(F)IR-FEL experiments on molecules and clusters

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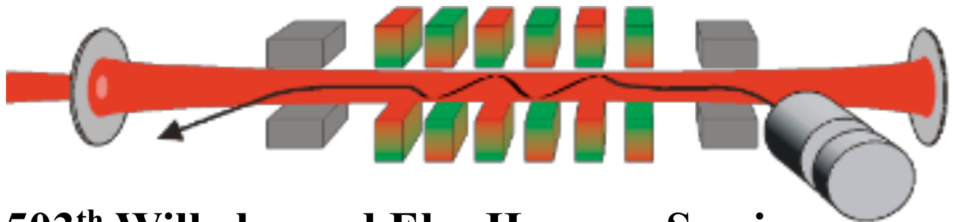
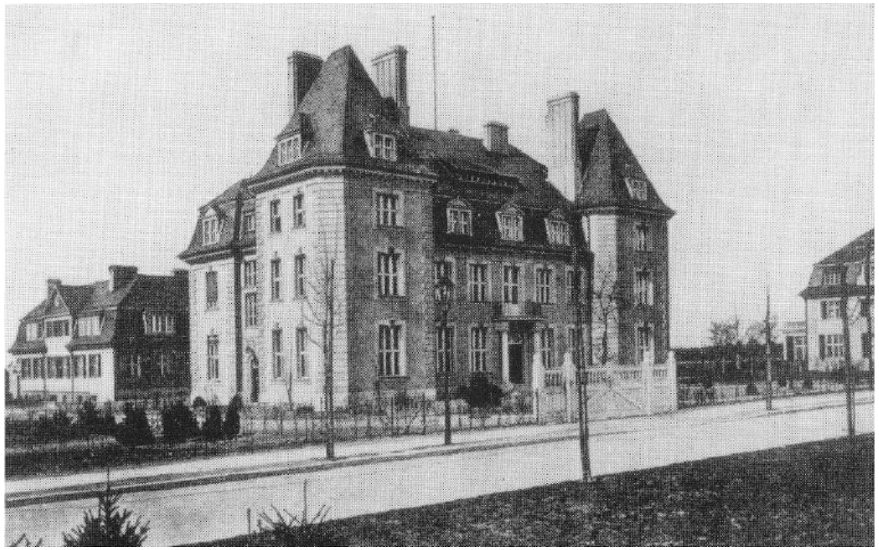
Some historical notes
Structure determination of gas-phase species
"Resonant heating" of molecules and clusters with IR light
Catching proteins in Helium droplets
Conclusions



503th Wilhelm and Else Heraeus Seminar
Free-Electron Lasers: from Fundamentals to Applications
April 10-13, 2012, Physikzentrum Bad Honnef

Some historical facts on the Fritz Haber Institute



Kaiser Wilhelm Institute for Physical Chemistry and Electrochemistry (1912)

1911 Founded by the Kaiser Wilhelm Society
1933 Fritz Haber leaves Germany; he dies in 1934
1953 Renamed into Fritz Haber Institute of the Max Planck Society
2011 Centenary celebrations
2012 First light of the IR-FEL

100 YEARS OF PHYSICAL CHEMISTRY IN BERLIN–DAHLEM
100 YEARS

Nobel Laureates

1914 Max von Laue (Physics)
1918 Fritz Haber (Chemistry)
1925 James Franck (Chemistry)
1927 Heinrich Wieland (Chemistry)
1963 Eugene Wigner (Physics)
1986 Ernst Ruska (Physics)
2007 Gerhard Ertl (Chemistry)

