diagram


H/C ratio
O/C ratio
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0.0
0.2
0.4
0.6
0.8
1.0
CRAM
SuwFA
+3O/-4C
+3O/-4C
a
17.1
b
283.5
c
1123.0
d
1113.3
e
202.8
f
2.6
a
525.3
b
304.2
c
8.1
a
7.5
b
6.0
series 1
series 2
series 3

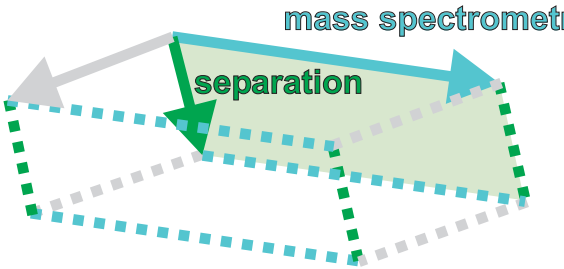

100000000
10000000
1000000
100000
10000
peak intensity
177.95
178.00
178.05
178.10
178.15
178.20
m/z
series 1
series 2
series 3
d
c
e
b
a
f
c
b
a
b
a

$10^{60\text{-}200}$

structure space

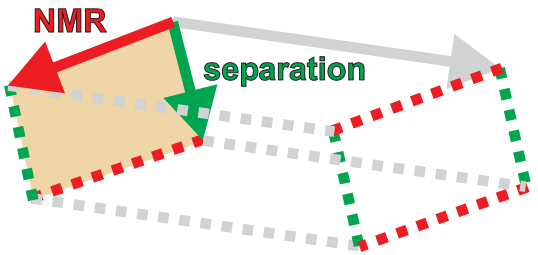


significant (analytical) bucket space: $10^{8\text{-}14}$



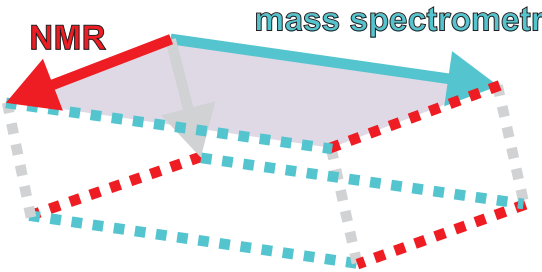
$10^{6\text{-}9}$

LC(CE) / MS



$10^{4\text{-}9}$

LC (CE) / NMR



$10^{6\text{-}10}$

NMR / MS statistical hetero-spectroscopy (SHY)