Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Photodissociation spectroscopy of protonated leucine enkephalin

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Electronic Supplementary Information

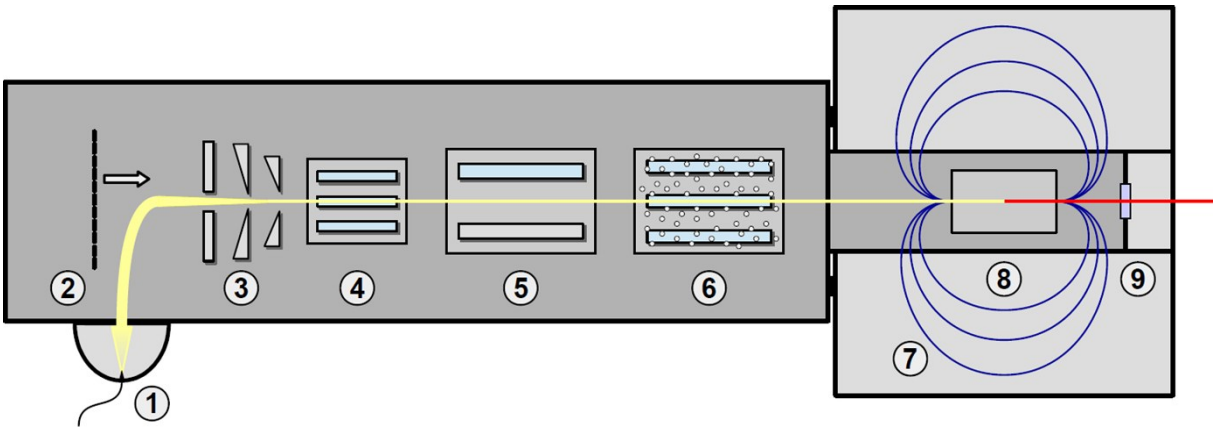


Figure S1. Simplified schematic view of the commercial FT-ICR MS Bruker APEX Qe: **1)** Electrospray Source, **2)** Repeller, **3)** Electrostatic Lens and two Funnels, **4)** Hexapole, **5)** Quadrupole Mass Filter, **6)** Collision Cell, **7)** 9.4 T Superconducting Magnet, **8)** ICR Cell, **9)** Window for Laser Irradiation. Note that the cyclotron radius is smaller than the diameter of the laser beam. Additional electrostatic lenses for ion guiding are placed in between **4)**, **5)**, **6)** and **8)**.