Haber
1911-33

Wieland
1917-18

Franck
1918-20

Wigner
1923-32

Ruska
1949-74

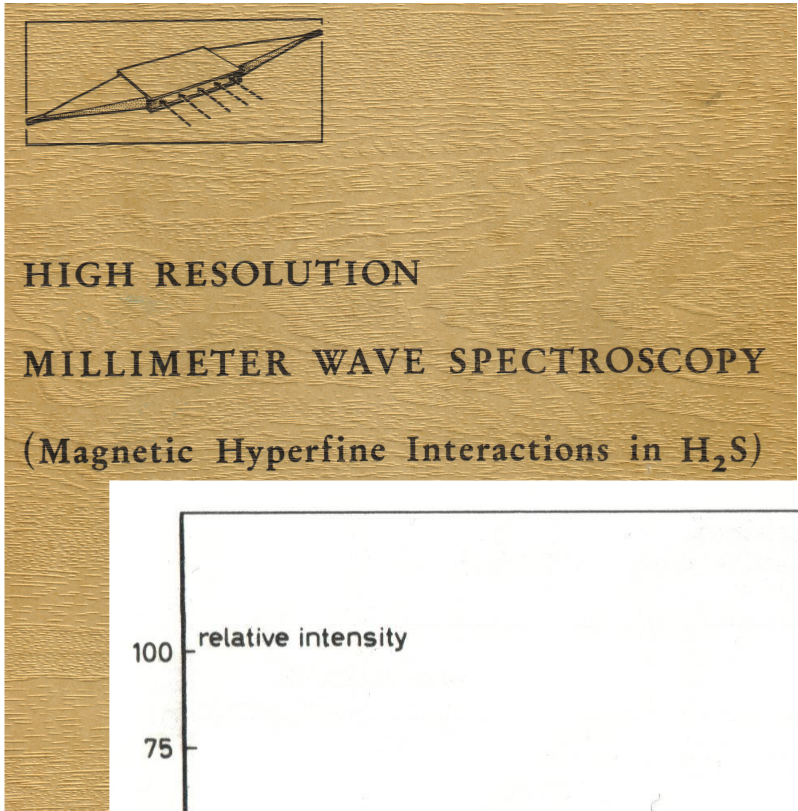
von Laue
1951-59

Ertl
1986-2004

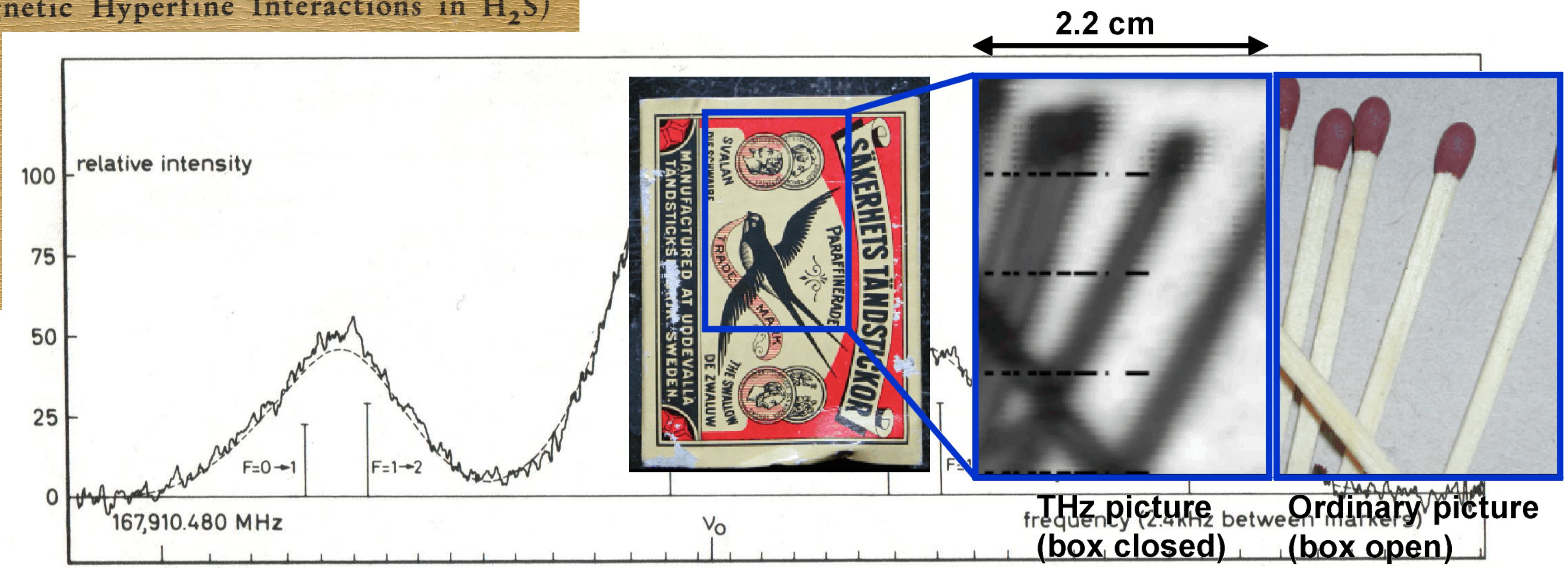
June 30, 1966:

1st PhD thesis of the Research Group on Atomic and Molecular Physics, University of Nijmegen, Nijmegen, The Netherlands

