HelmholtzZentrum münchen
German Research Center for Environmental Health

Fourier Transform Ion Cyclotron Resonance Mass Spectrometry and Computational Tools in Modern Analytical Chemistry

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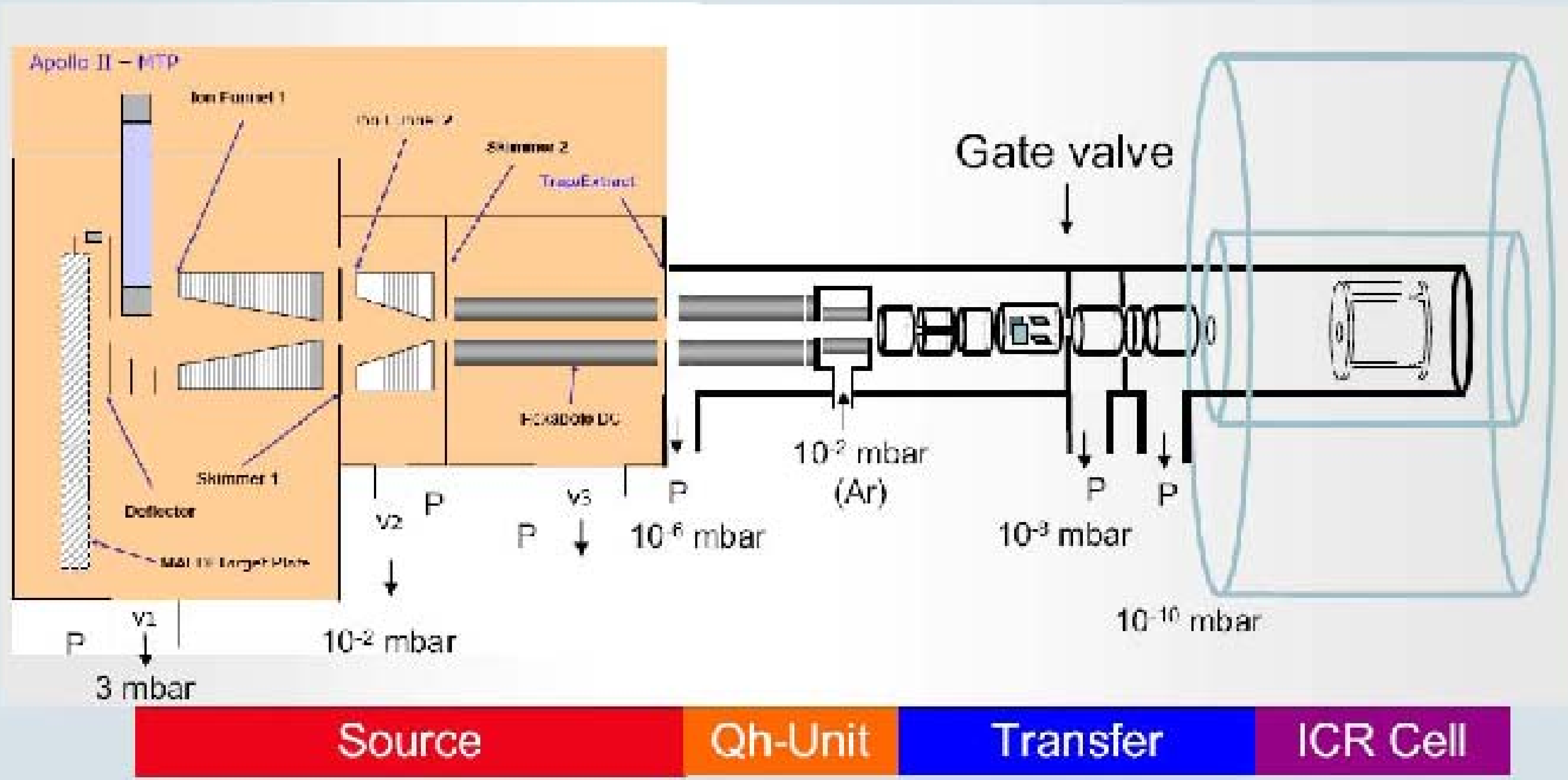
Overview

1. Introduction to the FTMS technique.

2. Instrumental developments in FT-ICR and ionization sources.

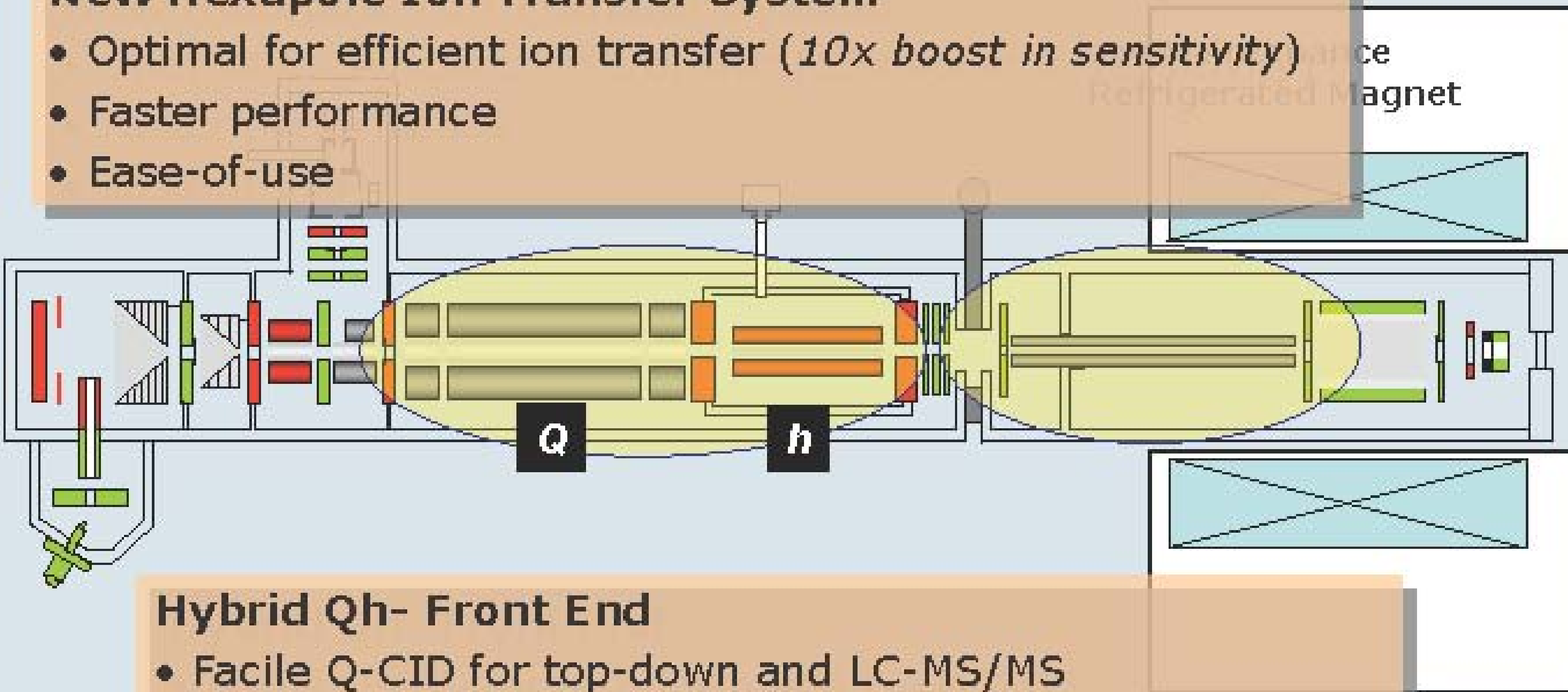
3. Some examples of structural elucidations in MS/MS CID experiments

Schematic presentation of the whole FTMS instrument



solarix

Instrument design



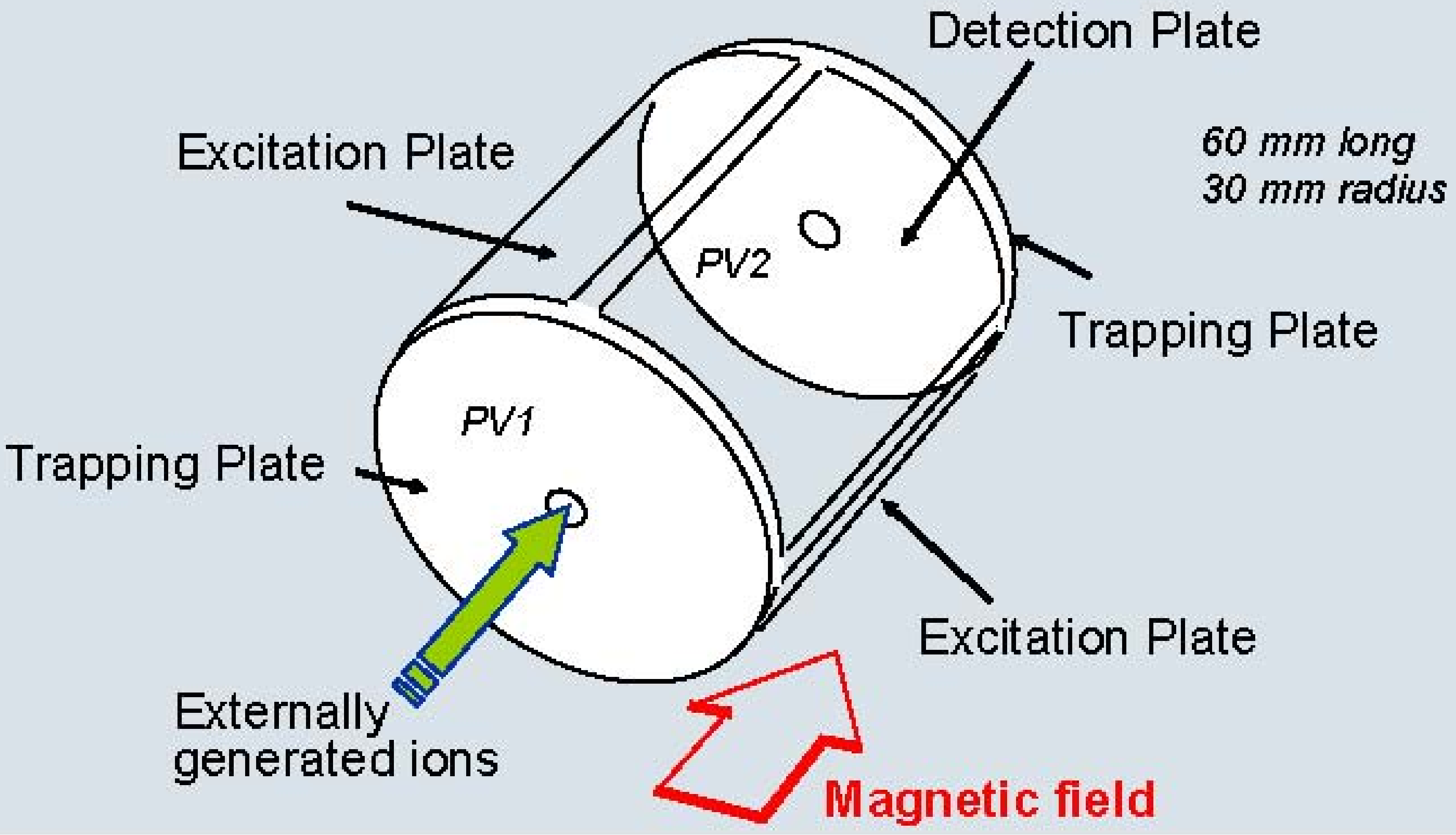
New Hexapole Ion Transfer System

- Optimal for efficient ion transfer (*10x boost in sensitivity*)
- Faster performance
- Ease-of-use

Hybrid Qh- Front End

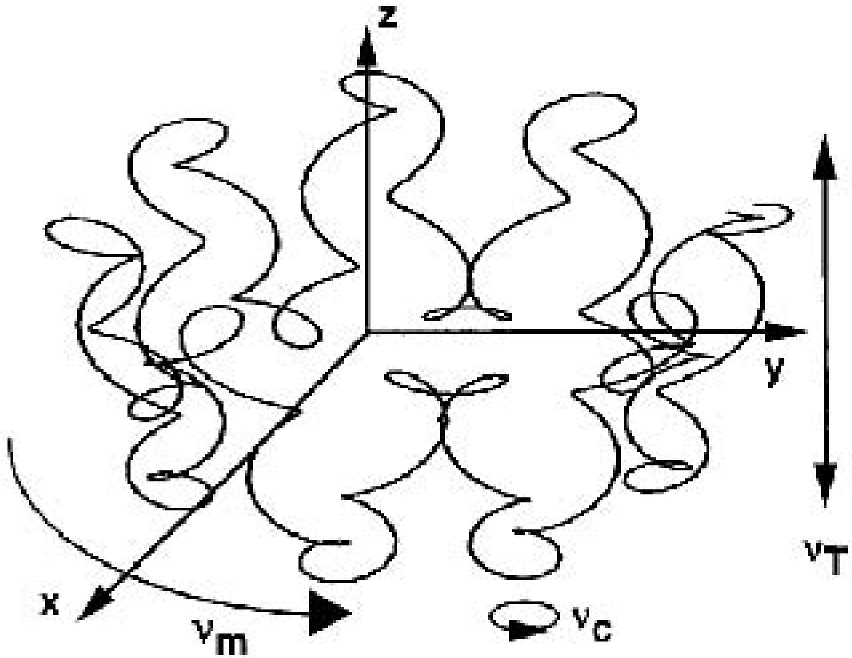
- Facile Q-CID for top-down and LC-MS/MS
- Supports CASI™ for enrichment of low abundant species

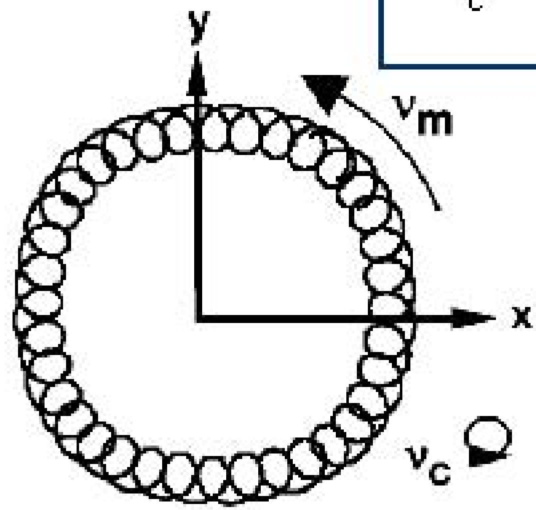
Cylindrical Ion Cyclotron Resonance Cell (ICR Cell, ICR Trap)

