Polyatomic ions in traps: from molecules via clusters to nanoparticles

Dieter Gerlich

Introduction

Ions in rf fields
Basics, buffer gas cooling

Typical tests
Spectroscopy
Association reactions, cluster
LIR: $\text{N}_2^+$ + Ar

Recent application
Reactions with H atoms
Deuteration, nuclear spin
State selective preparation

Nanoparticles
NPMS
HT - SRET, Decay of C$_{60}^+$

Summary and outlook
Gasentladungs- und Ionenphysik
DFG FG Laboratory Astrophysics
1993 - 2009

TV-22PT
S. Schlemmer, O. Asvany (Köln)

AB-22PT + H-beam
A. Schlemmer, A. Luca, G. Borodi
J. Glosik, R. Plasil, C. Mogo

RET + Cₙ-beam
I. Savic, S. Decker, I. Cermak

Black body radiation
S. Decker, M. Kämpf

Beam-Trap
M. Smith

Astrochemistry

22PT-spectroscopy
J. Maier, Basel

Cold TrpH⁺, TyrH⁺
T. Rizzo, O. Boyarkin
buffer gas cooling
ultracold ions: N$_2^+$

Reactions with H atoms
Neg ions
H$-$ + H
Big Bang Nucleosynthesis

$< 1 \text{s} : n/p \sim 1$

$p + e^- \leftrightarrow n + \nu$

$n + e^+ \leftrightarrow p + \bar{\nu}$

$> 1 \text{s}, \tau_{\nu/2} \sim 615 \text{s}$

$n \rightarrow p + e^- + \bar{\nu}$

$100 \text{s}, n/p \sim 1/7$

$10^9 \text{K}, kT \sim 0.1 \text{MeV}$

$p + n \leftrightarrow d + \gamma + 2.2 \text{MeV}$

$d + n \rightarrow H^3 + \gamma$

$H^3 + p \rightarrow He^4 + \gamma$

$d + p \rightarrow He^3 + \gamma$

$He^3 + n \rightarrow He^4 + \gamma$
Early universe chemistry: end of dark age

\[
\text{H}^- + \text{H} \rightarrow \text{H}_2 + \text{e}^-
\]

- important for cooling primordial clouds (8,000 - 200 K)
- uncertainties affect predictions for star formation

Volker Bromm, Physik Journal 7 (2008) Nr.4, 29
H$_2$ formation in the early Universe

radiative association
very slow
H + H → H$_2$ + h$_\nu$

early times
H$^+$ + He → HeH$^+$ + h$_\nu$
HeH$^+$ + H → H$_2^+$ He
H$_2^+$ + H → H$_2$ + H$^+$

later times
H$^+$ + H → H$_2^+$ + h$_\nu$
H* + H → H$_2$ + h$_\nu$
→ H$_2^+$ + e$^-$

H$^-$ channel
H + e$^-$ → H$^-$ + h$_\nu$
H$^-$ + H → H$_2$ + e$^-$

The periodic table of astronomers

H

He

Mg

C  N  O  Ne

Si  S  Ar

Fe
Formation and destruction of CH$_n^+$ in space

- C$^+$, CH$^+$, CH$_2^+$, CH$_3^+$, CH$_4^+$, CH$_5^+$, H$_2$, H$_3^+$, He$^+$, CO, HCO$^+$, H$_2$CN$^+$, N, O, H$_2$O, CH$_5$O$^+$, CH, CH$_2$, CH$_4$, CH$_2$
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Summary and outlook
INHOMOGENEOUS RF FIELDS: A VERSATILE TOOL FOR THE STUDY OF PROCESSES WITH SLOW IONS