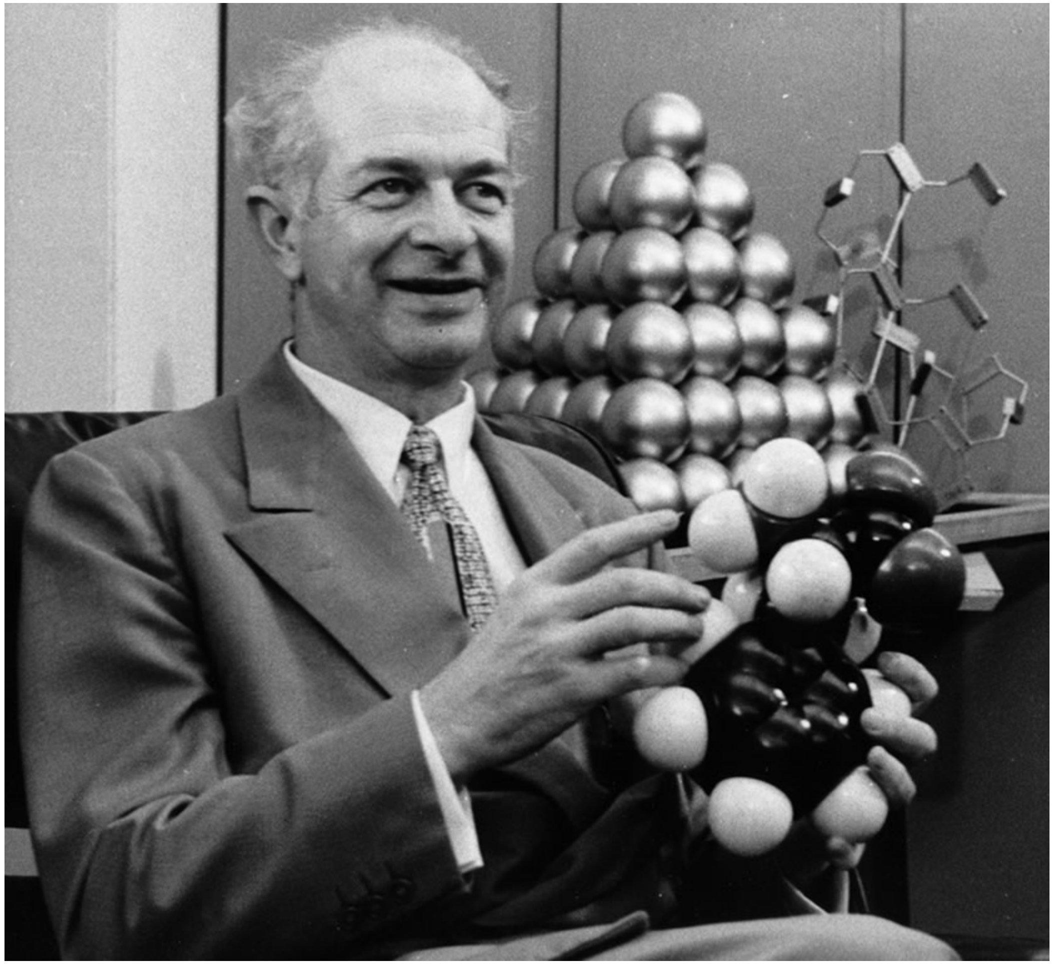
Cees Huiszoon (& Frans van Rijn)   Thesis advisor: Prof. A. Dymanus



From millimeter, or sub-millimeter, spectroscopy, to THz imaging:



It is structure…



Linus Carl Pauling (1901-1994)
Nobel Prize in Chemistry 1954
Nobel Peace Prize 1962

…that we look for whenever we try to understand anything. All science is built upon this search;

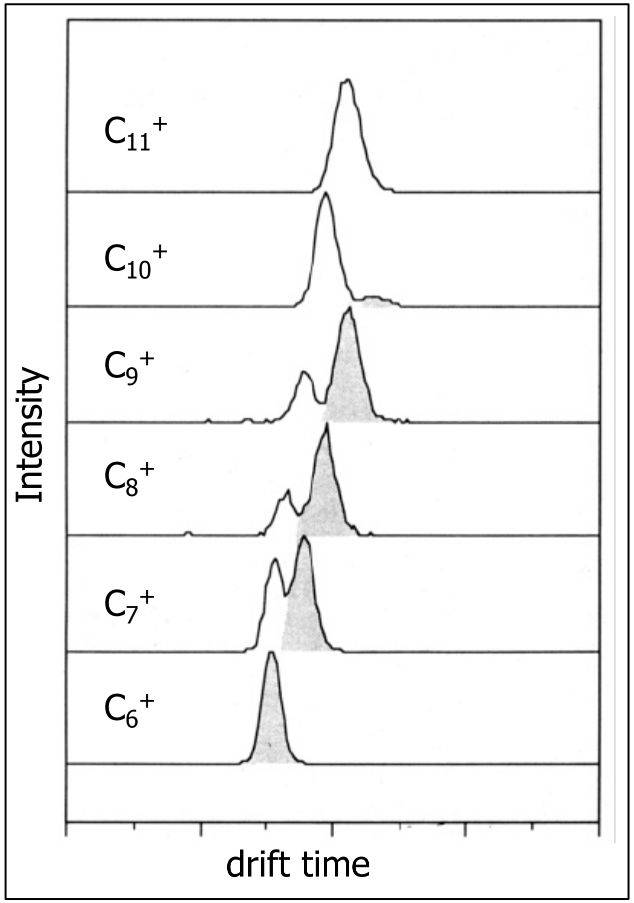
…

We like to understand, and to explain, observed facts in terms of structure.