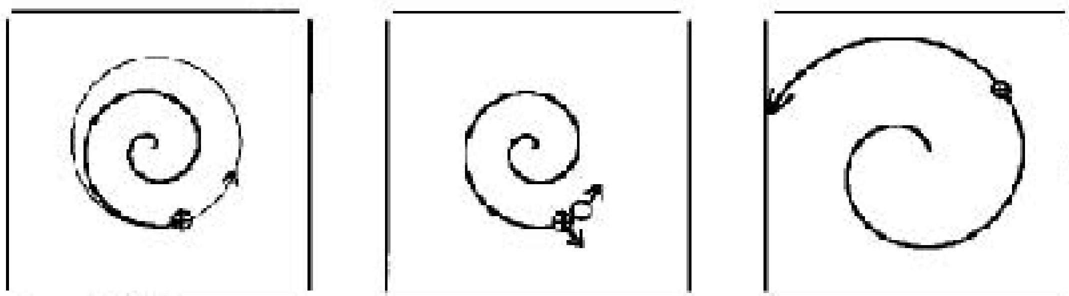


Ion motion in FT-ICR cell

$$w_c = \frac{q.B_0}{m}$$





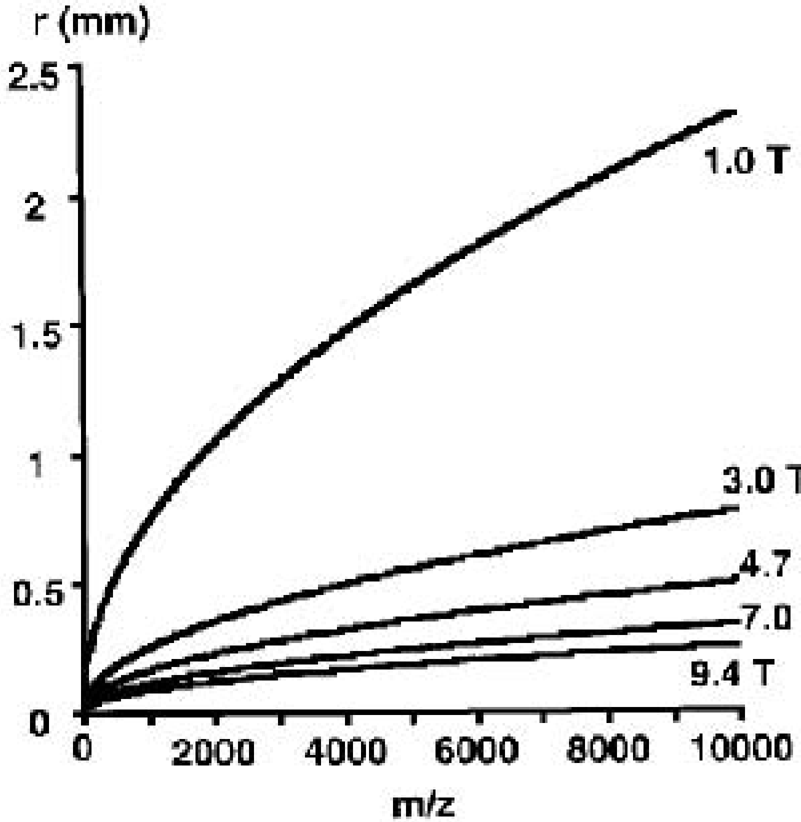


Excitation CID Radial quenching

MARSHALL, HENDRICKSON, AND JACKSON

Before radial ion excitation

$$r = \frac{1}{qB_0}\sqrt{2mkT}$$

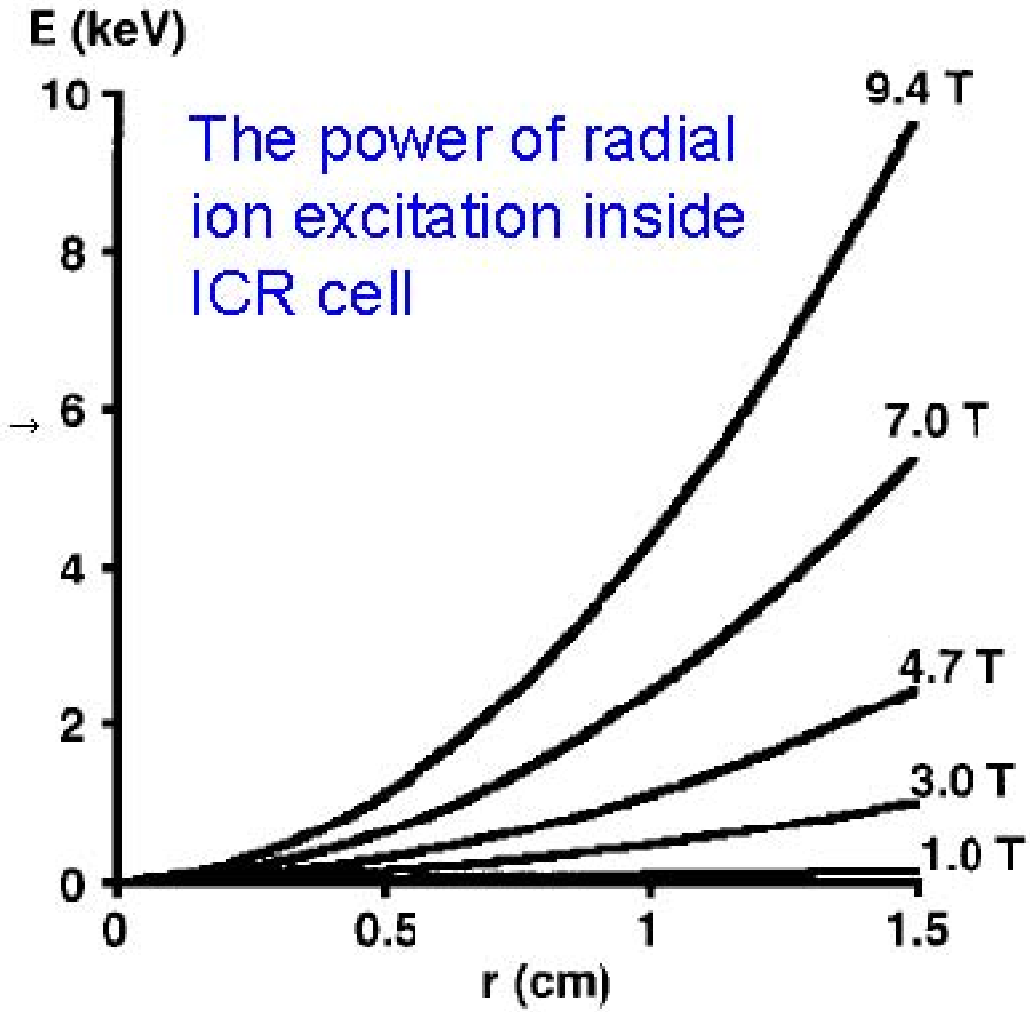


Ions are better confined in the ICR cell, if the magnetic field strength is relatively high.

Evolution of the thermal (unexcited) cyclotron radius as a function of m/z at different magnetic field strengths.

After radial ion excitation

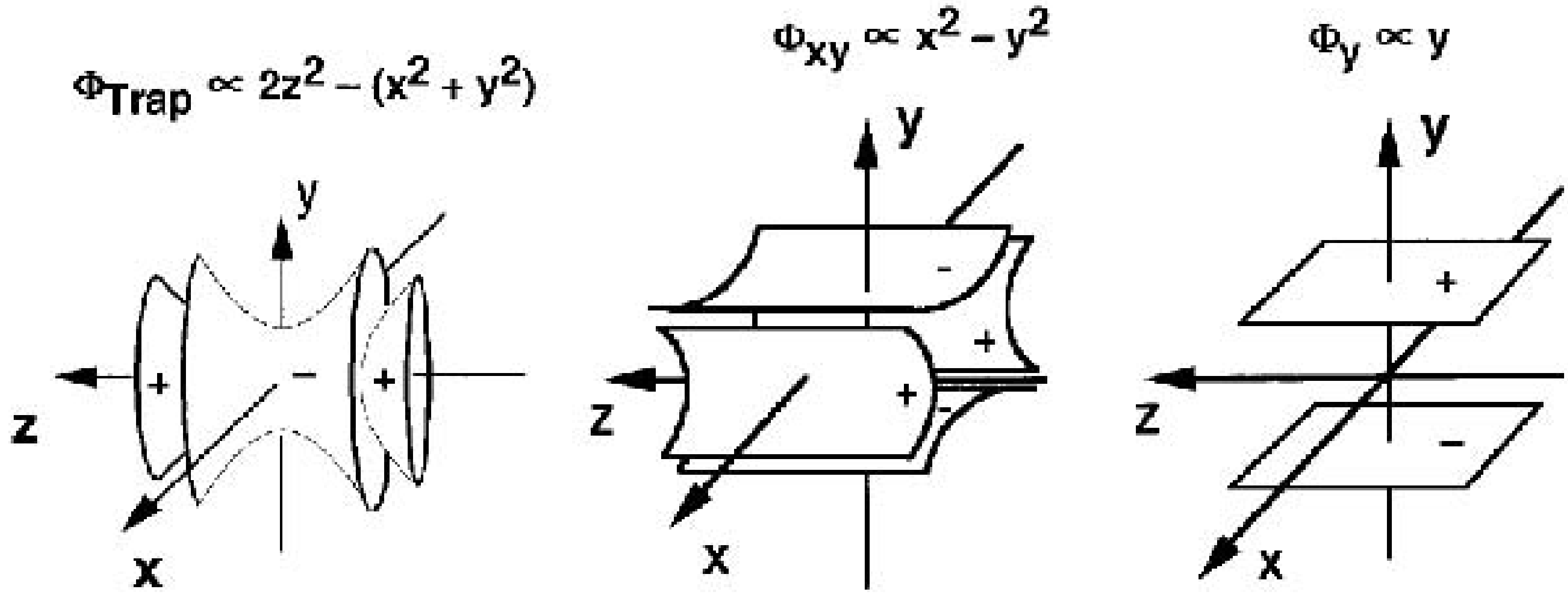
$$w_c = \frac{q.B_0}{m} = \frac{v_{xy}}{r}$$



$$v_{xy} = \frac{qB_0 r}{m}$$

$$KE = \frac{1}{2} m v_{xy}^2 = \frac{q^2 B_0^2 r^2}{2m}$$

End cyclotron radius (after excitation) versus translational kinetic energy



Axial dipole | Radial quadrupole | Radial dipole

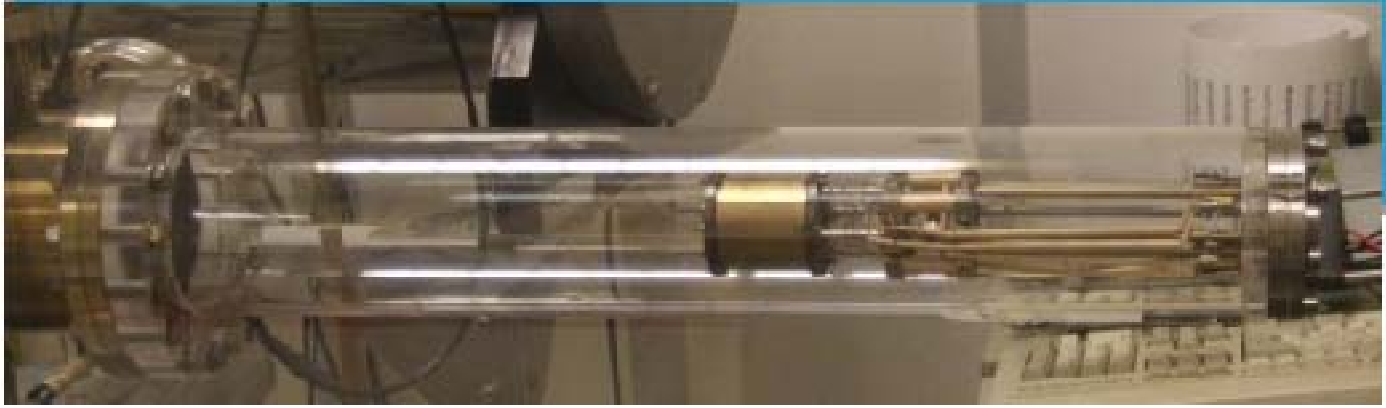
Plots of isopotential surfaces for trapping, quadrupolar, and dipolar electric fields.

Trapping electric field is axial, while the excitation electric field has a major radial component.

Radial excitation electric field can be dipolar or quadrupolar in nature.

Marshall, Hendrickson, Jackson, Mass. Spec. Rev. 1998, 17, 1-35

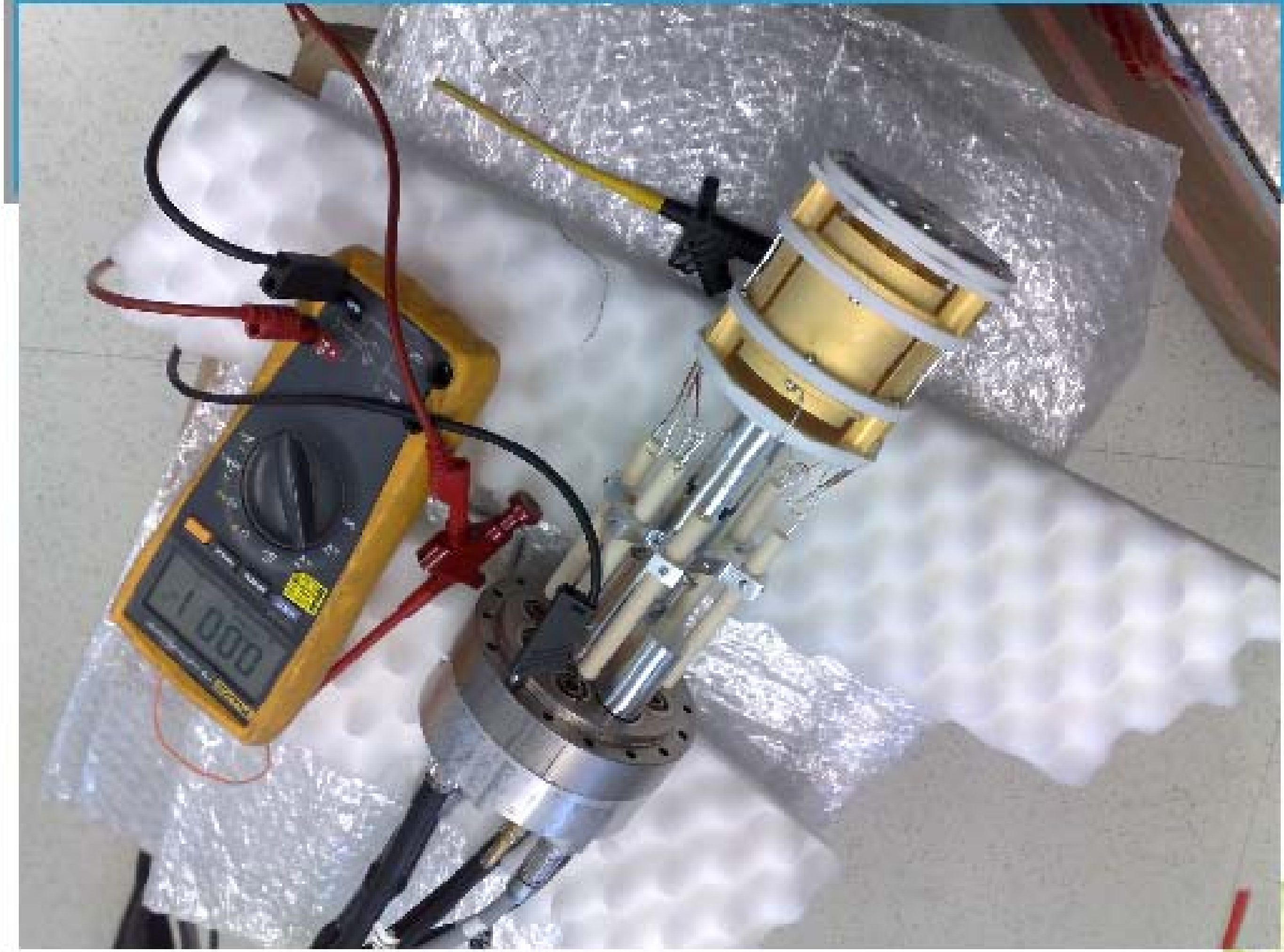
New ICR cell for simultaneous trapping and detection of positive & negative ions