DIETER GERLICH

I. Introduction

II. Motion of Charged Particles in Fast Oscillatory Fields

III. Experimental Applications and Tests of Several rf Devices

IV. Description of Several Instruments

V. Studies of Ion Processes in RF Fields: A Sampling

VI. Conclusions and Future Developments
Motion in a fast oscillating field

\[ m\ddot{r} = qE_0(r) \cos(\Omega t + \delta) + qE_s(r) \]

homogen

inhomogen

Kapitza 1951, Landau-Lifschitz Classical Mechanics 1962
Motion in a fast oscillating field

\[ r(t) = r(0) - a \cos(\Omega t) \]
\[ a = qE_0/m\Omega^2 \]

\[ r(t) = R_0(t) + R_1(t) \]
\[ R_1(t) = -a(t) \cos \Omega t \]

\[ E_0(R_0 - a \cos \Omega t) = E_0(R_0) - (a \cdot \nabla)E_0(R_0) \cos \Omega t + \cdots \]

Effective potential
\[ V^*(R_0) = \frac{q^2 E_0^2}{4m\Omega^2} \]

Adiabaticity parameter
\[ \eta = 2q |\nabla E_0| / m\Omega^2 \]

Kapitza 1951, Landau-Lifschitz Classical Mechanics 1962
Ion trapping in rf fields

Effective Potential:

\[ V_{\text{eff}} = \frac{q^2 E_0^2}{4m\Omega^2} \quad \eta = \frac{2q|\nabla E_0|}{m\Omega^2} \]

2n-Pole:

\[ V_{\text{eff}} = \frac{n^2 q^2 V_0^2}{4m\Omega^2 r_0^2} \left( \frac{r}{r_0} \right)^{2n-2} \]

\[ \eta = 2n(n-1) \frac{qV_0}{m\Omega^2 r_0^2} \left( \frac{r}{r_0} \right)^{n-2} \]
Kinetic energy distribution

8-pole

16-pole

32-pole

$dN/dE$

$E/E_0$

$\langle E \rangle / E_0$

$time$

$0$ $1$ $3$

$0$ $1$ $2$ $3$

$+2 \cdot 10^{-4}$

$-2 \cdot 10^{-4}$
Confinement of charged particles in rf or AC fields
8-Pol (1969) / wire 4-Pol (1985)
Storage ion source

5.8 cm

10 cm

Gerlich 1977
History: thermalizing ions

Liquid N2 cooled trap (1988)
l-N$_2$ cooled RET (1990)
**TV 22-pole trap**

- **Effective potential** \( V^* \)
  \[ V^* = \frac{q^2 E_0^2}{4m\Omega^2} \]

- **Adiabaticity parameter** \( \eta \)
  \[ \eta = 2q \left| \nabla E_0 \right| / m\Omega^2 \]

- Parameters: \( q, m, E_0, \Omega, \) scaling: \( m\Omega^2 \)

\[ \eta \sim E_{\text{max}}^{(n-2)/(2n-2)} = E_{\text{max}}^{9/20} \]

\[ d = 1 \text{ mm} \]
\[ 2r_0 = 10 \text{ mm} \]
\[ r_0 = (n-1)d/2 \]
\[ 2n = 22 \]

D. Gerlich Physica Scripta, **T59** (1995) 256
22: a powerful number

„The 22 is the most powerful of all numbers. It is often called the Master Builder. The 22 can turn the most ambitious of dreams into reality. It is potentially the most successful of all numbers“.

Source:
http://www.decoz.com/Masternumbers.htm
Buffer gas cooling in an rf trap

Dynamic traps such as Penning, storage rings, cone trap do not work

Paul trap does not work

$\eta = \text{const}$

Only way to cool efficiently internal degrees of freedom are

rf multielectrode traps

sub K: cold pulsed effusive beam

He density / cm$^{-3}$

$10^{15}$

$10^{14}$

$10^{13}$

$10^{12}$

$10^{11}$

$t / \text{ms}$
\[ T_{\text{coll}} = \frac{m_{\text{ion}} T_{\text{He}} + m_{\text{He}} T_{\text{ion}}}{m_{\text{ion}} + m_{\text{He}}} \]

\[ T_{\text{He}} = 5 \text{ K} \]
\[ T_{\text{rot}} = T_{\text{coll}} = 25 \text{ K} \]
\[ T_{\text{ion}} = 245 \text{ K} \]
Sub-K cooling of stored ions