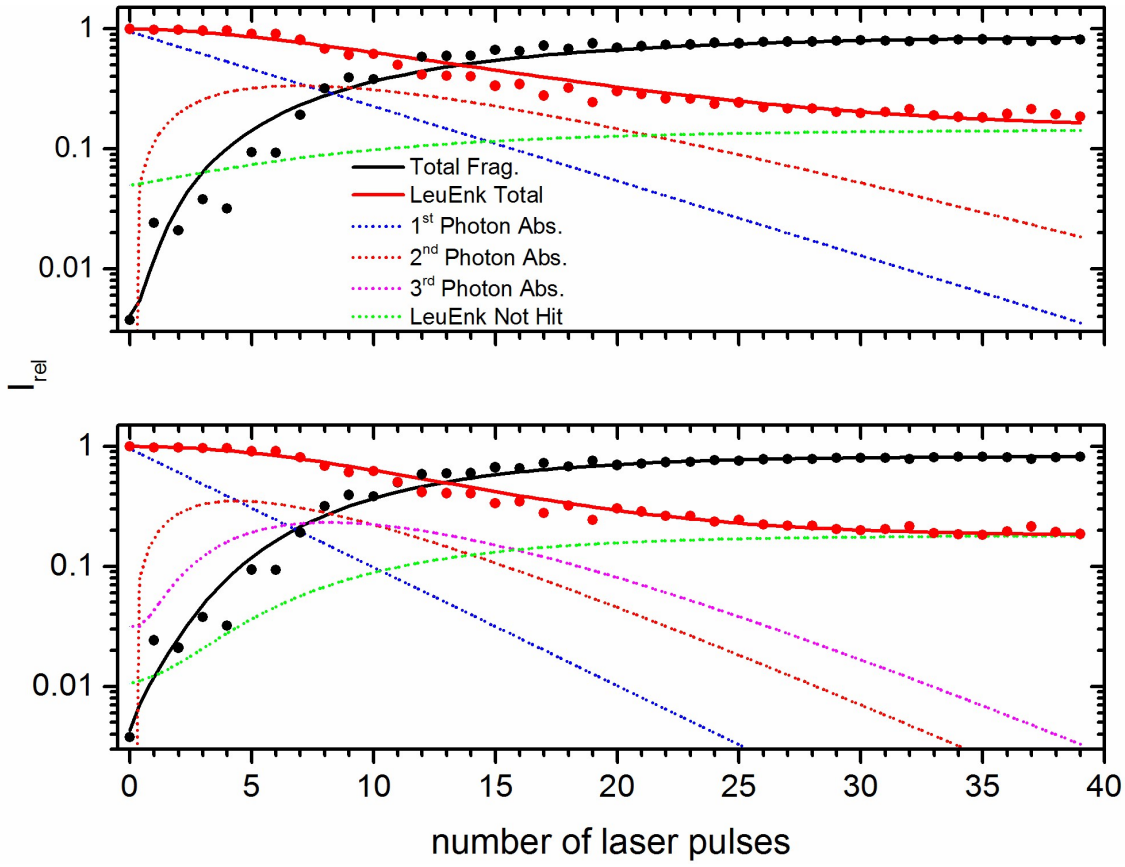


Figure S2: Kinetics fit assuming sequential absorption of two (top) and three photons (bottom).

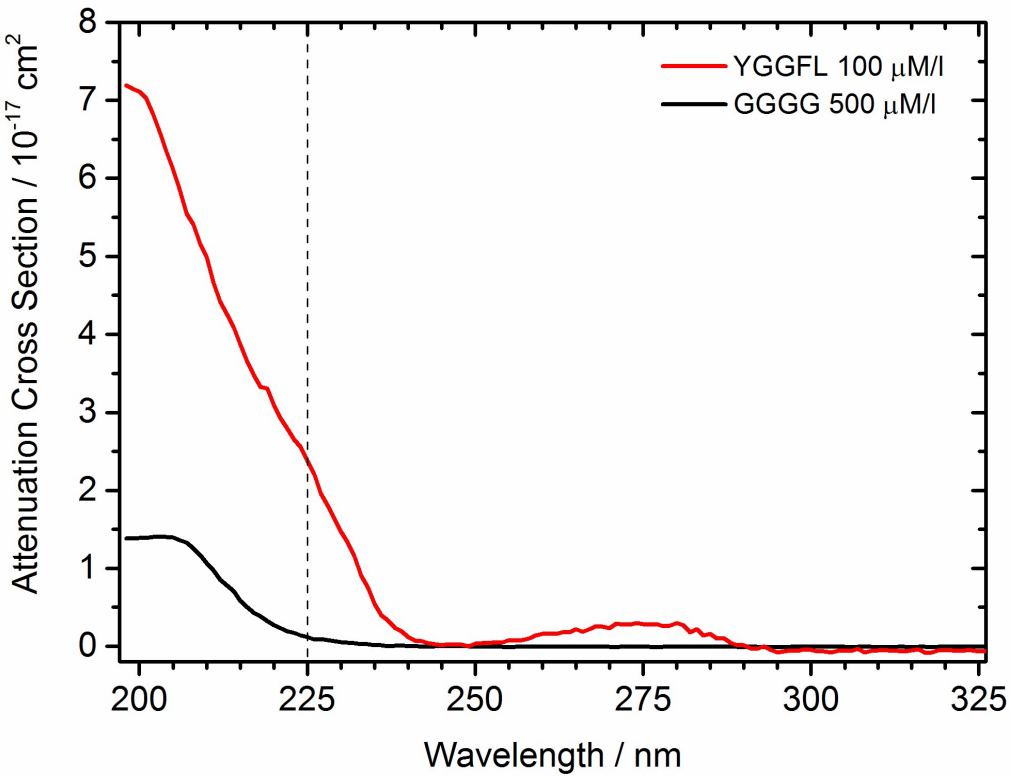


Figure S3: Solution phase UV-VIS spectrum of YGGFL and GGGG for comparison.