Simple ICR cell inside a vacuum tube

Multi section ICR cell with correction ring electrodes

Infinity ICR cell



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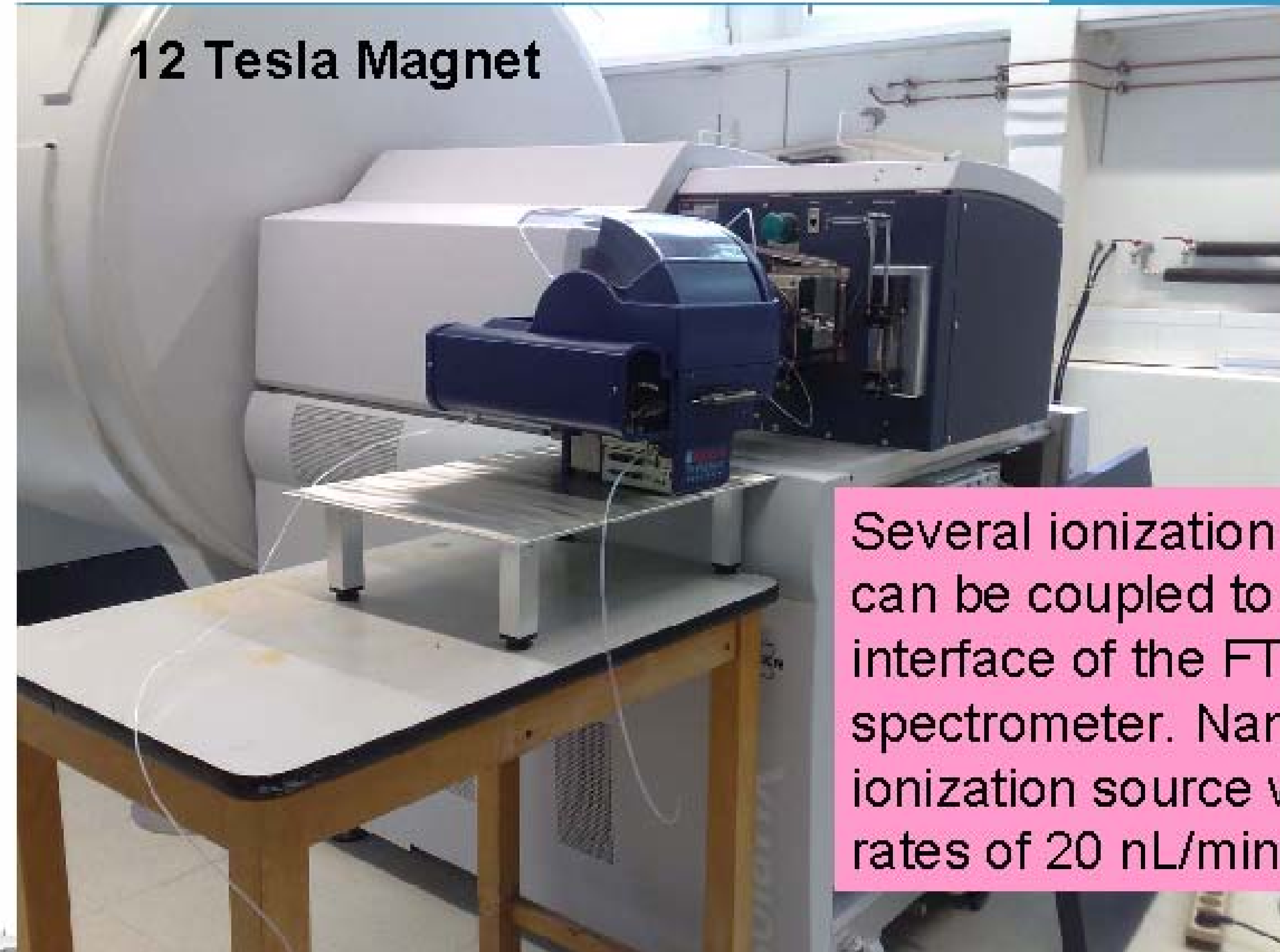
12 Tesla Magnet



Several ionization sources can be coupled to the interface of the FTMS mass spectrometer. Nanomate ionization source with flow rates of 20 nL/min.

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Excimer UV Laser with Telescope – Homogenizer & focusing units

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Implemented method:

B3LYP/6-311+G(2d,p) // B3LYP/6-31+G(d,p)

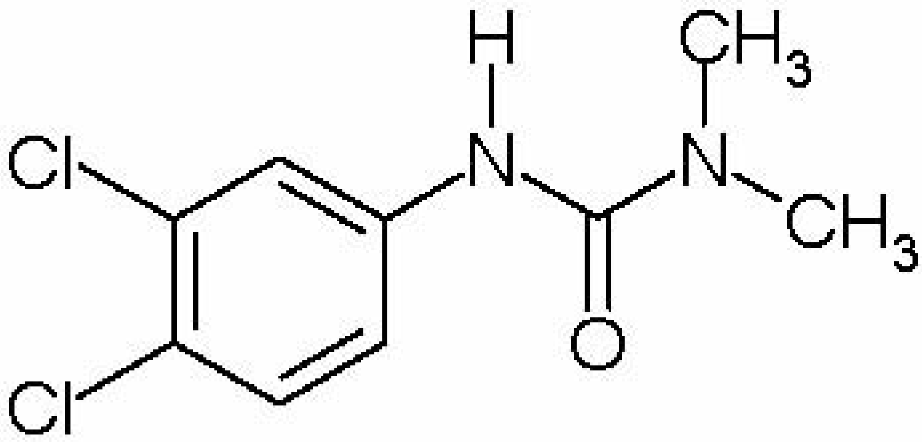
TS structures where traced along the reaction coordinate by running intrinsic reaction coordinate (IRC) calculations.

Stability tests were performed to ensure that the singlet state of each structure is that which describe the lowest energy solution to the SCF equations.

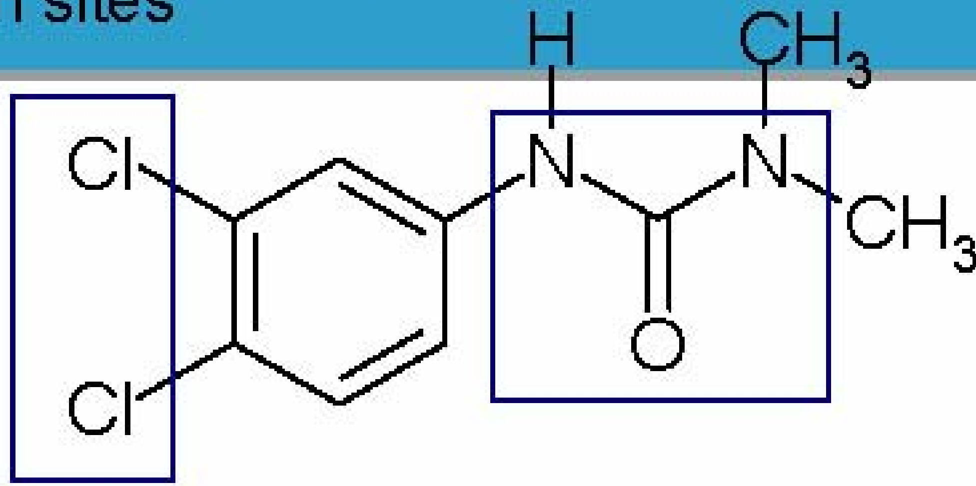
Diffuse functions are necessary to correctly describe the ion energetics

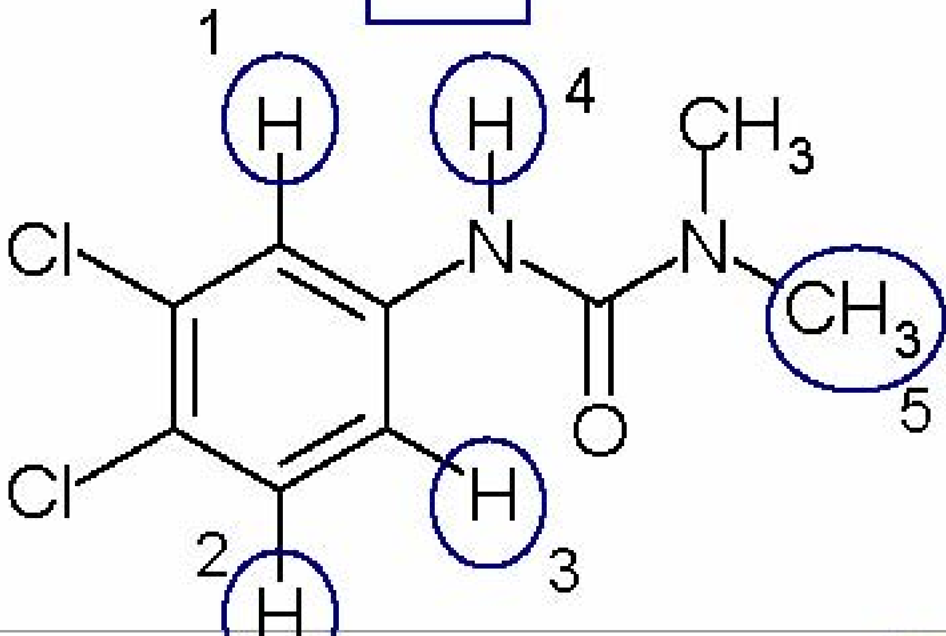
Part 1

Fragmentation of the quasi molecular anion $[M-H]^-$ of DCMU



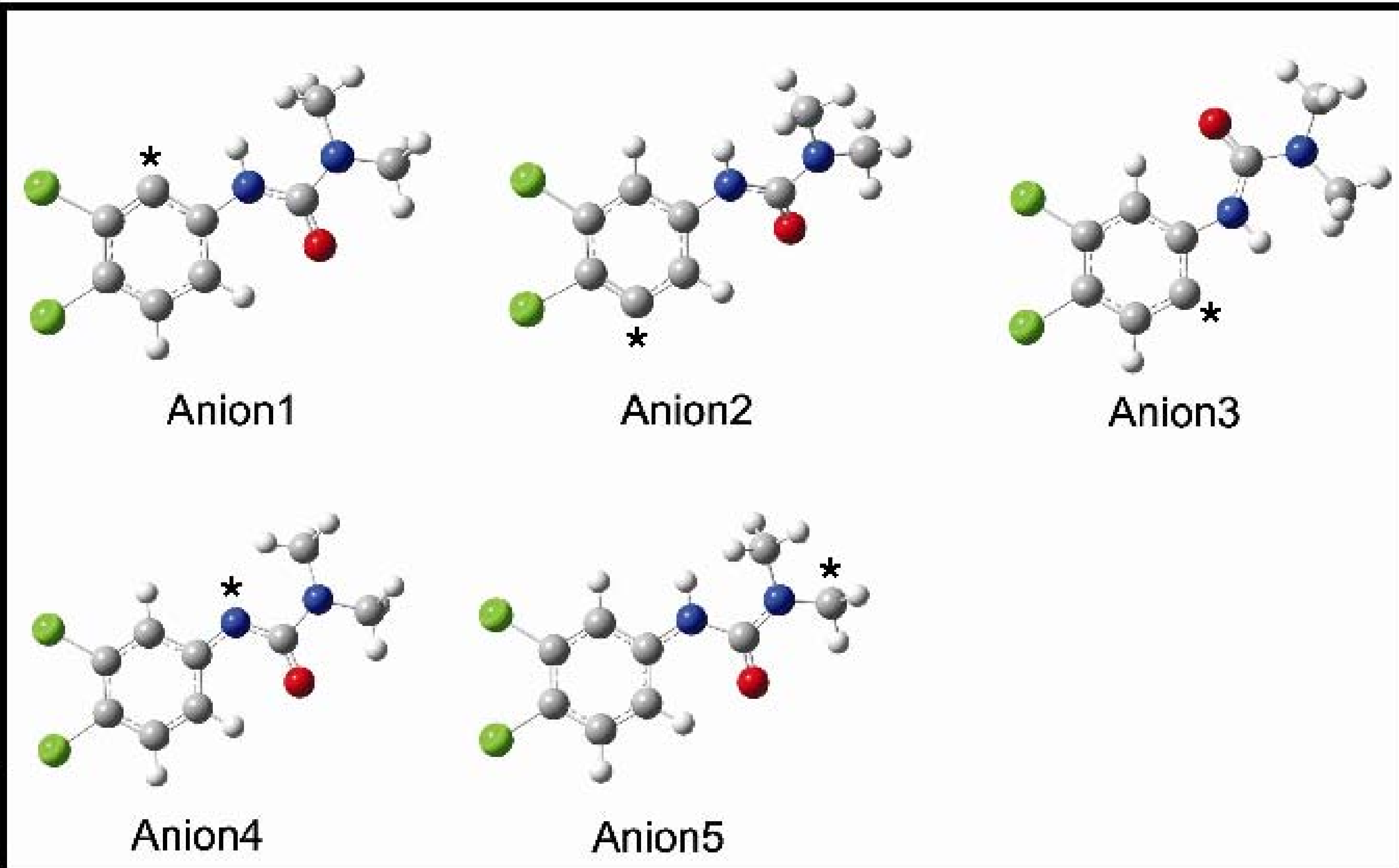
Structure, Functional groups and Deprotonation sites