Phase space compression in ion chemistry

Liouville theorem

Mass spectrometer and method and improved ion transmission

**Patent suit 2002**
Applied Biosystems and MDS won against Micromass to the tune of $47.5M.

Ion funnel PNNL, Richland 1998
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Summary and outlook
The Lausanne cooled ion spectrometer

O. Boyarkin, S. Mercier, A. Kamariotis, and T. Rizzo

Electronic spectra of cold, protonated amino acids

O. Boyarkin, S. Mercier, A. Kamariotis, and T. Rizzo
Electronic spectra: the Basel 22PT

A. Dhzonson, J. P. Maier

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Summary and outlook
Ternary association: \( \text{N}^+ + 2 \text{He} \)

\[ T = (15 \pm 5) \text{K} \]

\[ [\text{He}] = 4.8 \times 10^{14} \text{ cm}^{-3} \]

Collision rate: \( 10^6 \text{ s}^{-1} \)

\[ k_{\text{eff}} = 8.7 \times 10^{-16} \text{ cm}^3 \text{ s}^{-1} \]

\[ k_3 = 4.6 \times 10^{-31} \text{ cm}^6 \text{ s}^{-1} \]

Complex life time: \( 1.6 \times 10^{-11} \text{ s} \)

D. Gerlich "Experimental Investigation of Ion-Molecule Reactions Relevant to Interstellar Chemistry"  
He$^+$ + 2 He: ternary association

$\text{He}^+ + 2\text{He} \rightarrow \text{He}_2^+ + \text{He}$

$k_3 = 1.4 \times 10^{-31} \left(\frac{T}{300 \text{ K}}\right)^{0.6\pm0.1} \text{ cm}^6\text{s}^{-1}$

22PT: [pau94], DRIFT: Böhringer Arnold 1983
Formation of Methanol in space?

CH$_3^+$ + H$_2$O + He → CH$_5$O$^+$ + He

CH$_3^+$ + H$_2$O → CH$_5$O$^+$ + hv

\[ k_3 = 5 \times 10^{-25} \text{ cm}^6\text{s}^{-1} \]

\[ k_c \geq 3.4 \times 10^{-9} \text{ cm}^3\text{s}^{-1} \]

\[ g k_c = 5.1 \times 10^{-10} \text{ cm}^3\text{s}^{-1} \]

\[ \tau_{\text{dis}} = 0.3 \mu\text{s} \]

\[ \tau_r > 2.0 \text{ ms} \]

\[ k_r = 5 \times 10^{-13} \text{ cm}^3\text{s}^{-1} \]
$H_n^+$ cluster growth stationary equilibrium: $n = 19$

$T = 10 \, \text{K}, [H_2] = 10^{14} \, \text{cm}^{-3}$, storage time 10 s

Growth and destruction of $((\text{H}_3^+\text{H}_2)_n$ cluster

p-H$_2$ is more destructive!

large cluster grow better with o-H$_2$

deuteration:

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Summary and outlook
$N_2^+ + \text{Ar}$: LIR

$N_2^+ + \text{Ar}$  \hspace{1cm}  $\text{Ar}^+ + N_2$

Energy level diagram:

- $A^2\Pi$ (786 nm, $v = 2$)
- $X^2\Sigma$ (0, $v'' = 2$)

Transition:

- $2P_{1/2}$
- $2P_{3/2}$

Energies:

- 270 meV
- 178 meV
- 179 meV

Mass spectrum:

- $N_2^+$
- $O_2^+$
- $^{36}\text{Ar}^+$
- $^{40}\text{Ar}^+$

Labels:

- ohne Laser
- 800 ms Laseranregung

Graphical representation of the mass spectrum with various peaks corresponding to the ions of interest.
Low lying states \( \text{N}_2^+ \)

![Graph showing transitions in \( \text{N}_2^+ \) and matching table of measurements.](image)