"The place of Chemistry in the Integration of the Sciences"
Main Currents in Modern Thought 7 *(*1950) 110

Structural investigation in the gas phase

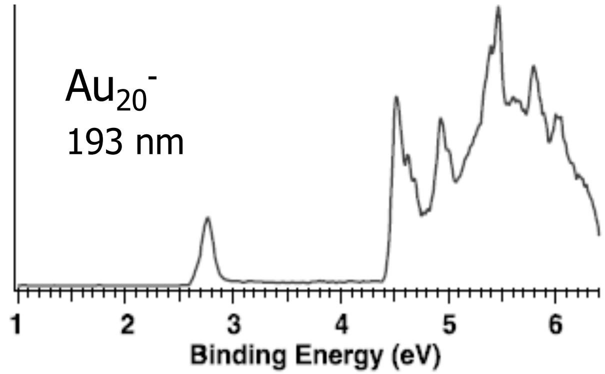
Ion mobility

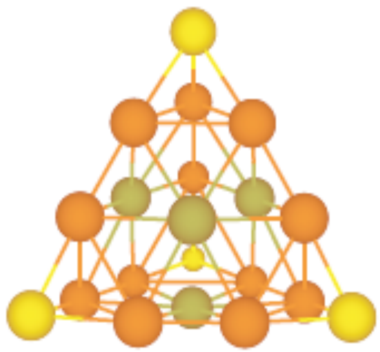


C_n^+

von Helden *et al.*, JPC 97 (1993) 8182.

Photo-electron spectroscopy

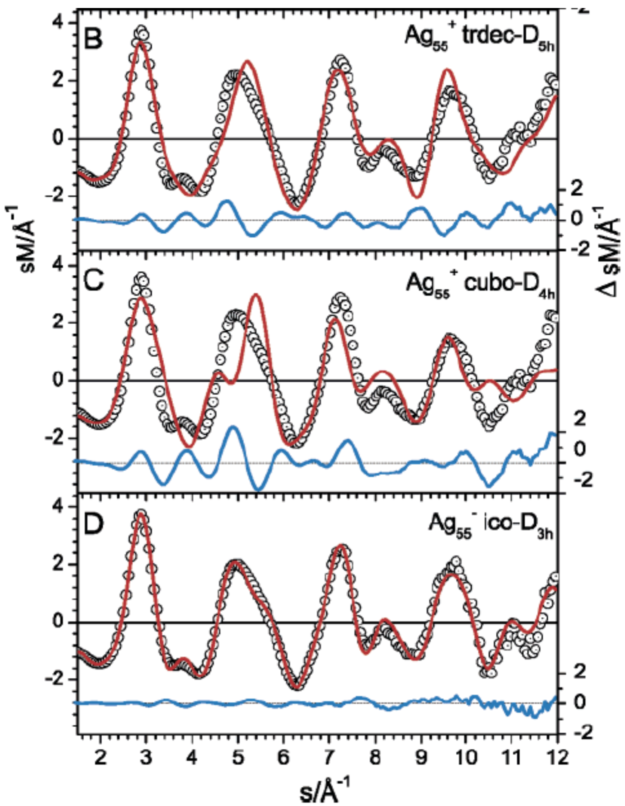




Au_{20}^-

Li *et al.*, Science 299 (2003) 864.