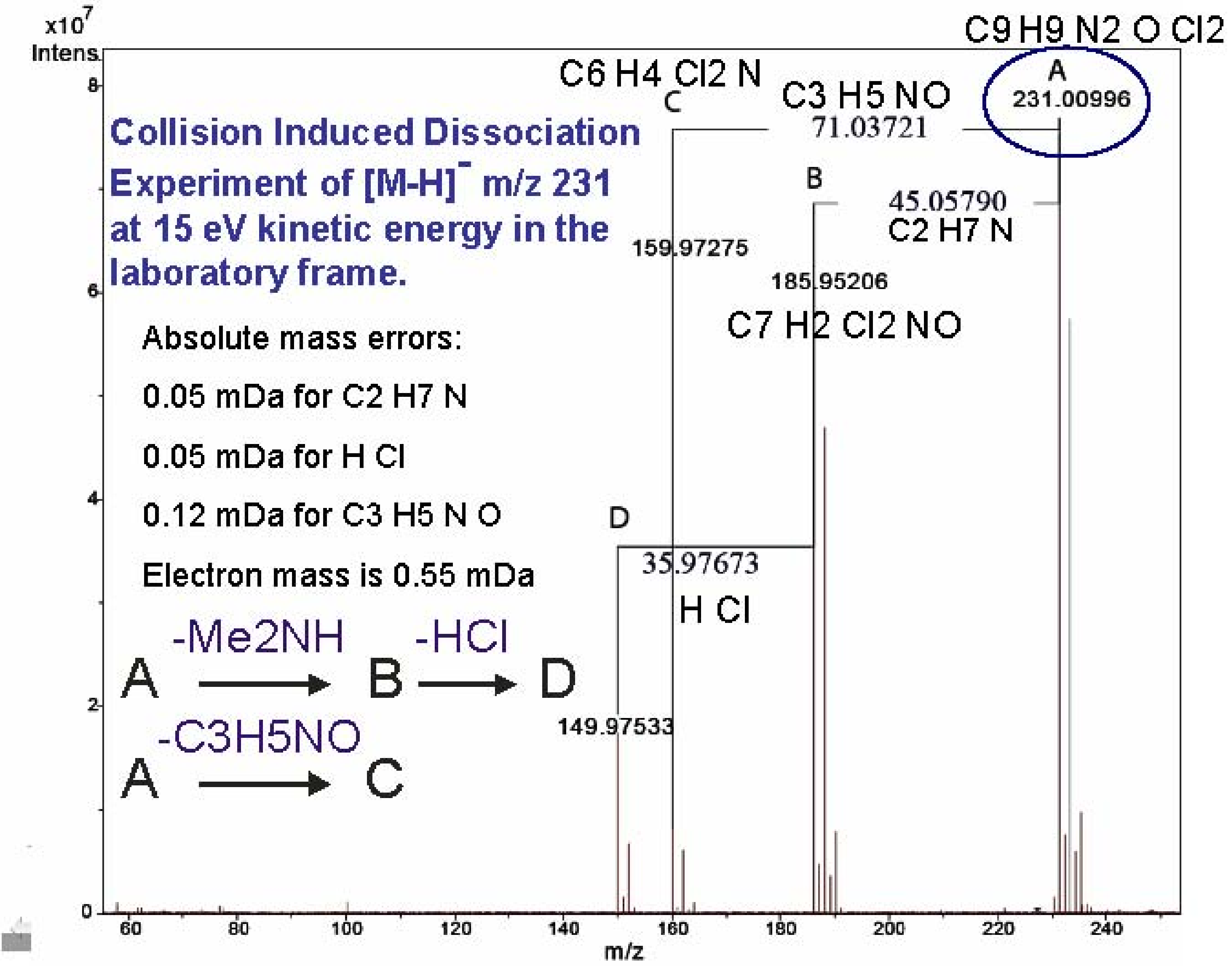




Isomer	DP B3LYP/6-311+G(2d,p)
Anion1	368
Anion2	380
Anion3	374
Anion4	335
Anion5	388

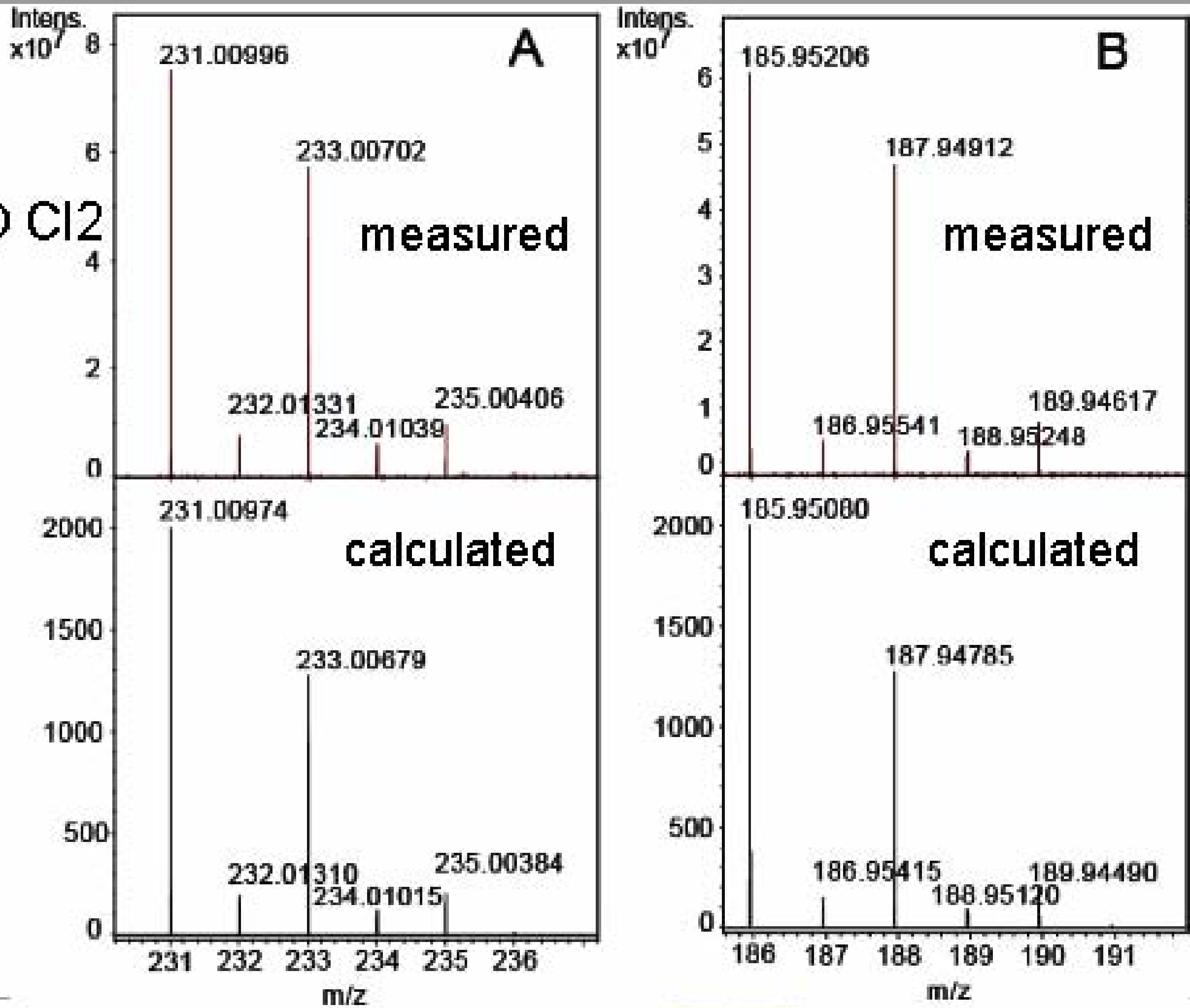
Optimized geometries for the five possible isomeric anions





Collision Induced Dissociation Experiment of [M-H]- m/z 231 at 15 eV kinetic energy in the laboratory frame.
Absolute mass errors:
0.05 mDa for C2 H7 N
0.05 mDa for H Cl
0.12 mDa for C3 H5 N O
Electron mass is 0.55 mDa
A -Me2NH → B -HCl → D
A -C3H5NO → C
C9 H9 N2 O Cl2
A
231.00996
C6 H4 Cl2 N
C
C3 H5 NO
71.03721
B
45.05790
C2 H7 N
159.97275
185.95206
C7 H2 Cl2 NO
D
35.97673
H Cl
149.97533
x10^7
Intens.
m/z

C9 H9 N2 O Cl2



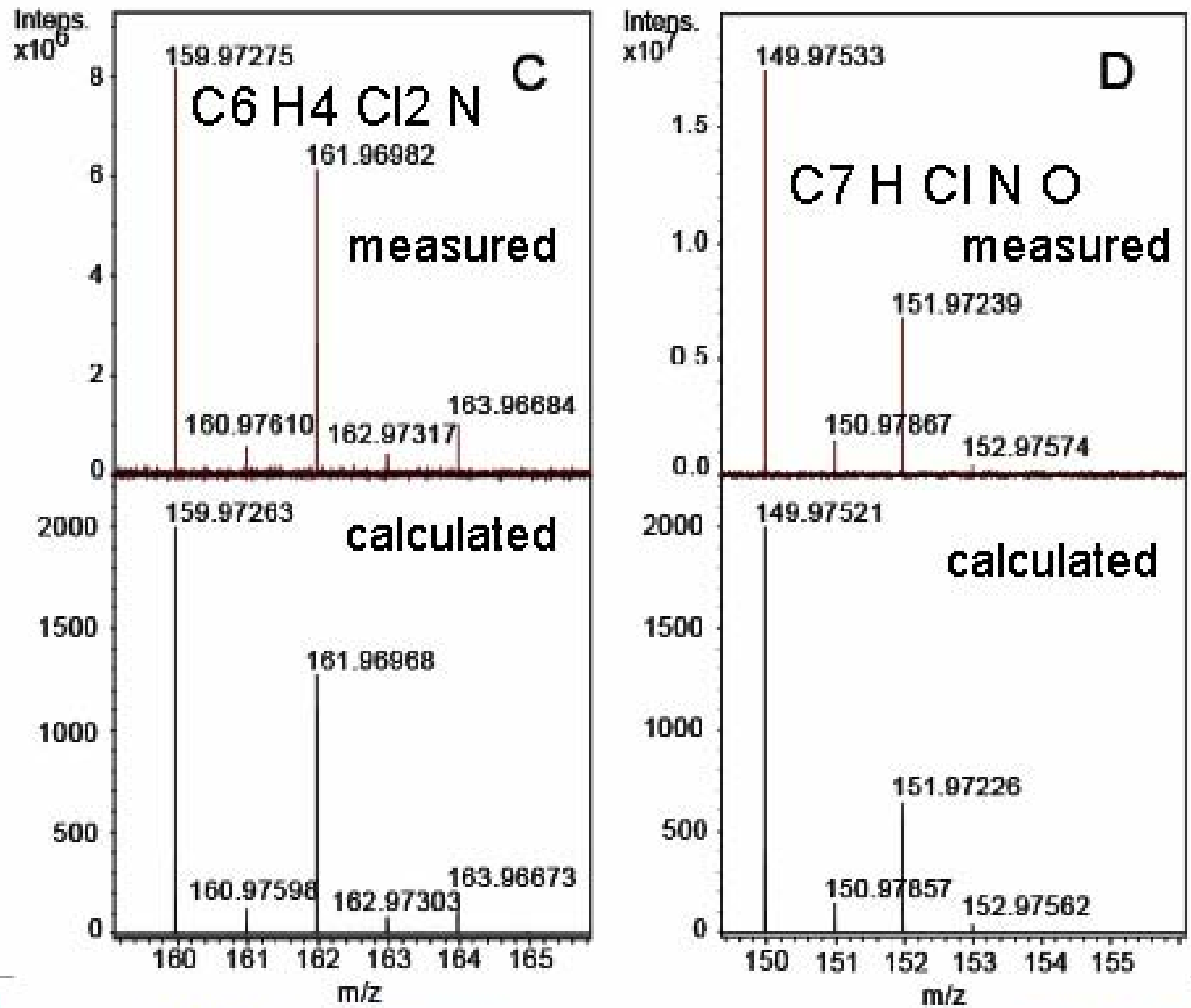
C7 H2 Cl2 N O

Isotopic distribution patterns

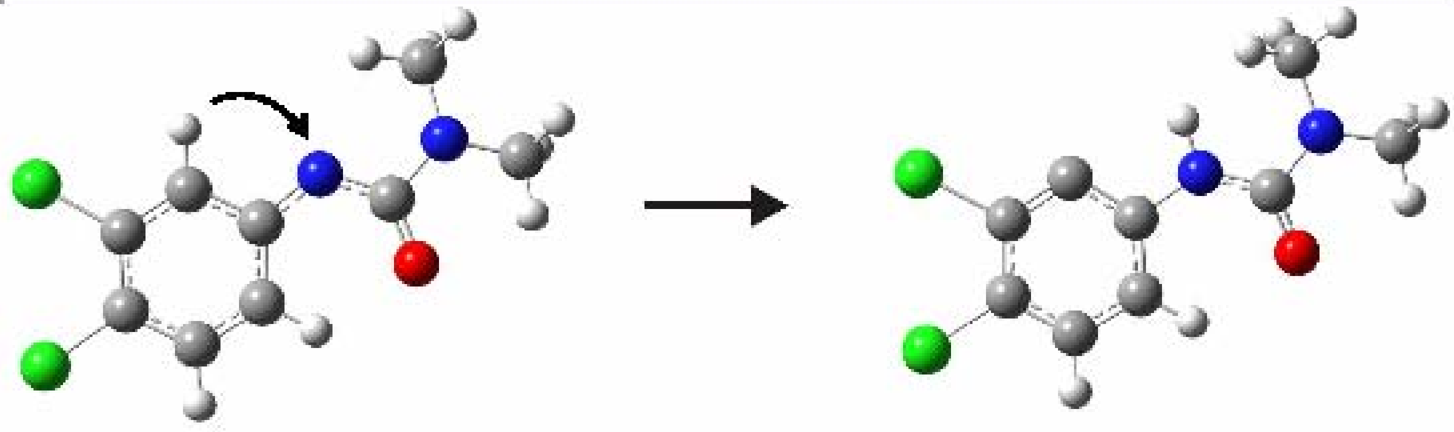
Number of scans: 30

Length of transient:
1 MWord

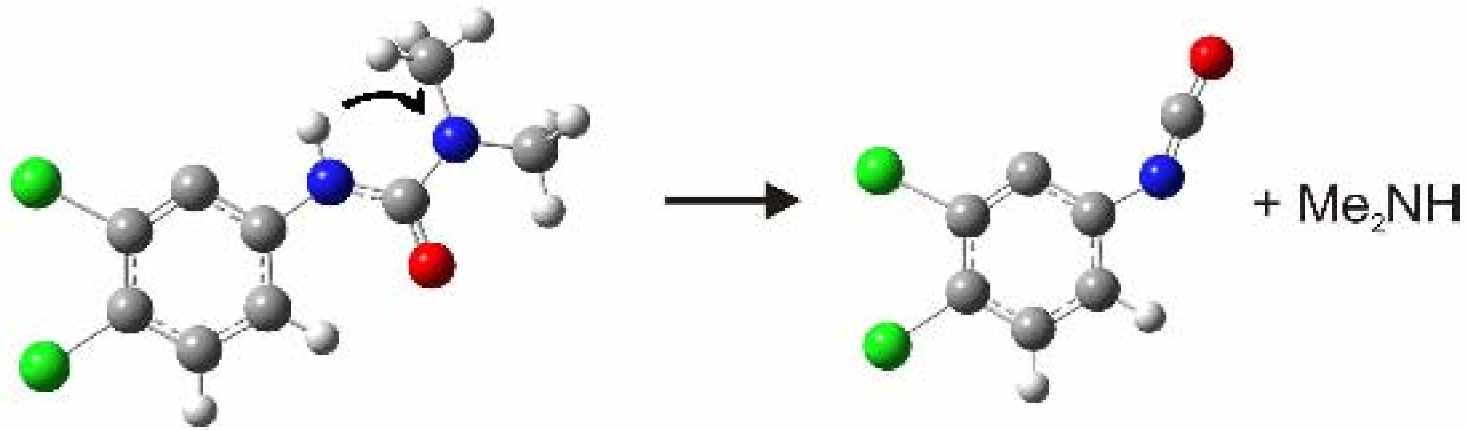
The FTMS instrument is capable of aquiring
4 MWords