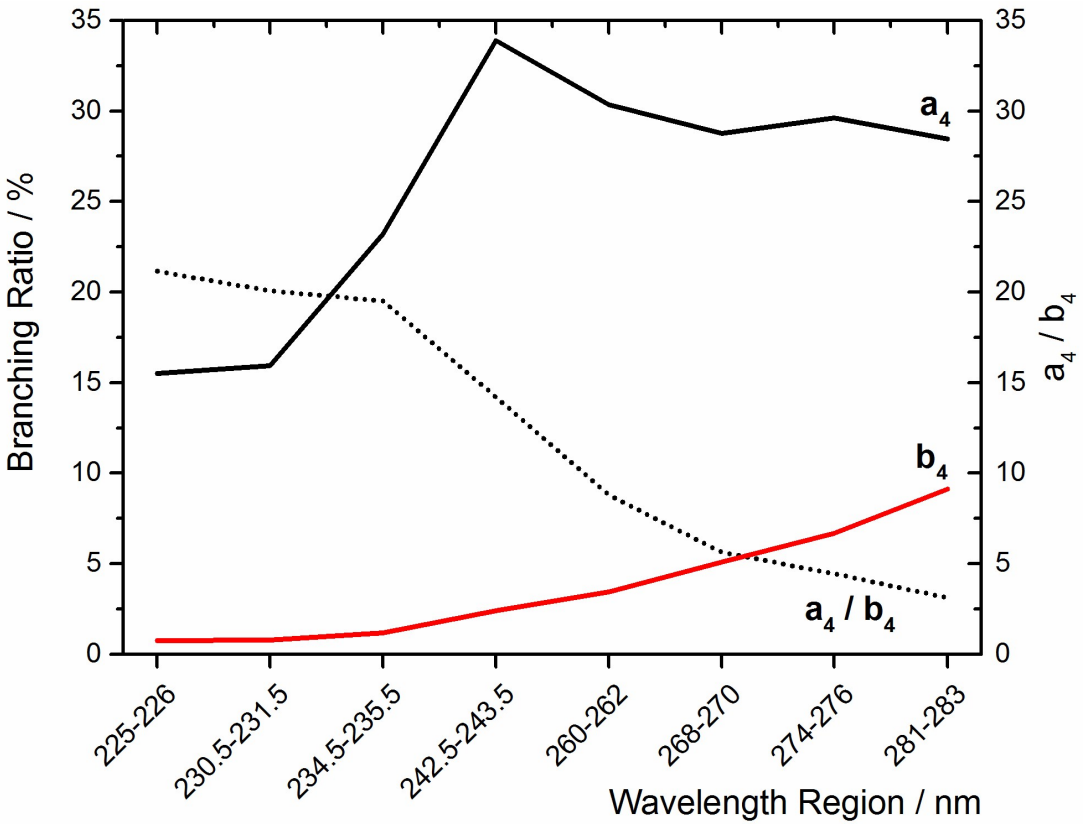


Figure S4: Ratio of a_4 vs. b_4 as a function of wavelength.