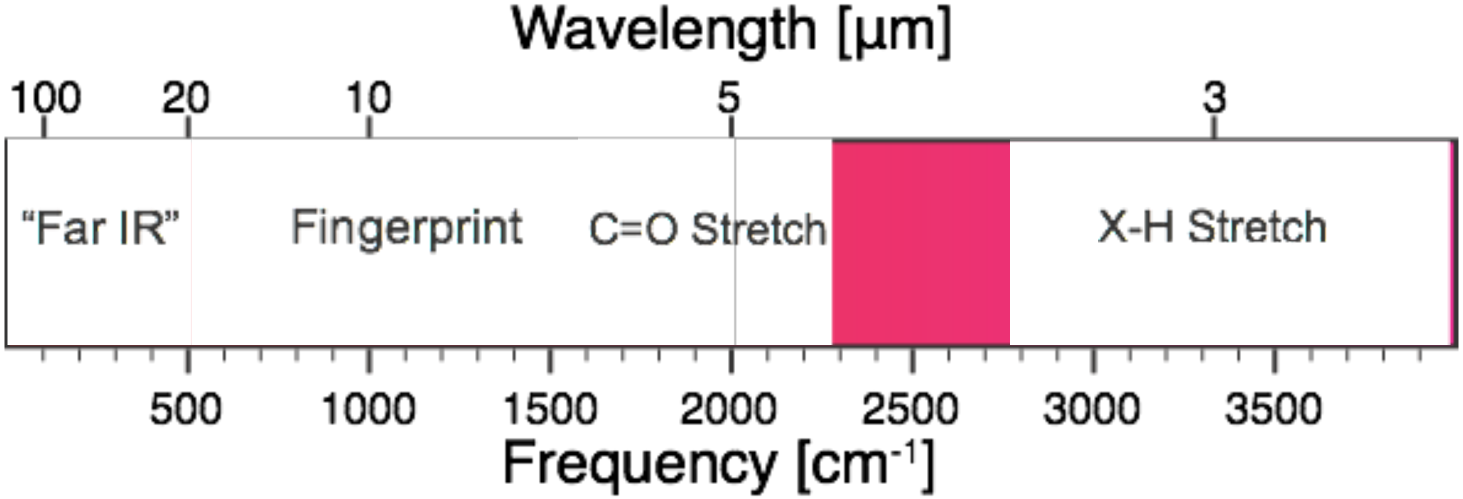
Electron diffraction



Ag_{55}^+

Schooss *et al.*, Nano Lett. 5 (2005) 1972.

The interaction of molecules and clusters with IR light



Fingerprint:
skeletal motion in molecules

X-H Stretch:
H-bonding
conformation of small biomolecules

"Far IR" or THz:
large amplitude motion / folding
metal-metal stretch
van der Waals modes
adsorbate modes on surfaces
rotational transitions

C=O Stretch:
"Amide I" in biomolecules
C=O on surfaces

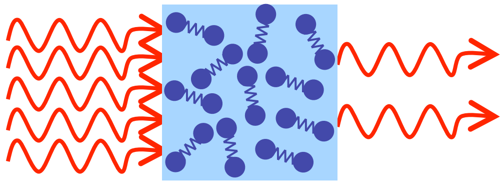
Measure absorption cross-section as a function of IR frequency; $\sigma(\nu)(\approx 10^{-20} cm^2)$

Compare measured and calculated spectra to draw conclusions about structure

In absorption spectroscopy:

one detects what the molecules do to the light

$$I(\nu) = I_0(\nu)e^{-\sigma(\nu)nl}$$



needed: large number of molecules-per-square-centimeter (nl)

not many photons needed

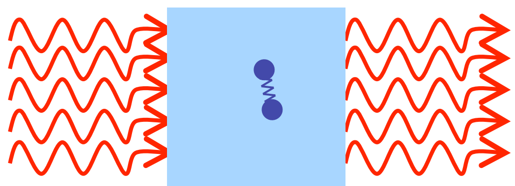
(as long as there are enough to be detected with sufficient statistics)

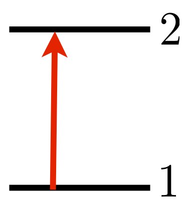
In “action” spectroscopy:

one detects what the light does to the molecules

$$N_1(\nu) = Ne^{-\sigma(\nu)F}$$

$$N_2(\nu) = N(1 - e^{-\sigma(\nu)F})$$





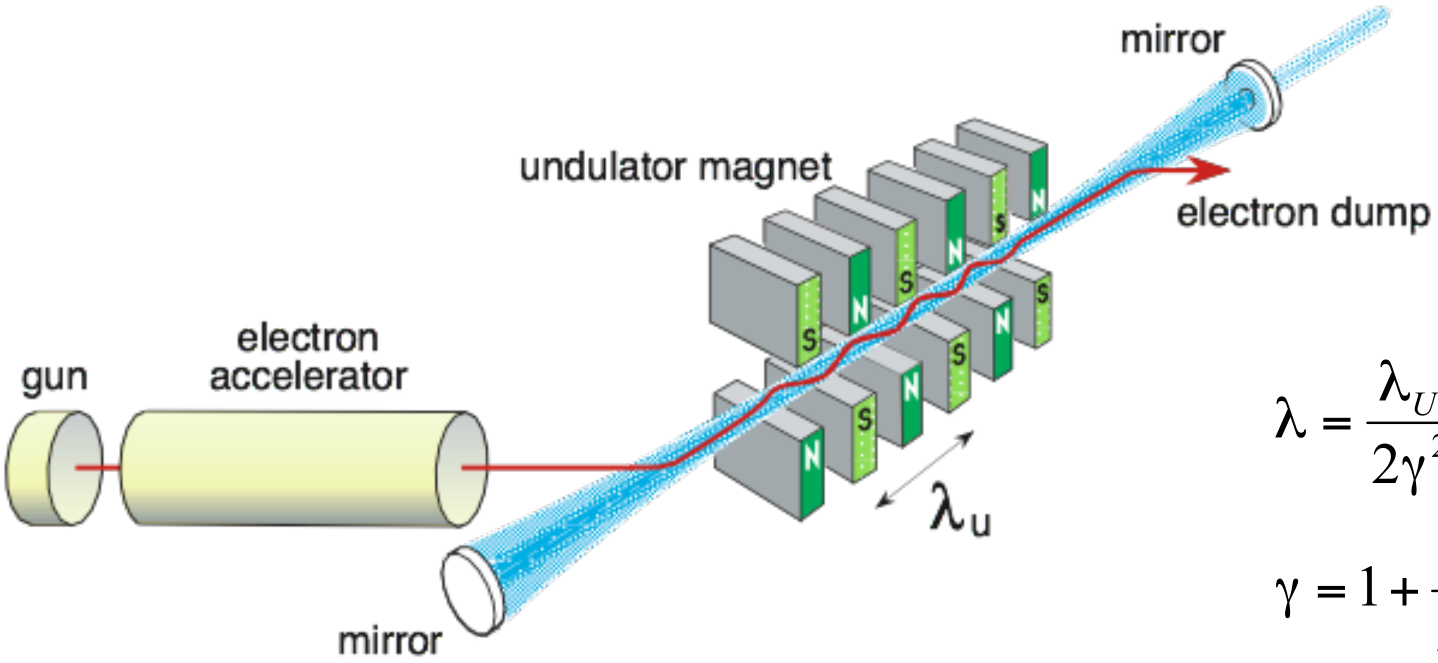
“zero background” detection

needed: large number of photons-per-square-centimeter (fluence; F)

not many molecules needed

(as long as there are enough to be detected with sufficient statistics)

The Free Electron Laser; general operation principle



$$\lambda = \frac{\lambda_U}{2\gamma^2}(1 + K^2)$$

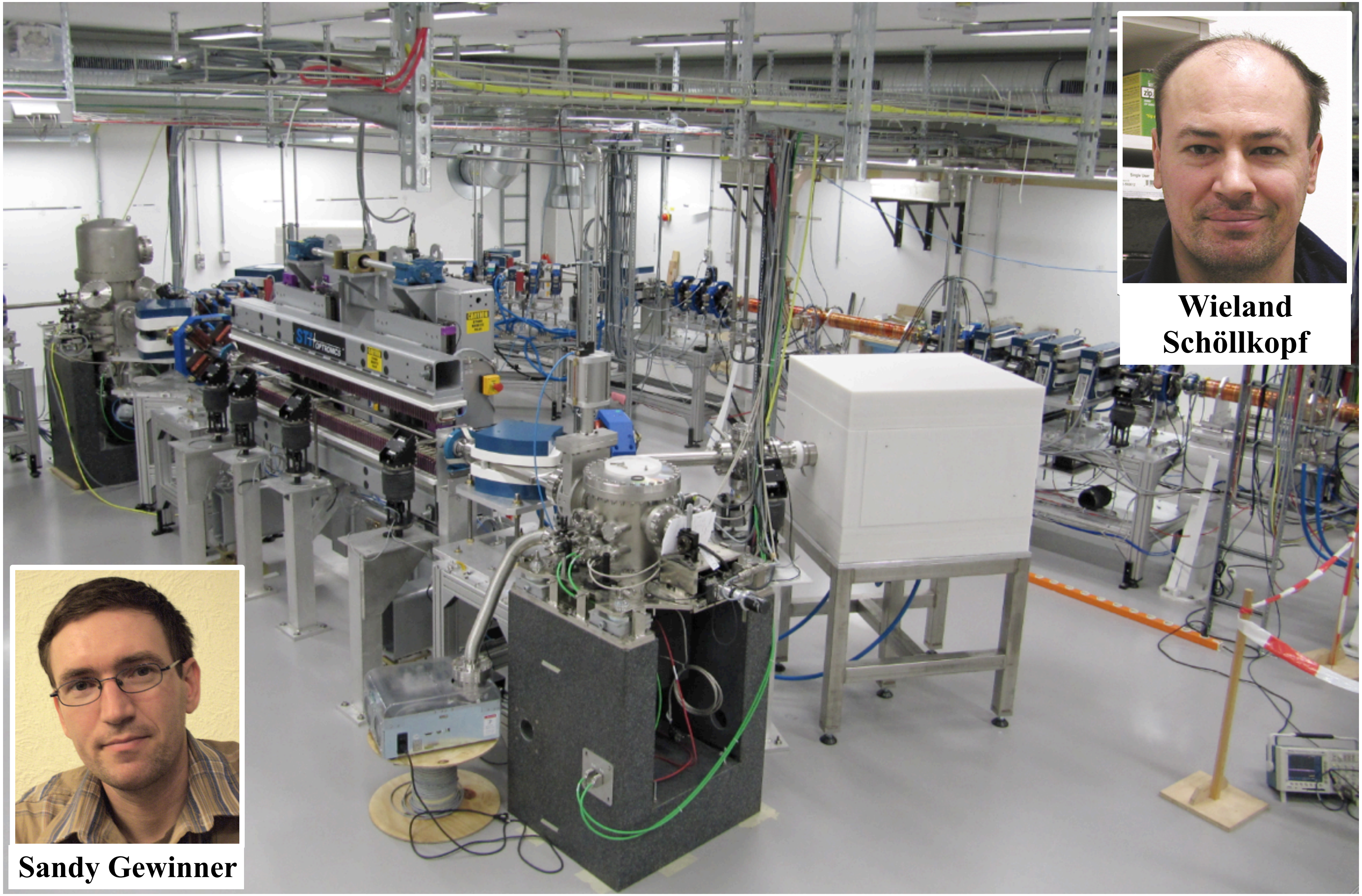
$$\gamma = 1 + \frac{E}{m_e c^2} \approx 2E[MeV]$$