Intramolecular Rearrangement in the $[M-H]^-$ anion

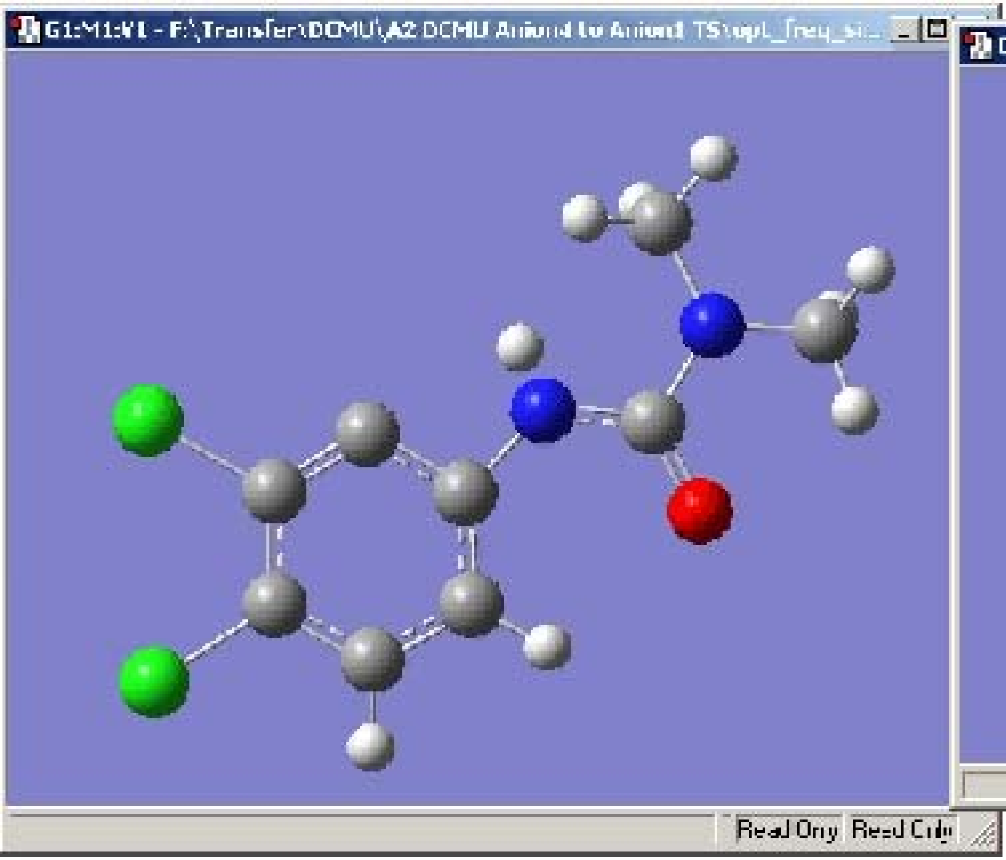


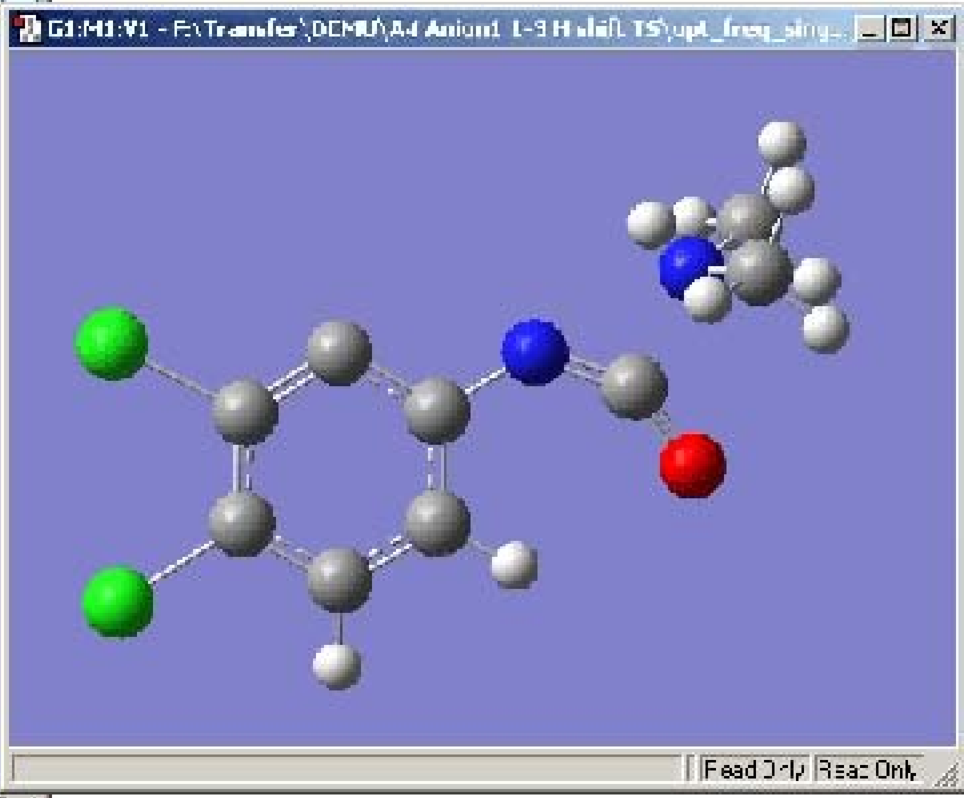
Anion4 Anion1



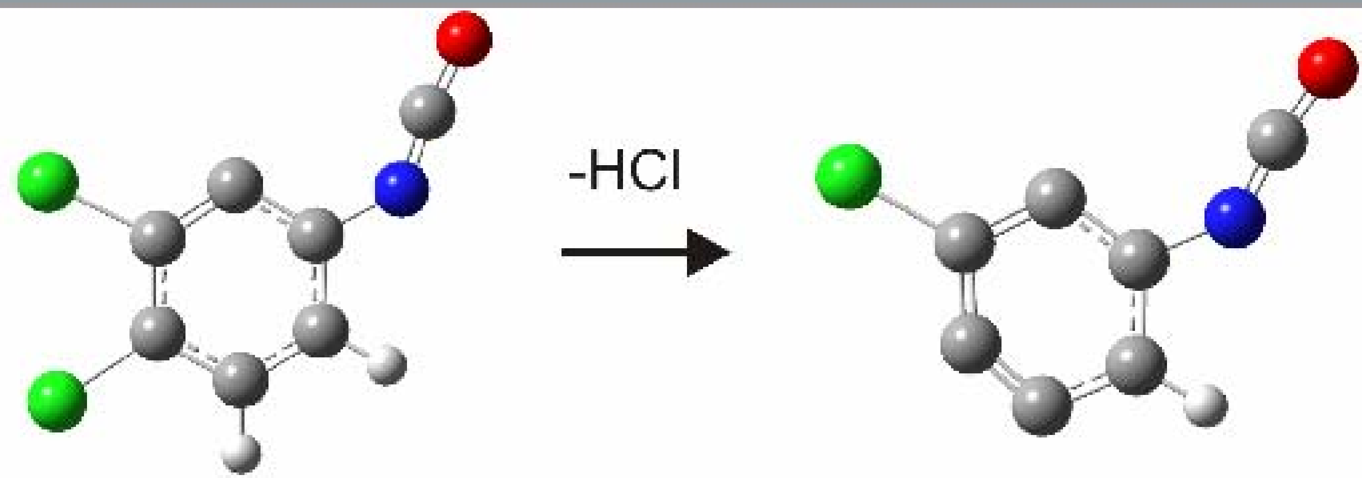
Anion1

Two steps for the concerted elimination of Dimethylamine



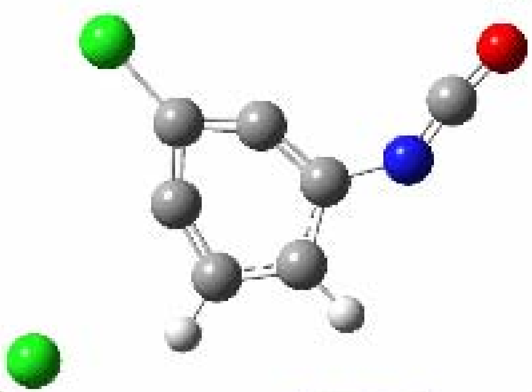


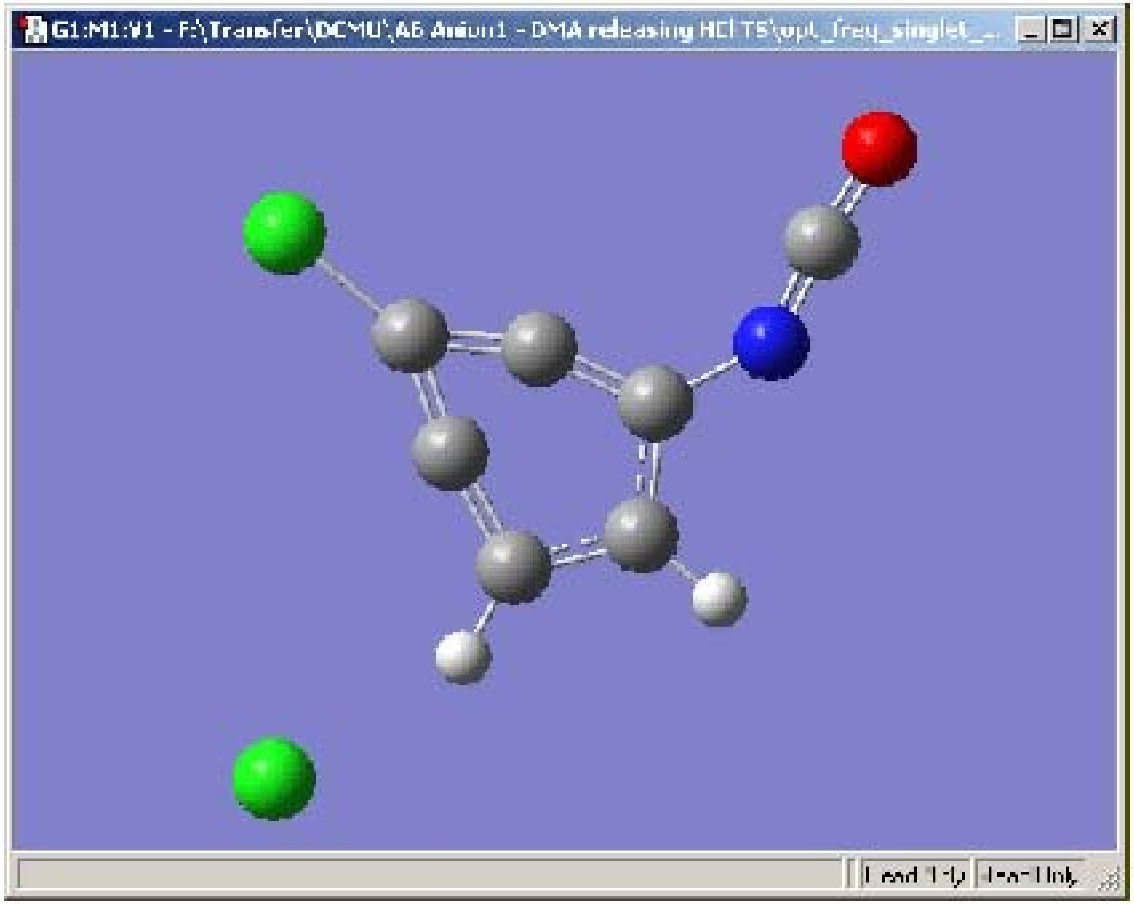
HCl elimination from the primary product ion