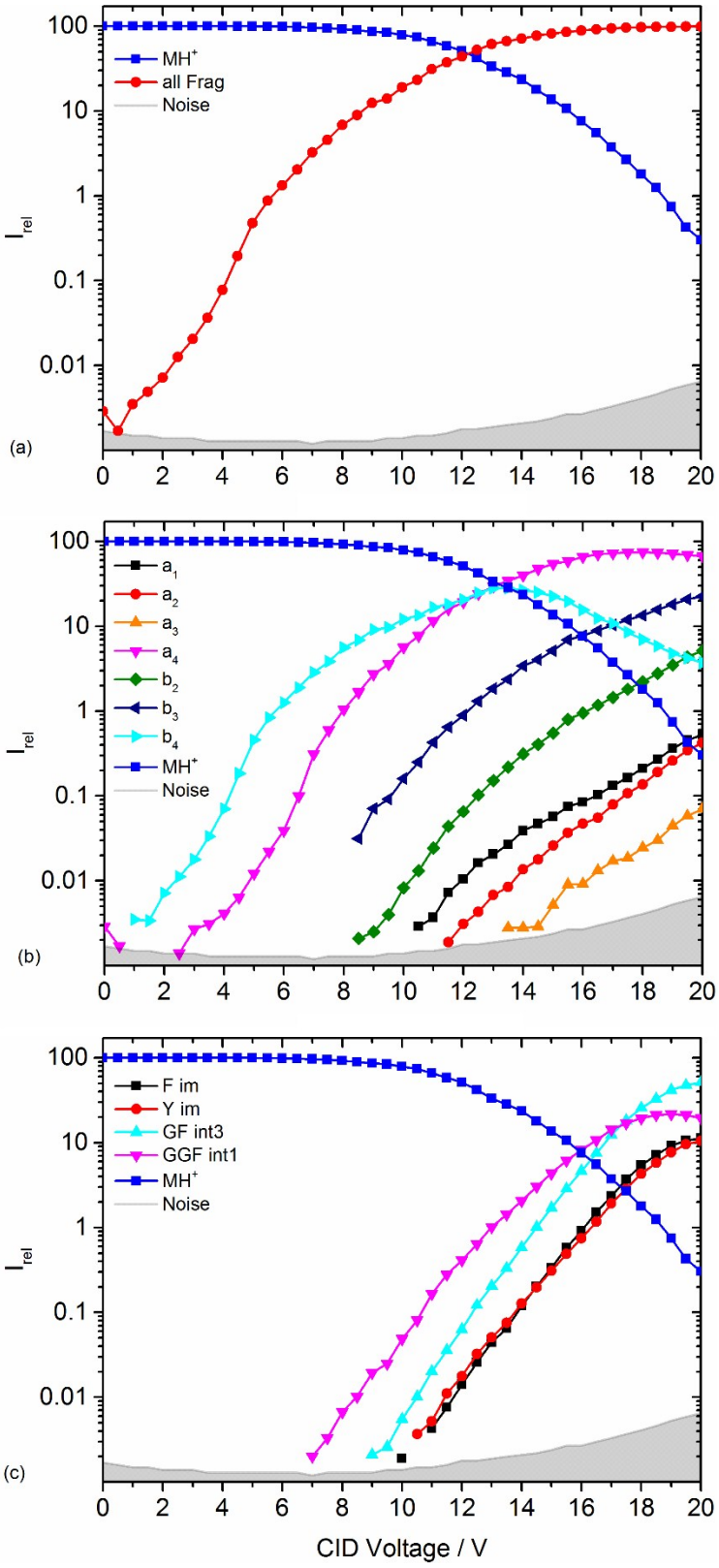


Figure S5: (a) Collision induced dissociation of protonated leucine enkephalin with argon for CID voltages from 0 to 20 V (< 1% of precursor ion remaining). (b) a- and b-type fragments and (c) internal fragments. All abundant ions have been included into the analysis.