<table>
<thead>
<tr>
<th>Linie</th>
<th>Messung</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_{12} ) ( J'' = 0.5 )</td>
<td>12694.9641</td>
</tr>
<tr>
<td>( Q_{11} ) ( J'' = 1.5 )</td>
<td>12694.9460</td>
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<tr>
<td>( R_{12} ) ( J'' = 1.5 )</td>
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<td>( Q_{11} ) ( J'' = 2.5 )</td>
<td>12695.5675</td>
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<tr>
<td>( R_{12} ) ( J'' = 2.5 )</td>
<td>12695.6875</td>
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<tr>
<td>( Q_{11} ) ( J'' = 3.5 )</td>
<td>12695.6548</td>
</tr>
<tr>
<td>( R_{12} ) ( J'' = 3.5 )</td>
<td>12695.2586</td>
</tr>
<tr>
<td>( Q_{11} ) ( J'' = 4.5 )</td>
<td>12695.2149</td>
</tr>
</tbody>
</table>
Temperature: LIR $\text{N}_2^+ + \text{Ar} \rightarrow \text{Ar}^+ + \text{N}_2$

$T_n = 260 \text{ K}$
$T_{\text{trans}} = 288 \text{ K}$

$T_n = 90 \text{ K}$
$T_{\text{trans}} = 106 \text{ K}$

$T_n = 52 \text{ K}$
$T_{\text{trans}} = 70 \text{ K}$

A. Sorgenfrei, PhD thesis, Freiburg, 1994
First LIR with an Ar beam

22-Pole Ion Trap

Pulsed Valve
Ion Deflector

Ar

N$_2^+$

T < 5 K
cooling with slow He or H$_2$

← hv
→ Ar$^+$

$T_{22PT}$ 10 K
$T_D$ (21 ± 5)K

Prag, 28.04.2010
The reaction shown in the figure is:

$$\text{N}_2^+ + \text{Ar} \rightarrow \text{Ar}^+ + \text{N}_2$$

The graph on the left shows the concentration of $\text{N}_2^+$ and $\text{Ar}^+$ over time at $T = 300$ K. The concentration of Ar is given as $[\text{Ar}] = 1.3 \times 10^{12}$ cm$^{-3}$. The graph on the right plots the rate constant $k$ (in cm$^3$ s$^{-1}$) against temperature $T$ (in K). The reaction rate is described by the Arrhenius equation:

$$k(T) = k_0 \exp\left(-\frac{E_a}{RT}\right)$$

where $k_0$ is the pre-exponential factor, $E_a$ is the activation energy, and $R$ is the gas constant.
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Summary and outlook
H-atom source + 22pole trap
Focusing H atoms

Diagram showing a setup for focusing hydrogen atoms, including a discharge tube, precoolers, hexapole magnets, a gas inlet, and a mass filter. The figure also includes a graph plotting relative density against TOF (time of flight) in ms, with peaks at 92 K, 8.2 meV, 21 meV, and 3.6 meV.
\[ \text{CH}^+ + \text{H}_2 \quad / \quad \text{CH}^+ + \text{H} \]

\[ T_{22\text{PT}} = 50 \text{ K} \]
\[ [\text{He}] = 1.5 \times 10^{13} \text{ cm}^{-3} \]
\[ [\text{H}] = 4 \times 10^8 \text{ cm}^{-3} \]
\[ [\text{H}_2] = 1.7 \times 10^9 \text{ cm}^{-3} \]
$\text{CH}^+ + \text{H}: \text{barrier!}$

$k (7 \, \text{K}, \text{CH}^+ (j=0)) = (5 \pm 3) \times 10^{-11} \, \text{cm}^3\text{s}^{-1}$
Where is the barrier?

\[ \text{CH}^{+}(^1\Sigma) + \text{H}(^2S) \rightarrow \text{C}^{+}(^2\Pi) + \text{H}_2(^1\Sigma) \]
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Summary and outlook
Deuteration $\text{H}_3^+ + \text{HD} \leftrightarrow \text{H}_2\text{D}^+ + \text{H}_2$: equilibrium constant $K$?

$$K \sim \exp(231.8 \text{ K} / T)$$

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>Adams and Smith</th>
<th>Herbst</th>
<th>Ramanlal</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>4.5 ($\pm$1.3)</td>
<td>5.9</td>
<td>6.82</td>
</tr>
<tr>
<td>200</td>
<td>2.4 ($\pm$0.7)</td>
<td>2.6</td>
<td>1.52</td>
</tr>
<tr>
<td>295</td>
<td>2.0 ($\pm$0.6)</td>
<td>2.1$^a$</td>
<td>1.07$^a$</td>
</tr>
</tbody>
</table>

$^a$The theoretical value is actually at 300 K.