Active medium: free electrons that travel through a periodically changing magnetic field (undulator) at (almost) the speed of light.

Wavelength depends on the electron energy and the undulator parameters.

The electron beam, and thereby the light output, is usually pulsed.

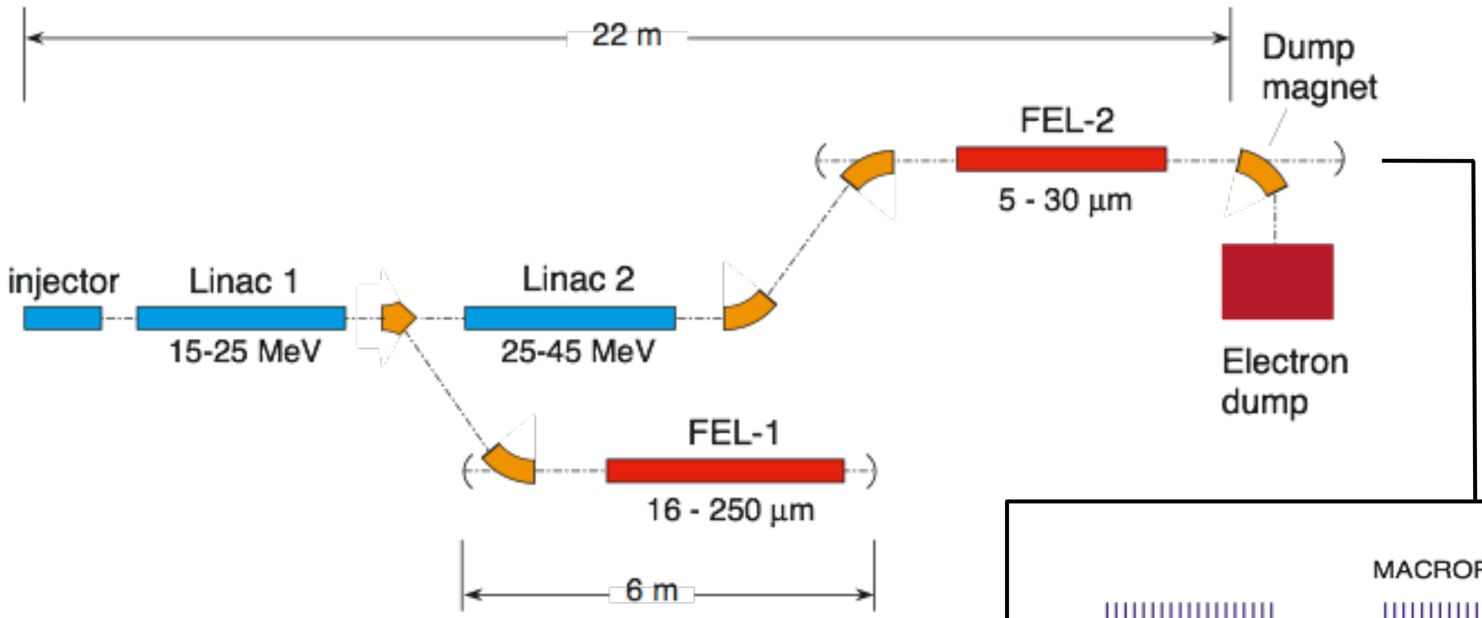
FHI-FEL: the FEL setup at the Fritz Haber Institute in Berlin