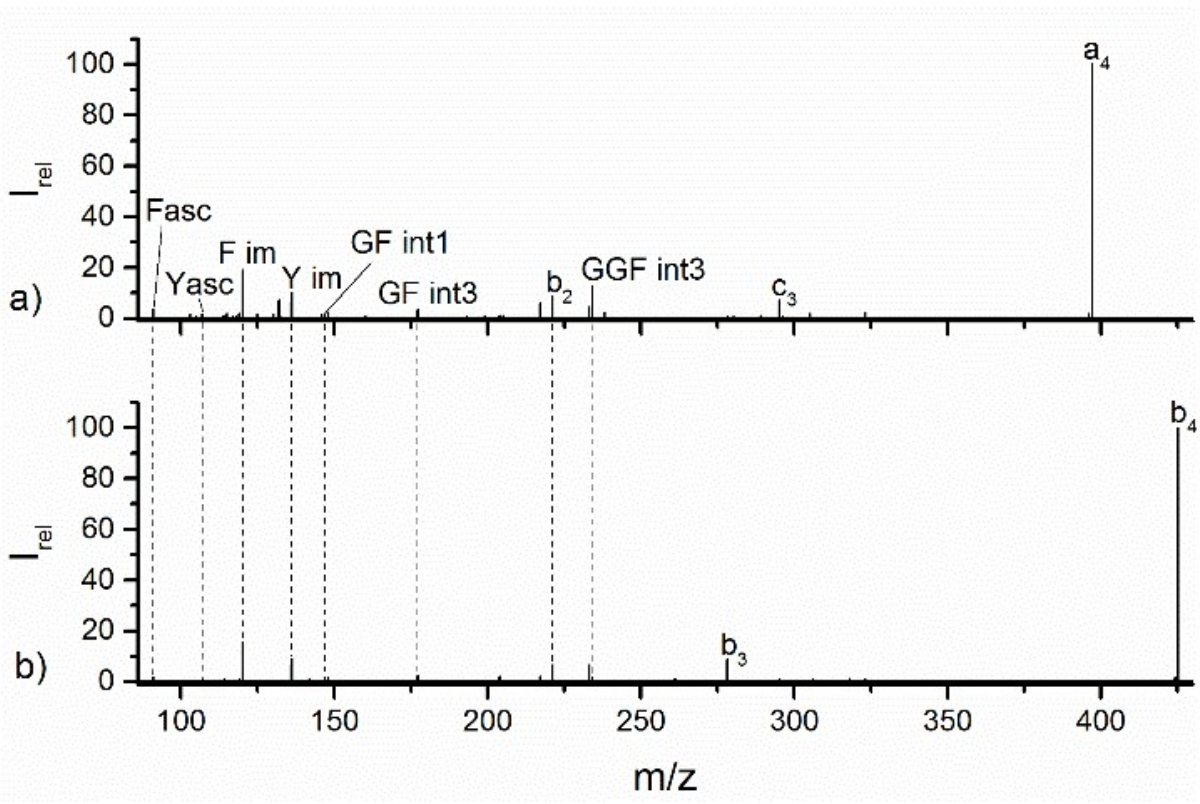


Figure S6: Fragment-LID: Mass spectra after irradiation of a_4 (a) and b_4 (b) for 1 sec. Mainly small (higher order) side chain and internal fragments are formed.

Table S1. List of all identified singly protonated sequence fragments upon LID (incl. protonated YGGFL). Measured mass, expected exact mass and deviation between measured and exact mass.

Fragment	m_{meas} / Da	m_{exact} / Da	Δm / mDa
a_1	136.0764	136.0762	0.1
a_2	193.0980	193.0977	0.3
a_3	250.1195	250.1192	0.4
a_4	397.1874	397.1876	0.2
b_1	164.0714	164.0712	0.2
b_2	221.0930	221.0926	0.3
b_3	278.1144	278.1141	0.3
b_4	425.1823	425.1825	0.3
c_1	181.0980	181.0977	0.3
c_2	238.1198	238.1192	0.6
c_3	295.1449	295.1407	4.3
x_3	362.1715	362.1716	0.1
x_4	419.1928	419.1931	0.3
y_1	132.1026	132.1025	0.1
y_2	279.1711	279.1709	0.2
y_3	336.1925	336.1924	0.1
y_4	393.2137	393.2138	0.1
$(YGGFL)H^+$	556.2761	556.2772	1

Table S2. List of re-assignments for LID.

Previous assignment	Reassignment	m_{meas} / Da	m_{exact} / Da	Δm / mDa
z_1	GGF int4+H	115.0508	115.0508	0.07
x_1	YGGF int3+H	158.0608	158.0566	4.2
z_2	YGGF int1	262.1194	262.1192	0.2
x_2	YGGFL int1	305.1252	305.1250	0.2

Table S3. List of all identified singly protonated internal and side chain fragments upon LID, as well as two intense unassigned fragment peaks iu1 and iu2. Measured mass, expected exact mass and deviation between measured and exact mass.

Fragment	m_{meas} / Da	m_{exact} / Da	Δm / mDa
F asc	91.0547	91.0548	0.05
Y asc	107.0497	107.0497	0.03
GGF int4+H	115.0508	115.0508	0.07
F im	120.0814	120.0813	0.04
Y im	136.0764	136.0762	0.1
GFint1	147.0686	147.0684	0.2
YGGF int3+H	158.0608	158.0566	4.2
GF int2	162.0921	162.0919	0.2
GF int3	177.1030	177.1028	0.2
GGF int1	205.0979	205.0977	0.2
GGF int2	219.1137	219.1134	0.4
GGF int3	234.1246	234.1243	0.3
YGGF int1	262.1194	262.1192	0.2
YGGF int2	290.1143	290.1141	0.2
YGGFL int1	305.1252	305.1250	0.2
iu1	323.1403		
y_4°	375.2033	375.2033	0.05
a_4^*	380.1610	380.1611	0.01
Iu2	426.1675		
MH^+-Y asc-H	448.2207	448.2196	1.1
MH^+-Y asc	449.2271	449.2275	0.3
MH^+-F asc	465.2220	465.2224	0.4
MH^+-(NH_3+HCOOH)	493.2444	493.2451	0.7
MH^+-HCOOH	510.2708	510.2717	0.8
MH^+-H_2O	538.2654	538.2666	1

Table S4. Center position of Gaussian fit functions in Figure 4.