Ramanlal & Tennyson

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>2.6(+12)</td>
</tr>
</tbody>
</table>

Gerlich et al. (2002)

| H$_2$: $K = 7.4$ |

$T_{22PT}$ 10 K, (2005)

<table>
<thead>
<tr>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$&gt;500$</td>
</tr>
</tbody>
</table>

Ramanlal & Tennyson wrote in 2004:

**Trap experiment disagrees with calculations by 12 orders of magnitude**

R. Adams and Smith Herbst Ramanlal

80 4.5 ($\pm$1.3) 5.9 6.82
200 2.4 ($\pm$0.7) 2.6 1.52
295 2.0 ($\pm$0.6) 2.1$^a$ 1.07$^a$

$^a$The theoretical value is actually at 300 K.

**Theoretical Value**

The theoretical value is actually at 300 K.

Ramanlal & Tennyson

$T = 10$ K

$2.6(+12)$

Gerlich et al. (2002)

n-H$_2$: $K = 7.4$

p-H$_2$: $K = 390$

$T_{22PT}$ 10 K, (2005)

$>500$

Nuclear spin: propensity rules

\[ \text{o-H}_3^+ + \text{HD} \rightarrow \text{H}_2\text{D}^+ \]
\[ \text{p-H}_3^+ + \text{HD} \rightarrow \text{H}_2\text{D}^+ \]

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Summary and outlook
LIR spectrum of $\text{H}_2\text{D}^+$ ($\Delta v_2$ or $\Delta v_3 = 1$)

$\text{H}_2\text{D}^+ + \text{H}_2 + hv \rightarrow \text{H}_3^+$

$[\text{H}_2] = 7 \times 10^{10} \text{cm}^{-3} \quad T = (25 \pm 5) \text{ K}$

$n$- $\text{H}_2 : \text{ o} : \text{ p} = 0.75 : 1$

"p"- $\text{H}_2 : \text{ o} : \text{ p} = 0.20 : 1$

Schlemmer, Asvany, Hugo, Gerlich, Astrochemistry, IAU Symposium 231, 2005
Overtone detection of $\text{D}_2\text{H}^+$ $(0_{00})$

**Doppler width**
- discharge 250 K
- trap 9 K

**Transition**
- calc. 6536.301
- measured 6536.319
THz radiation induced D-H exchange

First LIR spectra

$\text{H}_2\text{D}^+$ 1370084.880(20) MHz
$\text{D}_2\text{H}^+$ 1476605.708(15) MHz

<table>
<thead>
<tr>
<th></th>
<th>$\text{H}<em>2\text{D}^+$  $l</em>{01} \rightarrow 0_{00}$</th>
<th>$\text{D}<em>2\text{H}^+$  $l</em>{11} \rightarrow 0_{00}$</th>
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<tbody>
<tr>
<td>this work</td>
<td>1370084.880(20)</td>
<td>1476605.708(15)</td>
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<tr>
<td>$ab \text{ initio}^a$</td>
<td>1369991.8</td>
<td>1476628.0</td>
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<tr>
<td>unpublished value$^b$</td>
<td>1370146.0(3)</td>
<td>1476605.5(3)</td>
</tr>
</tbody>
</table>

O. Asvany et al. PRL 100 (2008) 233004
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Summary and outlook
Evaporation and erosion of dust particles

- **Silicate / Graphite Core**
  - Photons: heating, sublimation, photoionization, sputtering
  - Electrons: secondary e^- emission

- **Ice Mantle**
  - Ions: sputtering
  - Molecules: adsorption

- **Particles**
  - Sputtering, cratering, fragmentation
**Theory of Quadrupole Trap**

Effective Potential:
\[ E_{\text{pot}} = \frac{1}{2} M \omega^2 z^2 \]

Applied Field:
\[ \Phi_0 = U_0 - V_0 \cos(\Omega t) \]