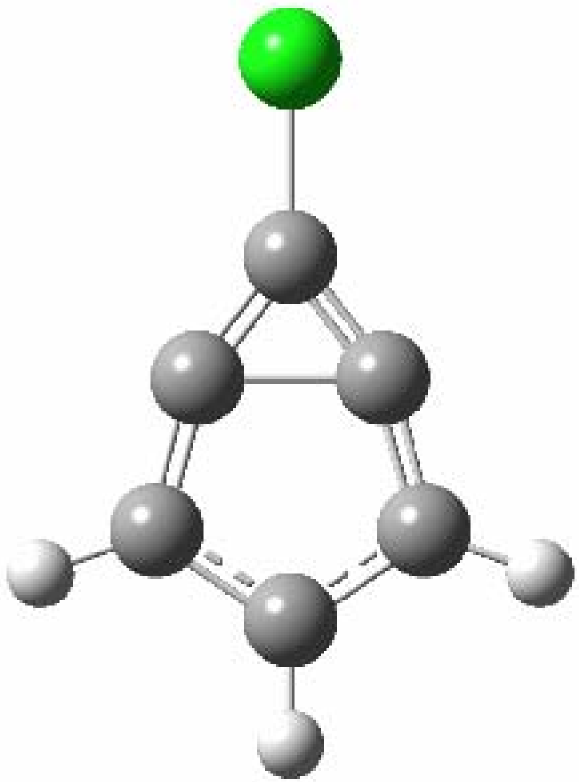


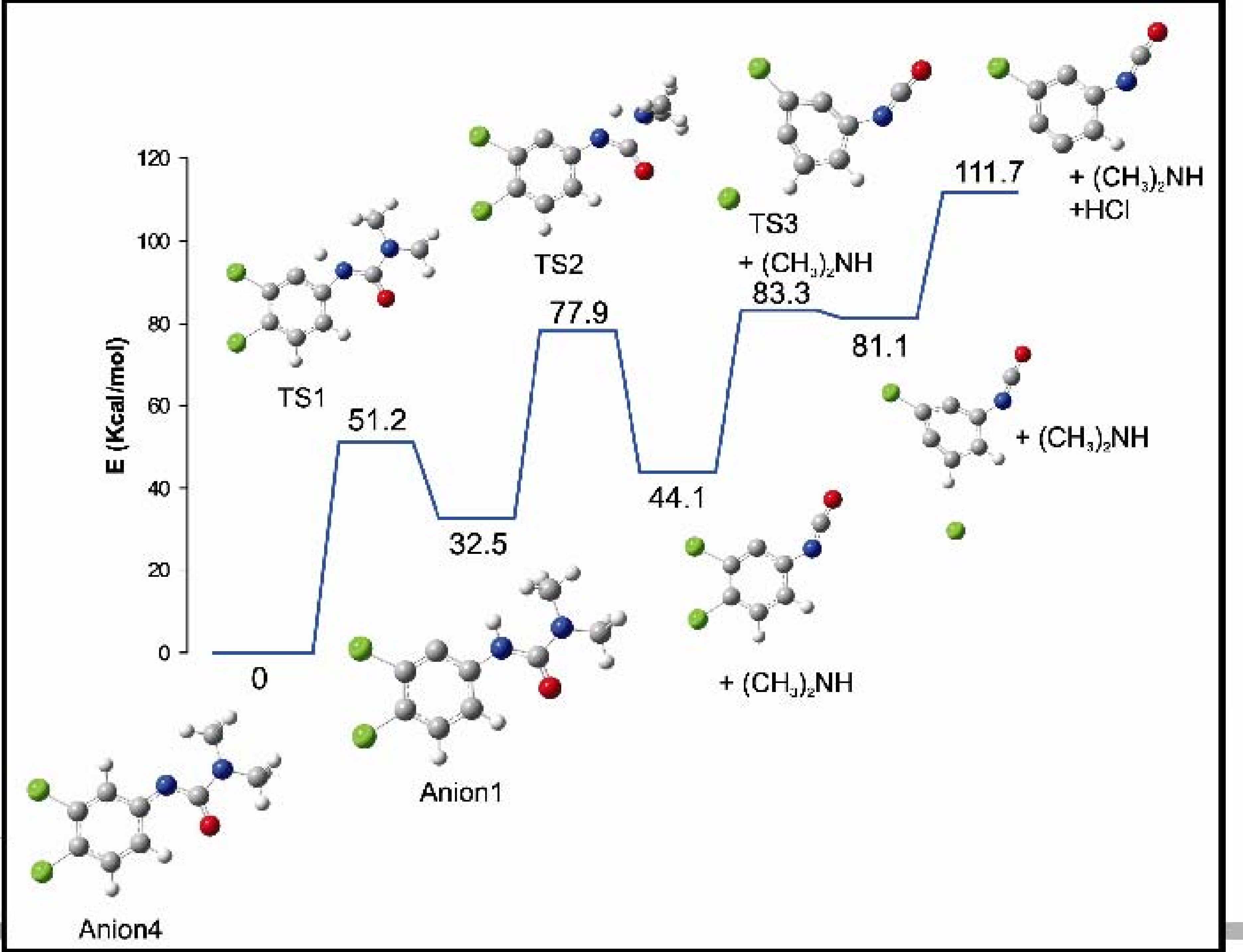
1,2-Dichloro-4-isocyanato-Benzene

10 π aromatic ring mono anion



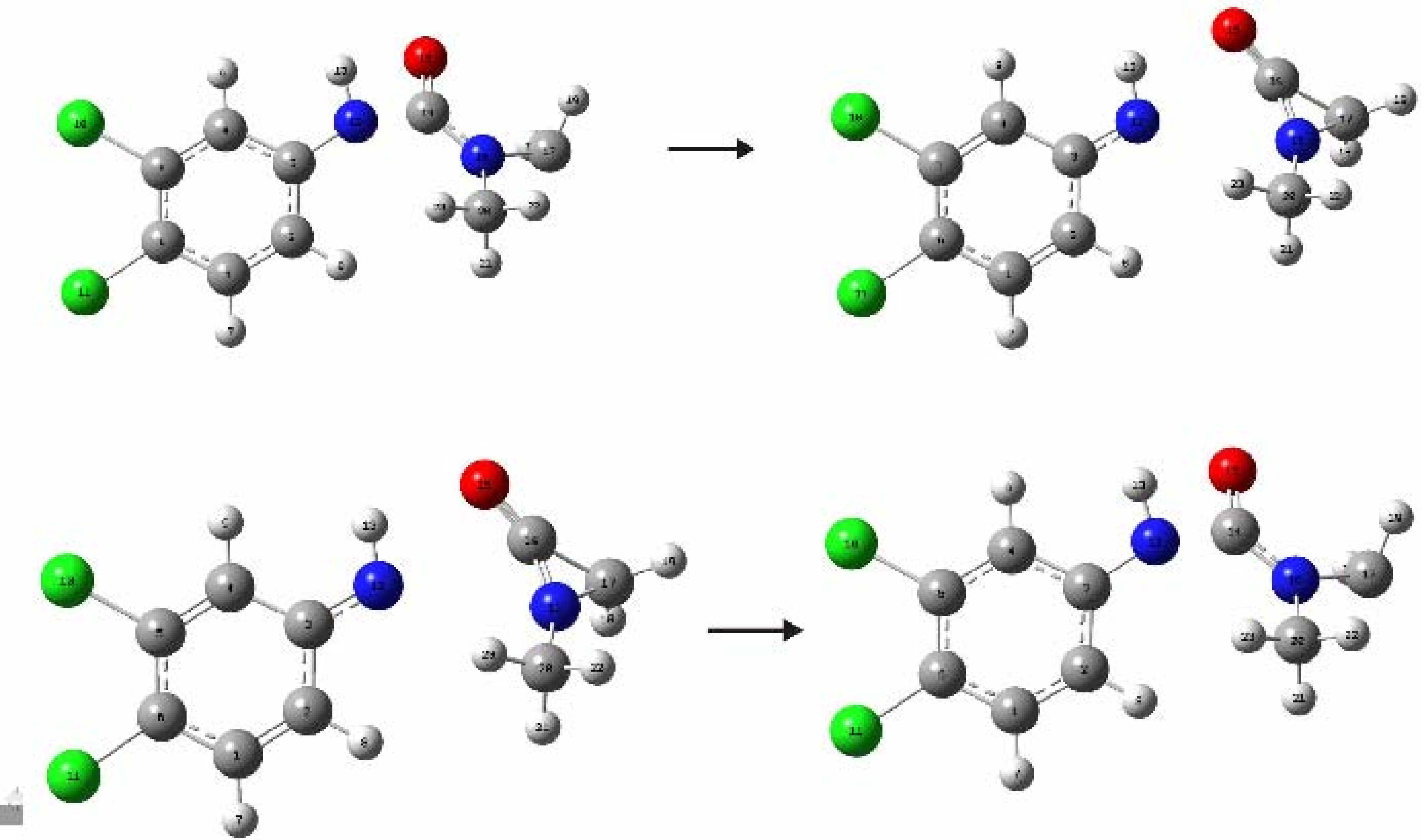

G1:M1:V1 - DMA releasing HCl TS



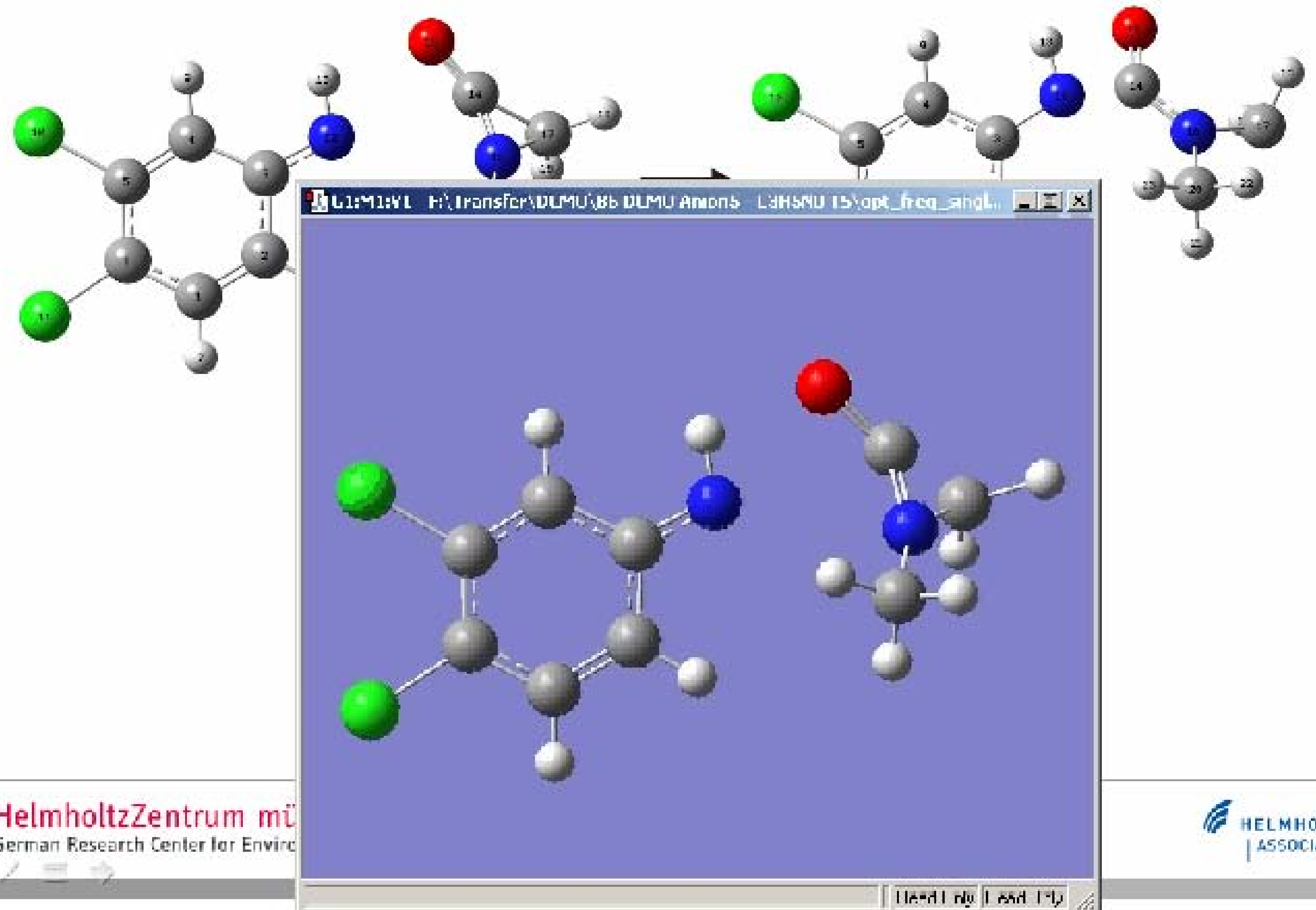


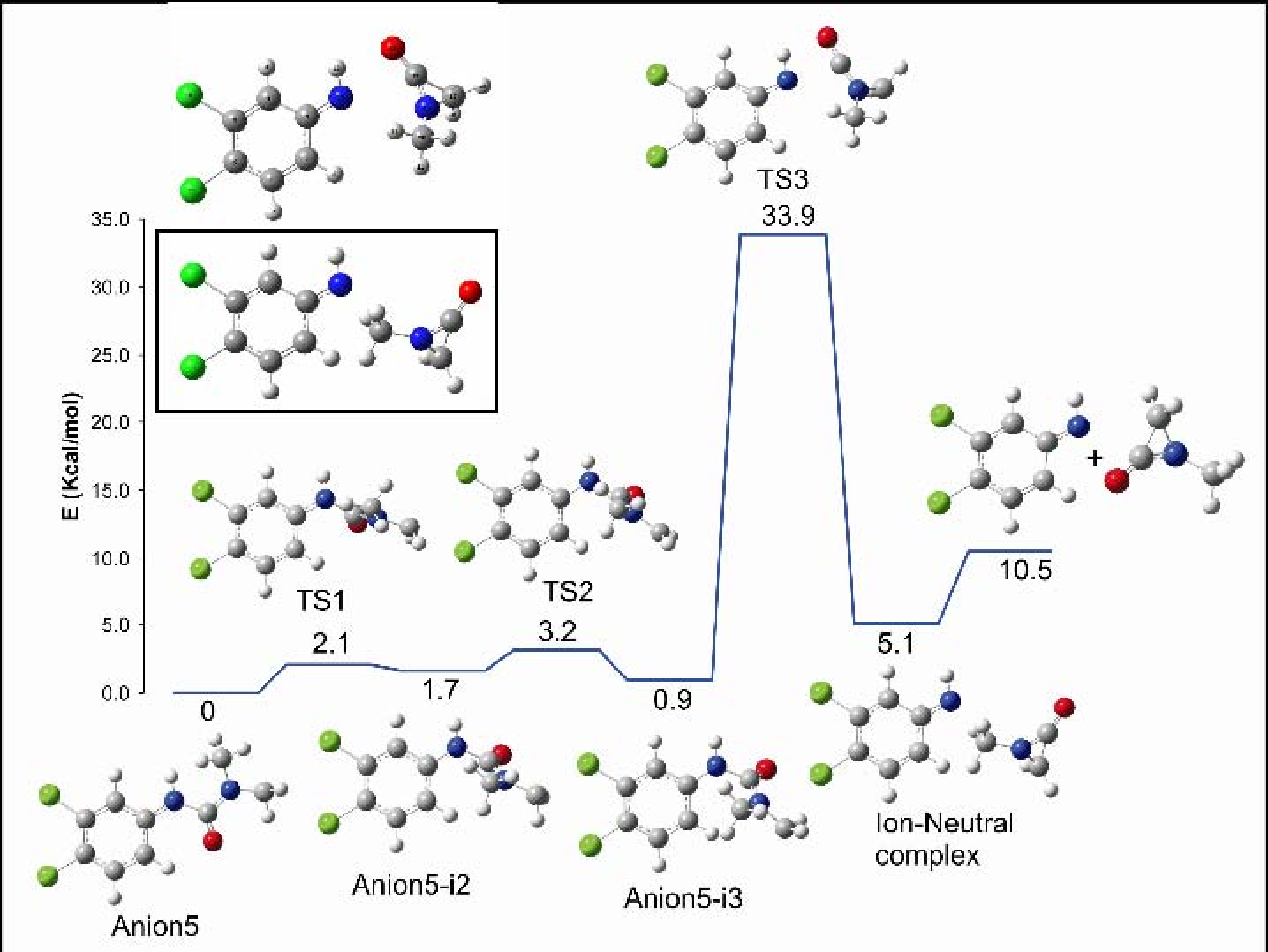
E (Kcal/mol)
120
100
80
60
40
20
0
0
51.2
32.5
77.9
44.1
83.3
81.1
111.7
TS1
TS2
TS3
+ (CH3)2NH
+ (CH3)2NH
+ (CH3)2NH
+ (CH3)2NH
+HCl
Anion1
Anion4

The second fragmentation pathway

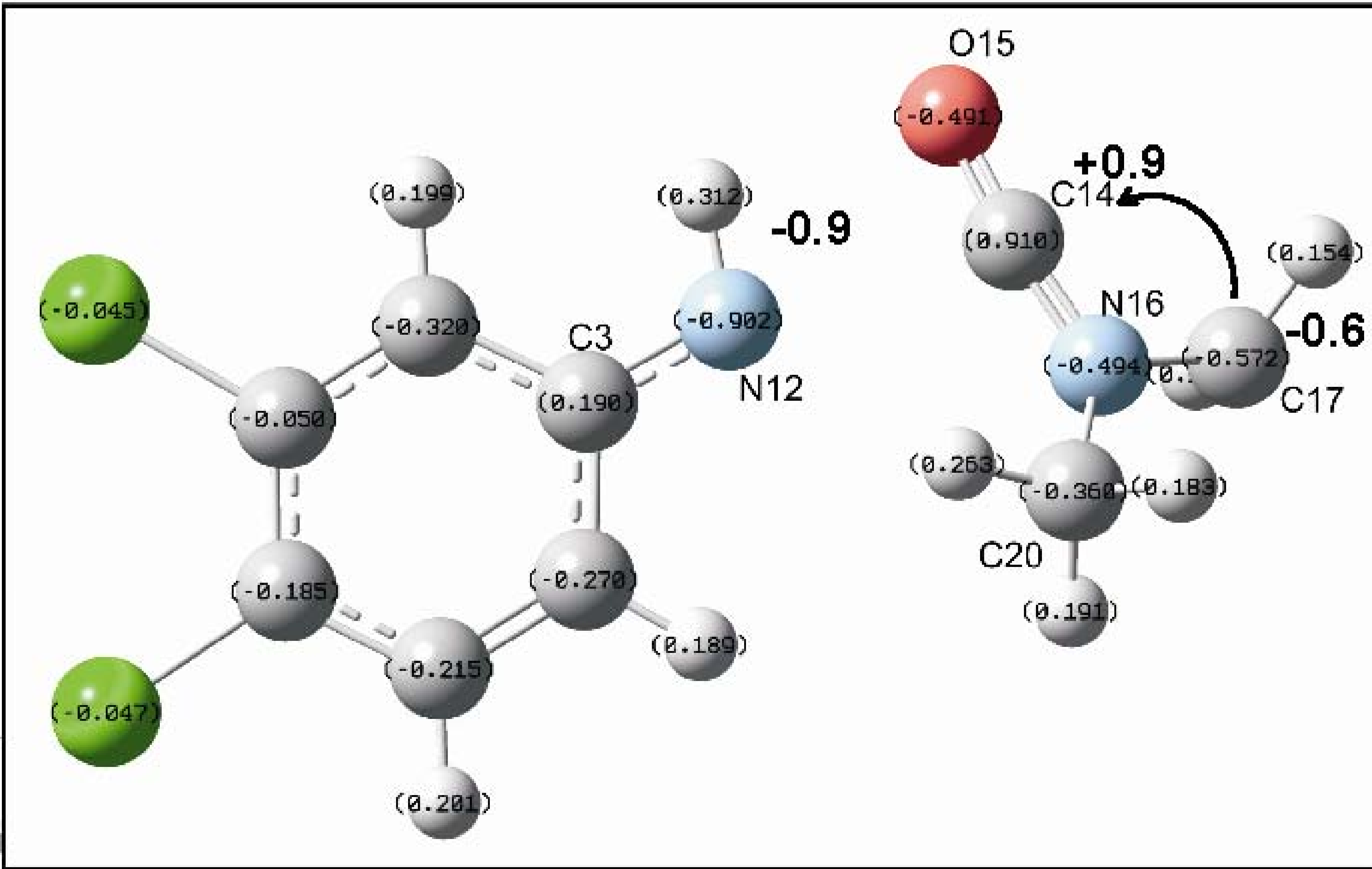


Nucleophilic addition of aniline anion to the carbonyl's Carbon atom of the aziridin ring