1-Photon / cm^{-1}	2-Photon / cm^{-1}	3-Photon / cm^{-1}	Average
52000	52000	52000	
38375	38420	38271	38355
36730	36646	36713	36696
35481	35448	35428	35452
		34053	

Table S5. List of all identified singly protonated fragments upon CID (incl. protonated YGGFL). Measured mass, expected exact mass and deviation between measured and exact mass.

Fragment	m_{meas} / Da	m_{exact} / Da	Δm / mDa
a_1	136.0761	136.0762	0.1
a_2	193.0977	193.0977	0.04
a_3	250.1192	250.1192	0.006
a_4	397.1875	397.1876	0.1
b_2	221.0927	221.0926	0.02
b_3	278.1142	278.1141	0.1
b_4	425.1818	425.1825	0.7
c_1	181.0977	181.0977	0.02
c_2	238.1232	238.1192	4
c_3	295.1447	295.1407	4
x_4	419.1920	419.1931	1
y_1	132.1023	132.1025	0.2
y_2	279.1710	279.1709	0.1
y_3	336.1925	336.1924	0.1
y_4	393.2134	393.2138	0.5
F im	120.0812	120.0813	0.2
Y im	136.0761	136.0762	0.1
GF int3	177.1027	177.1028	0.07
GGF int1	205.0977	205.0977	0.03
y°_4	375.2034	375.2033	0.2
a^{*}_4	380.1613	380.1612	0.2
MH^+-SC	465.2503	465.2502	0.1
MH^+-(NH_3+HCOOH)	493.2458	493.2451	0.6
MH^+-HCOOH	510.2725	510.2717	0.8
MH^+-H_2O	538.2670	538.2666	0.4
$(YGGFL)H^+$	556.2779	556.2772	0.7

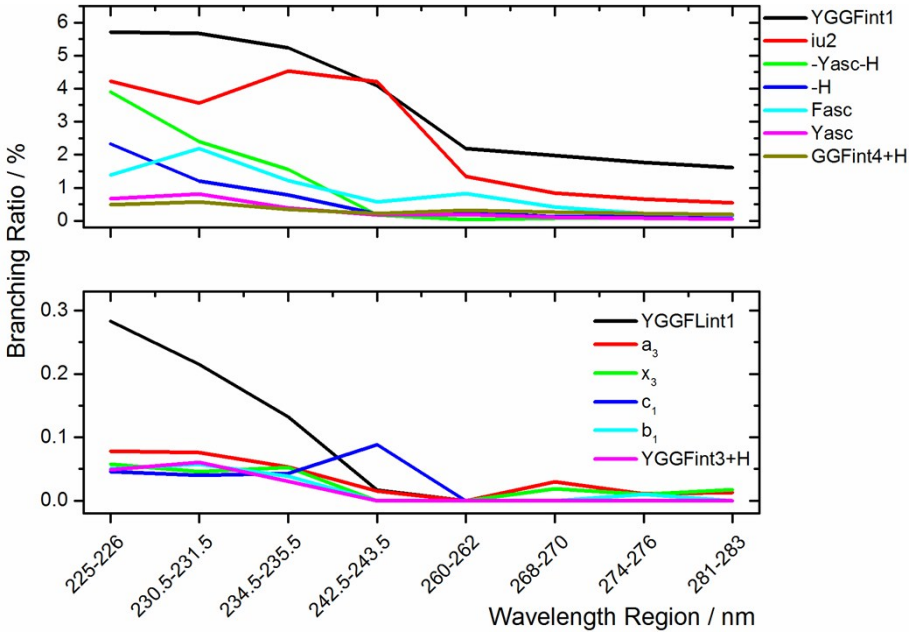
Table S6. List of re-assignments for previously published CID fragments.