Secular Motion:
\[ \omega_z = \frac{q_z \Omega}{\sqrt{2} \Omega} \]

Stability Parameter:
\[ q_z = \frac{4 Q \Omega}{M z_0^2 \Omega^2} < 0.3 \]

Q/M-Determination:
\[ Q/M = \frac{z_0^2 \omega_z \Omega}{\sqrt{2} V_0} \]
Determination of $q/m$

$$\omega_T = 2\pi \cdot 42.73 \text{ Hz}$$
$$\Omega = 2\pi \cdot 928 \text{ Hz}$$
$$V_0 = 1365 \text{ V}$$

$$Q/M = 98.13 \text{ mC/kg}$$
$$d\omega/\omega = 6 \cdot 10^{-5}$$
Cosmic rays induced change
Absolute charge state

![Graph showing the absolute charge state over time.](image)
Gas ad- and desorption
500 nm diameter SiO$_2$ sphere

$\Delta m = 33$ pg/h

CO$_2$ laser
2 W cm$^{-2}$
$\Delta T \approx 100$ K
$\Delta m = 0.2$ fg

$\Delta m = 17 \times 300$ amu/s

$\Delta m = -13$ pg/h

Molecular Ions and Nanoparticles in RF and AC Traps
D. Gerlich, Hyperfine Interactions 146 (2003) 293
mass spectrometers and scales

Penning-Traps

Quadrupol Mass Spectrometer

TOF-Mass Spectrometer

Molecules
Fluorescence
Particle
Scattered Light

New Trap

Commercial Balances

 fg  pg  ng  μg  mg  g  kg

Å  nm  μm  mm  cm  dm

m_e  amu  ^{12}C
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Summary and outlook
Hot carbon nanoparticles
Ions at high temperatures
Space charge, amplitude dependence

![Graphs showing space charge and amplitude dependence](image)
Thermal decay of $\text{C}_{60}^+$

Arrhenius parameter literature values: 3 - 12 eV
Thermal decay of $\text{C}_{60}^+$

$E_A = 2$ eV

$E_A = 4$ eV

$E_A = 5$ eV

$1/4$ h

Arrhenius parameter

literature values: 3 - 12 eV
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Summary and outlook
Cold ion chemistry in traps

Controlling all degrees of freedom
State to state reactions
Ultra slow relative velocities

Buffer gas cooling in RF traps
Cooling ions with cold effusive beams
Chopped, very slow beams of He
Cooling with slow H-atoms
Combination ion trap - H atom trap

Problems with ion traps
Potential distortions on surfaces
High Q resonance circuit without parasitic oscillations
Superconducting electrodes
Magnetic fields

Coulomb crystals in rf ion traps
Laser cooling, sympathetic cooling
Trapping cold H atoms

Hyperfine resonator

Confined atoms

Quadrupole magnet

Source solenoid

Transverse rf coil

Lower pinch solenoid

Bias solenoid

Upper pinch solenoid

Source

B (Z)

3T

2T

1T

0

Z
Combination: rf ion trap and MAC $e^-$ spectrometer

$$H^- + H \rightarrow H_2 + e^- \quad k(T) / E_T(e^-)$$
Carbocations

A cornerstone of the classical theory of structural chemistry since the time of Kekulé in the 1860s is that carbon can bind at most four other atoms (tetra-coordination).

Around 1950 S. Winstein in the USA found a short-lived carbocation that contained penta-coordinated carbon. He named the ion non-classical. Despite very great efforts by many leading physical organic chemists, the problem remained unsolved until Olah’s method of preparing long-lived carbocations was applied.

NPMS: perspectives

- long time trapping, isolation under UHV conditions
- non-destructive, absolute mass and charge determination
- high resolution of secular frequencies ($\Delta \nu / \nu < 10^{-6}$)
- single particle: average over time (not ensemble)

- experimental characterization of the trap, new trap design
  accuracy, precision, properties of the potential
- small particles (1-5 nm)
- optical detection (spectroscopy, light pressure,...)
- chemistry, agglomerates, magnetic properties
- temperature range: 5 K - 3000 K

Black body radiation of carbonaceous material