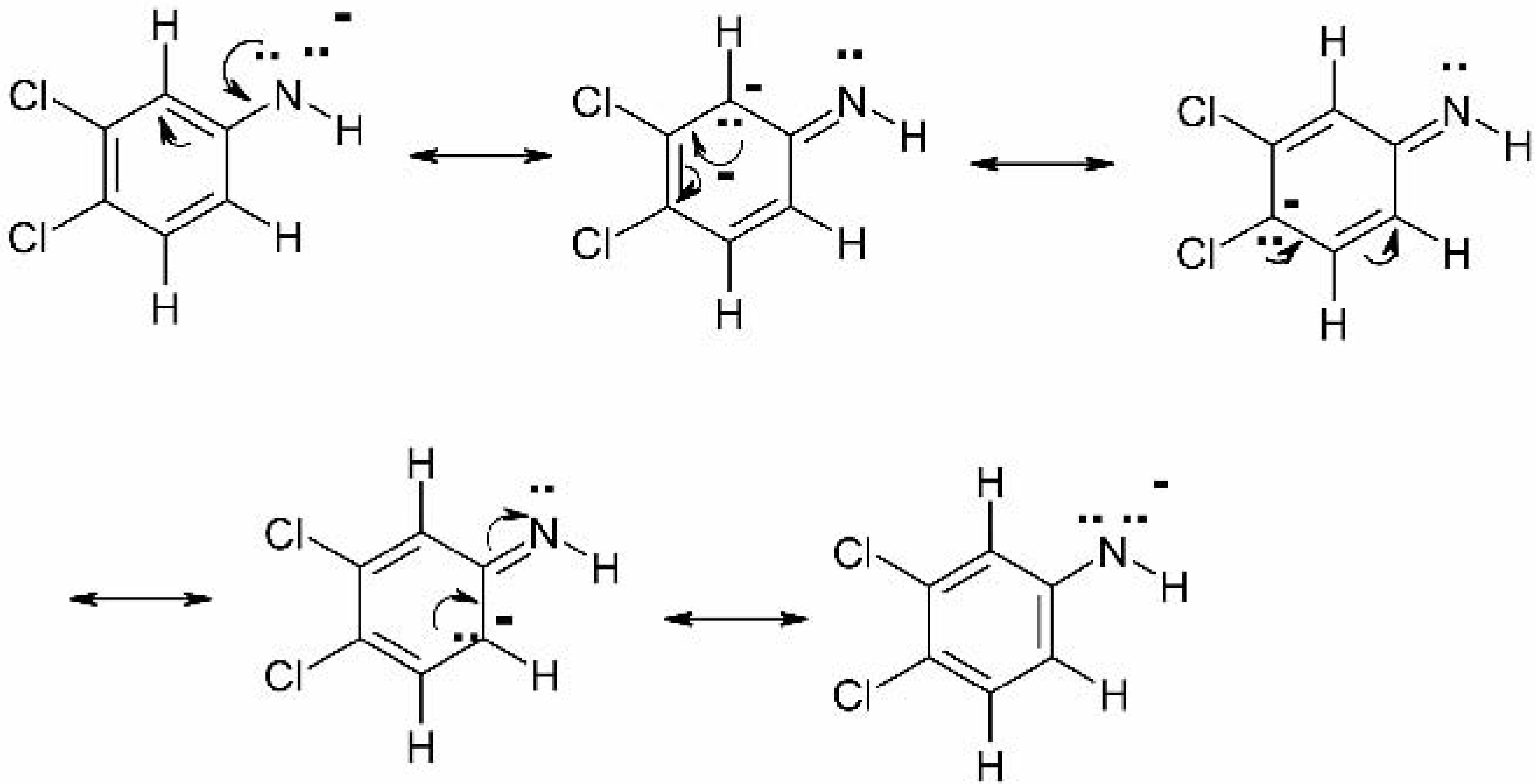



E (Kcal/mol)
35.0
30.0
25.0
20.0
15.0
10.0
5.0
0.0
TS3
33.9
TS1
TS2
2.1
3.2
1.7
0.9
0
5.1
10.5
+
Anion5
Anion5-i2
Anion5-i3
Ion-Neutral complex

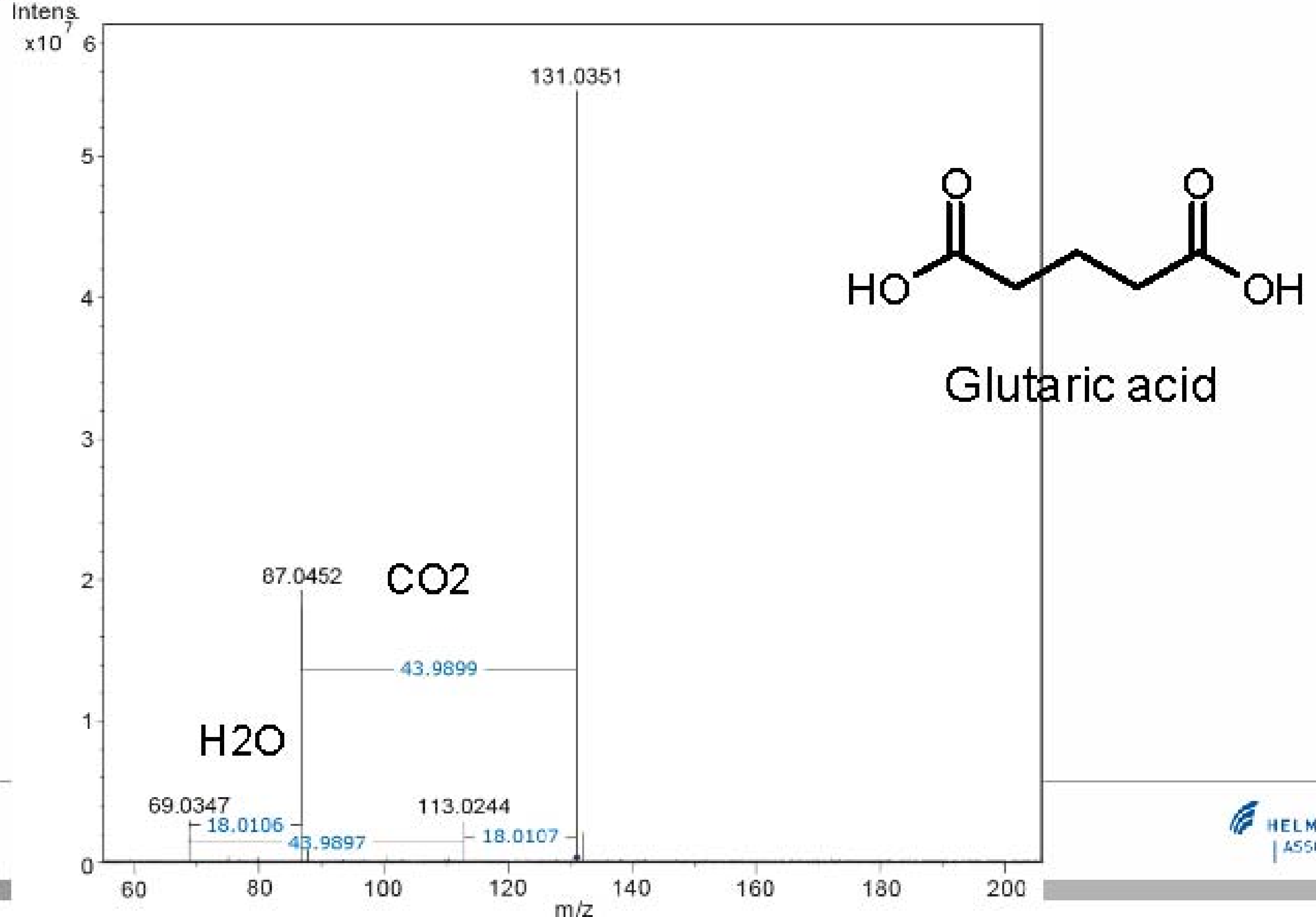
NBO charge distribution for the identidied transition State for C3H5NO elimination / Cyclization

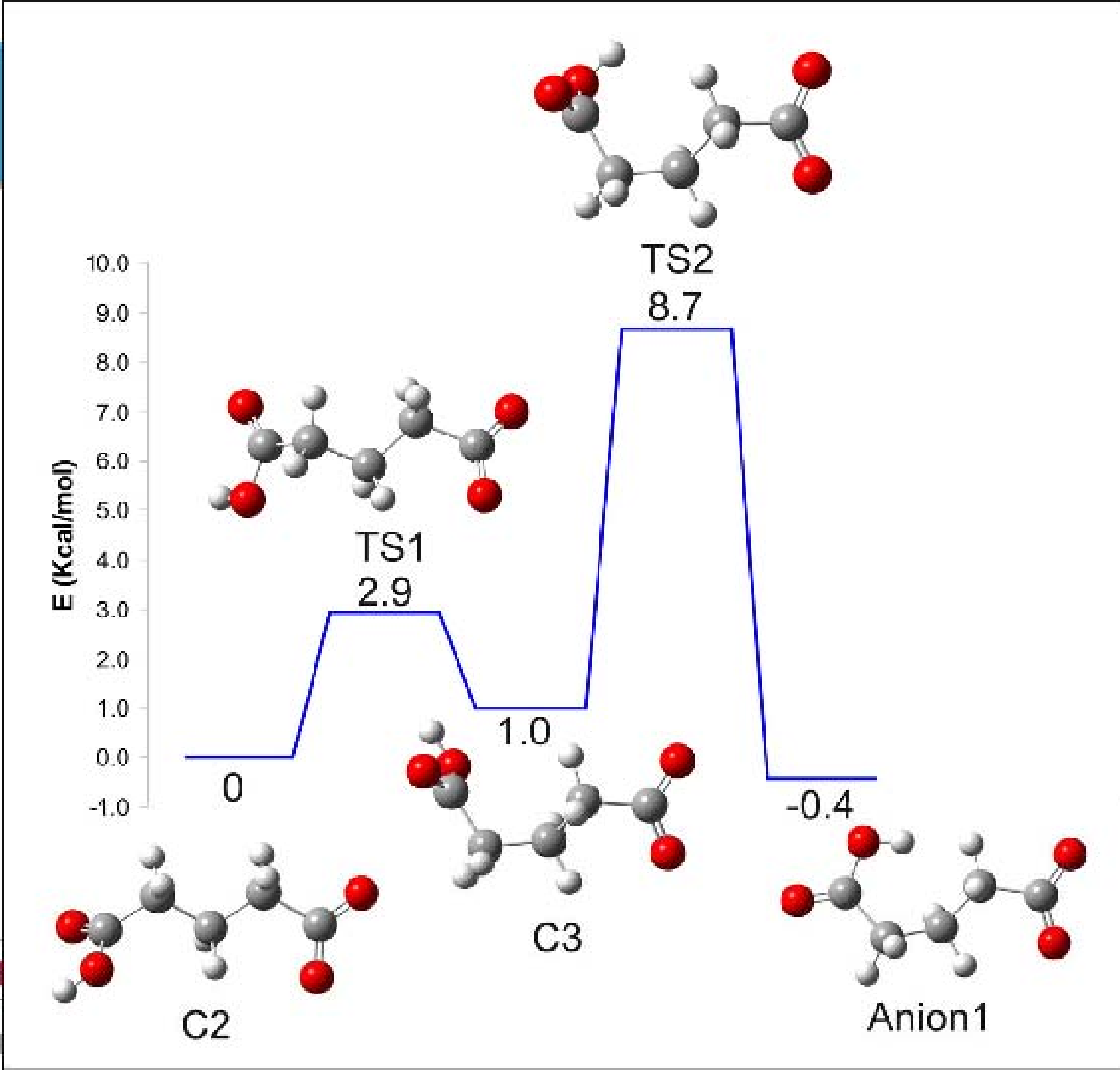


Stability of the formed aniline anion through electron delocalization – Five canonical forms exist



Fragmentation mechanisms of glutaric acid.