Previous assignment	Re-assignment	m_{meas} / Da	m_{exact} / Da	Δm / mDa
MH^+-F asc	MH^+-SC	465.2503	465.2502	0.1

Wavelength dependence of fragment branching ratios

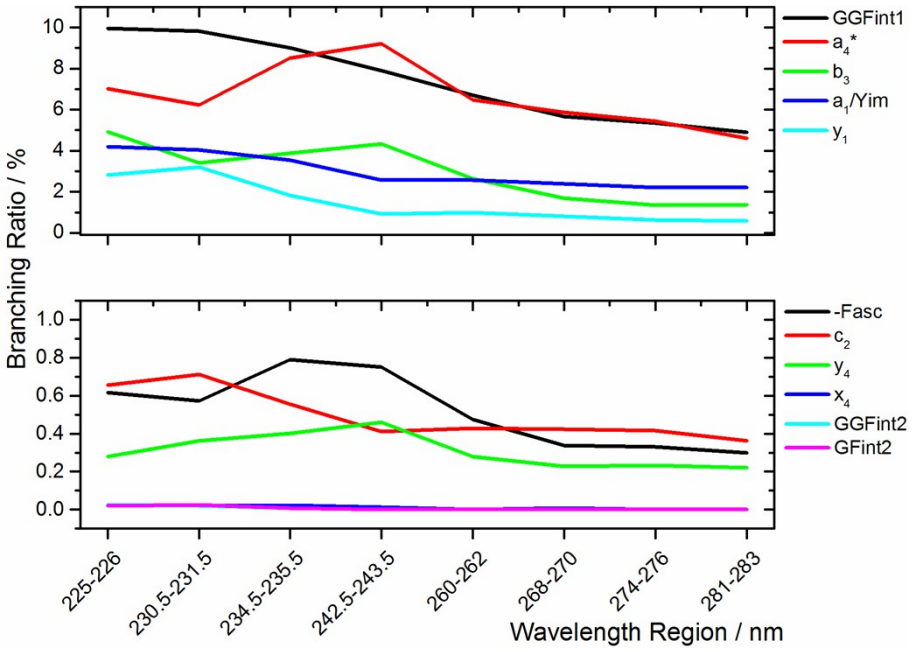
Very high abundance at short wavelengths (13):

YGGF int1, iu2, -Yas-H, -H, Fasc, Yasc, YGGFL int1, GGF int4+H, YGGF int3+H, a_3, x_3, c_1, b_1



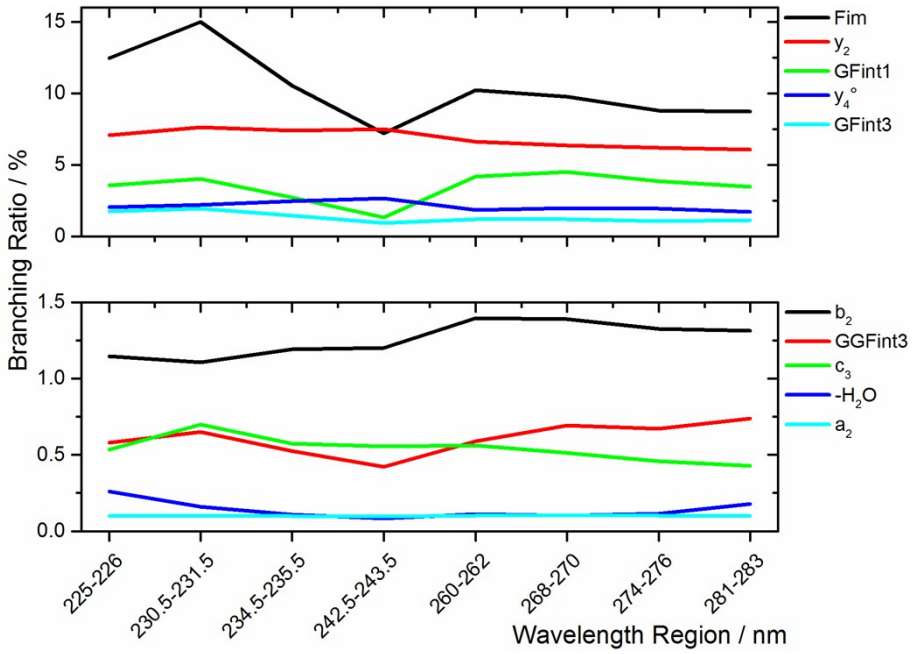
High abundance at short wavelengths (11):

GGF int1, a_4*, b_3, a_1/Yim, y_1, -Fasc, c_2, y_4, x_4, GGF int2, GF int2



Rather constant abundance at all wavelengths (10):

F im, y_2, GF int1, y_4°, GF int3, b_2, GGF int3, c_3, -H_2O, a_2



High abundance at long wavelengths (8):

a_4, iu1, b_4, -Yasc, y_3, -(NH_3+HCOOH), YGGF int2, -HCOOH