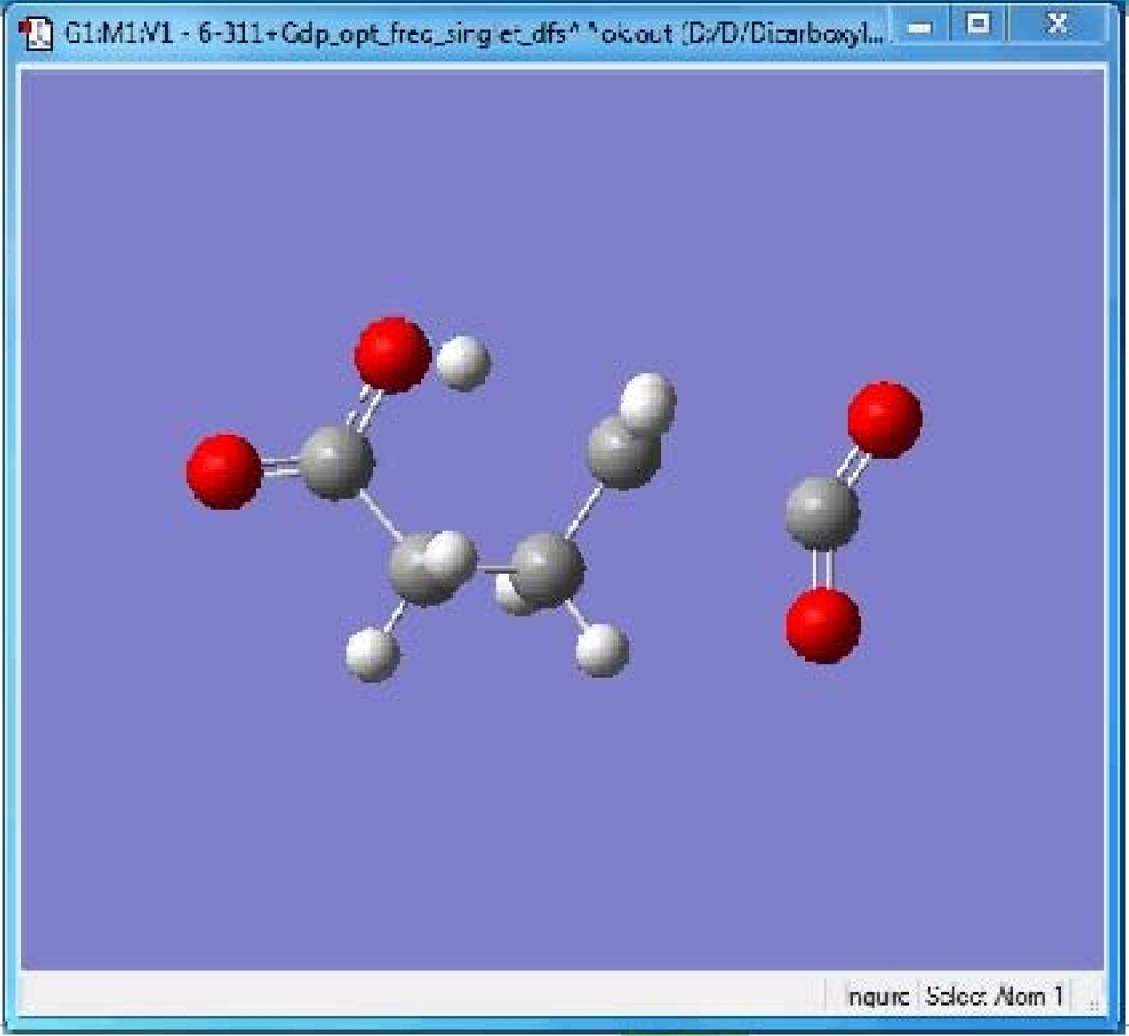


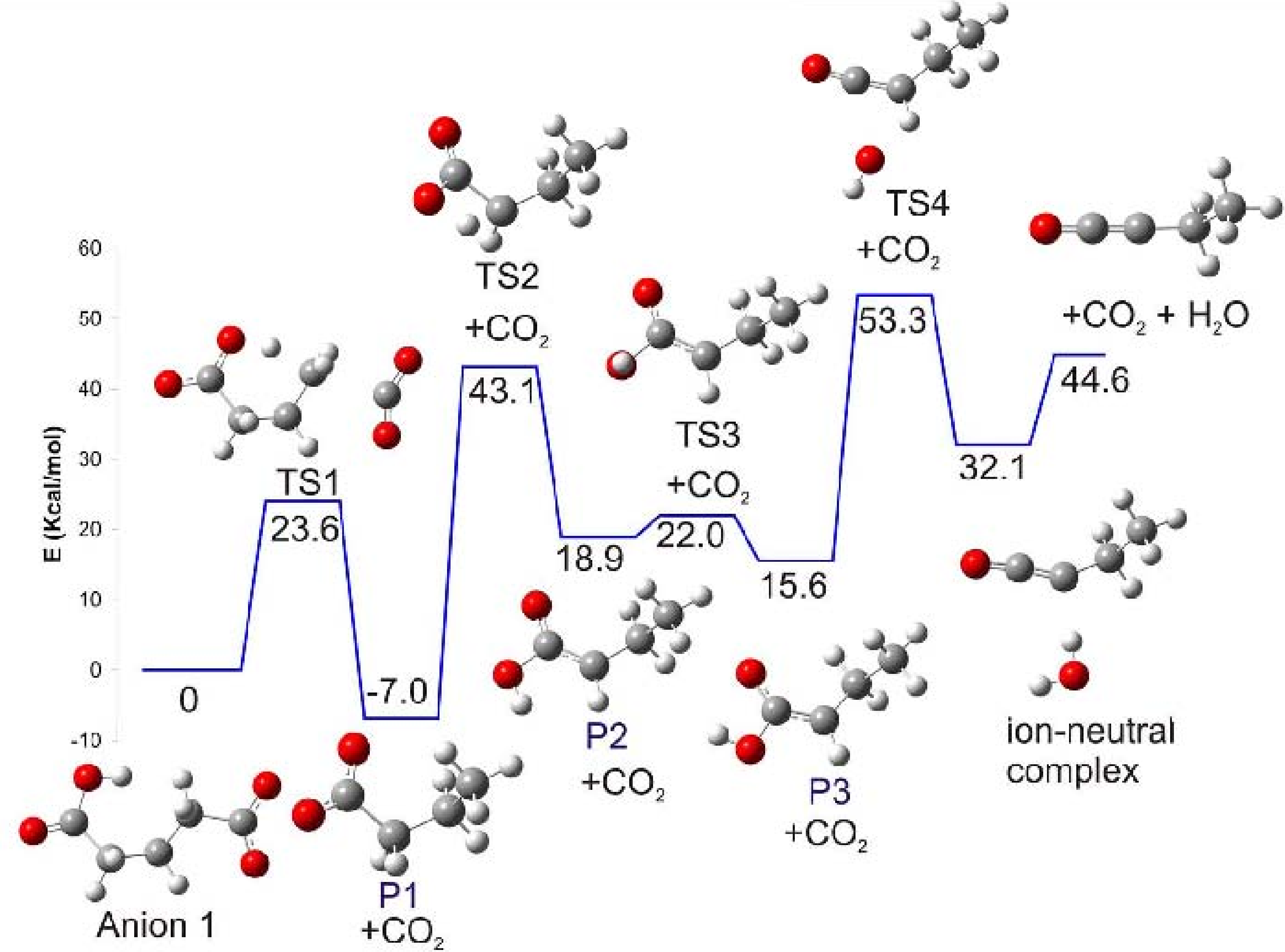

TS2
8.7
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
E (Kcal/mol)
TS1
2.9
1.0
0
-0.4
C2
C3
Anion1

Hel
Germ

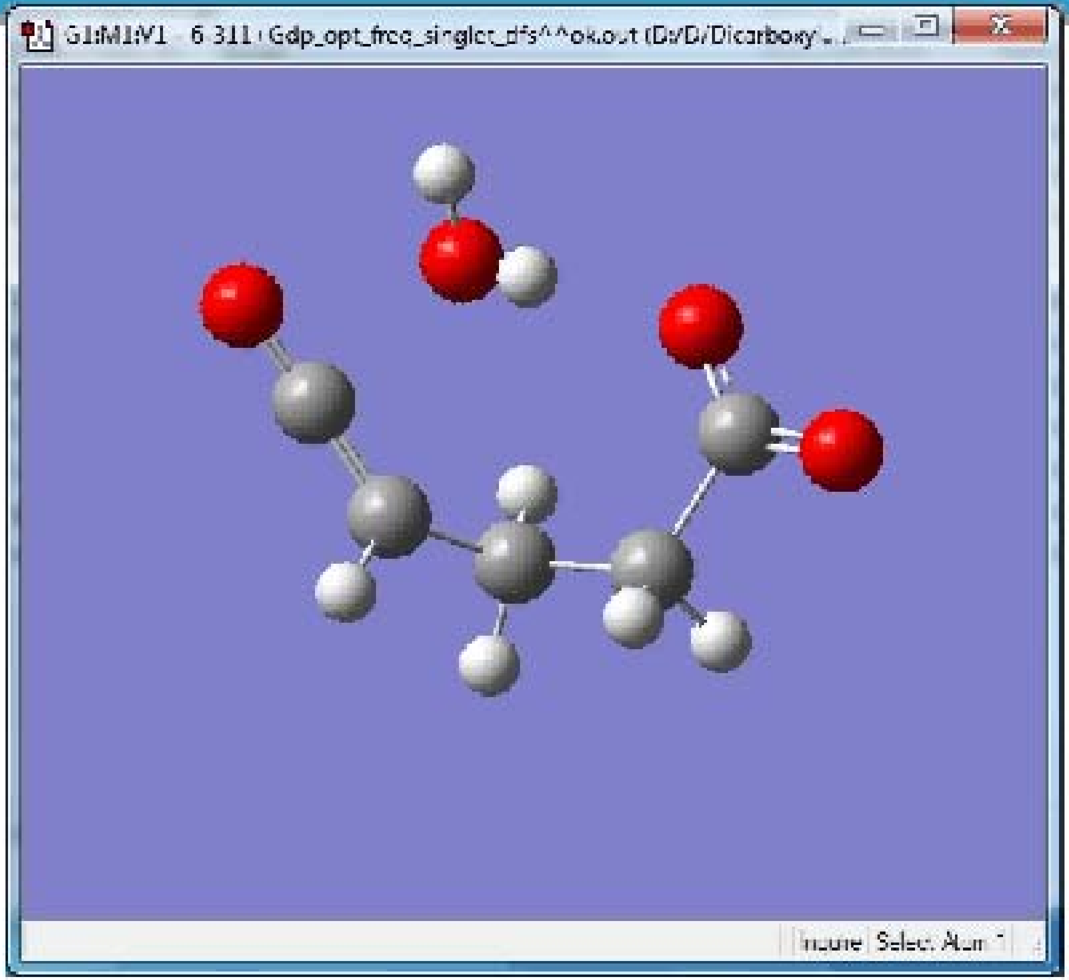
Z
ON

CO2 elimination concerted with intramolecular 1,5 proton shift





E (Kcal/mol)
60
50
40
30
20
10
0
-10
0
TS1
23.6
-7.0
TS2
+CO2
43.1
18.9
TS3
+CO2
22.0
15.6
TS4
+CO2
53.3
32.1
+CO2 + H2O
44.6
Anion 1
P1
+CO2
P2
+CO2
P3
+CO2
ion-neutral
complex



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RCM

Exploring rearrangements along the fragmentation of glutaric acid negative ion: a combined experimental and theoretical study

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Exploring rearrangements along the fragmentation pathways of diuron anion: A combined experimental and computational investigation

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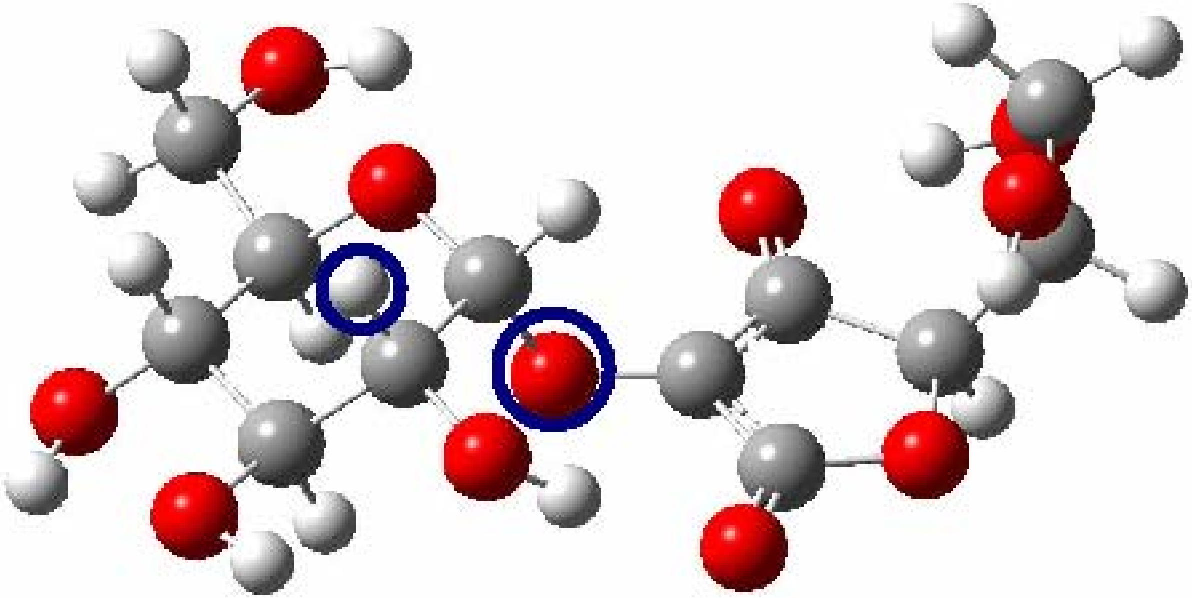
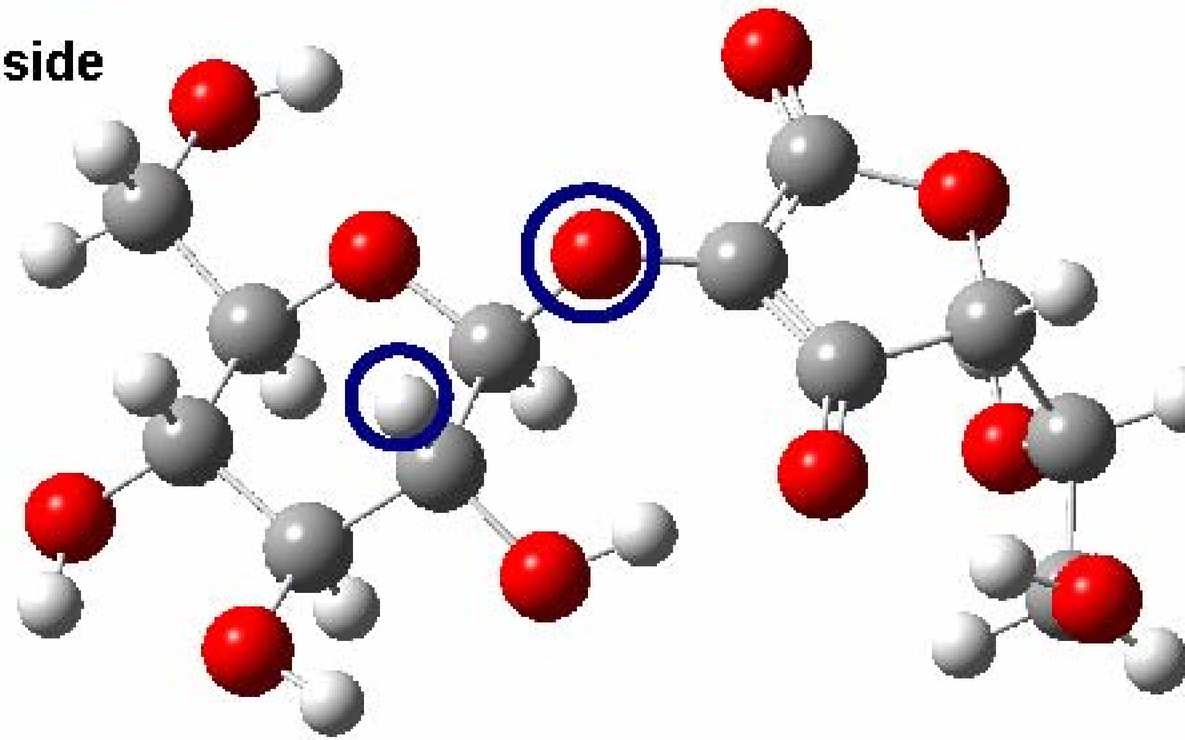


α- ascorbic acid 2-*O*-glucoside



β- ascorbic acid 2-*O*-glucoside

Conclusion

- An example for a chlorinated herbizide with multi-functional groups was given to show that measured isotopic patterns match the calculated ones exactly. This is a powerful feature of this ICR cell relative to others, which are dependent on the trapping voltages applied in the cell.
- Multi acceleration events are possible inside one device (the hexapole as a collision chamber). Thus, internal energy can be deposited many times and this leads to formation of product ions belonging to different generations.

Conclusion

- Intramolecular interaction between two terminal functional groups plays a key role in facilitaing new thermodynamically favourable fragmentation mechanisms.

- The implementation of a quantum mechanical approach together with mass spectrometric measuremnts is necessary to get deep insight about the physical organic chemistry which is taking place in the gas phase.

Conclusion

- All what was presented can be be of great help in regard to structural elucidation of interesting organic components, which bear multi-functional organic groups in humic and fulvic acids.

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Prof. Dr. Wanczek

All colleagues of our workgroup

Thank You for your attention