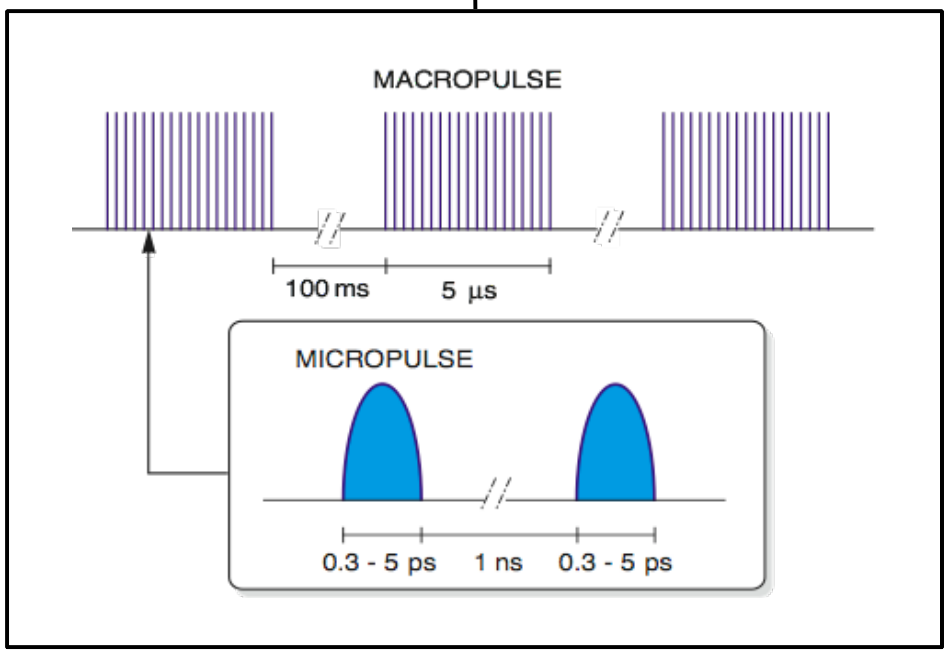


Wieland Schöllkopf

Sandy Gewinner

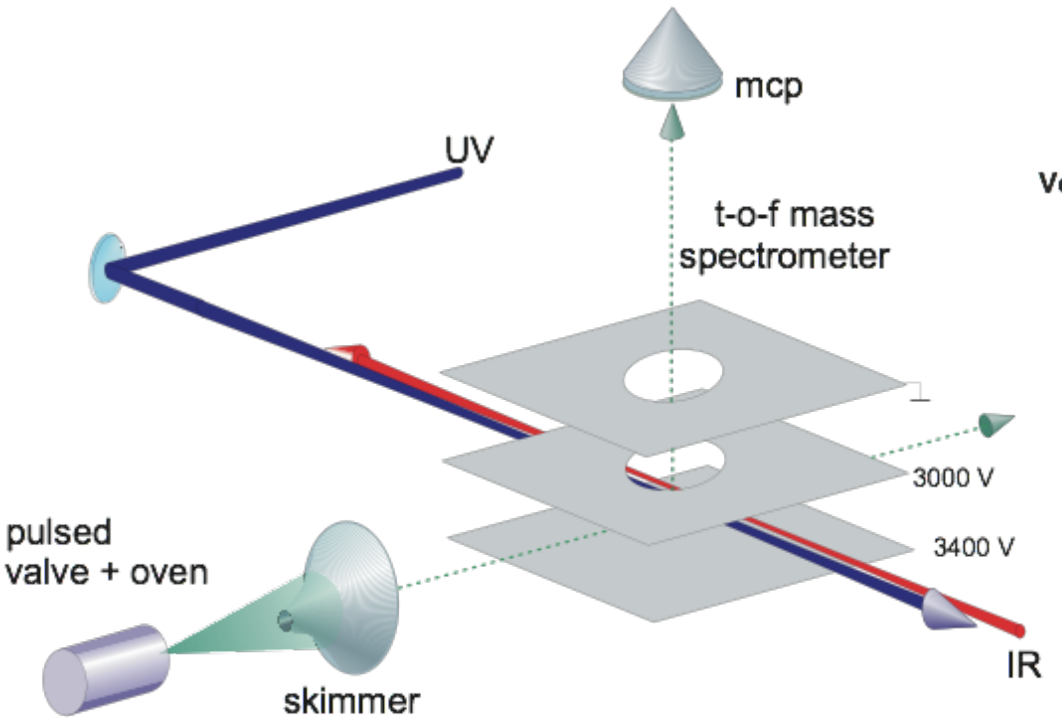
The Free Electron Laser for Infrared eXperiments (FELIX)

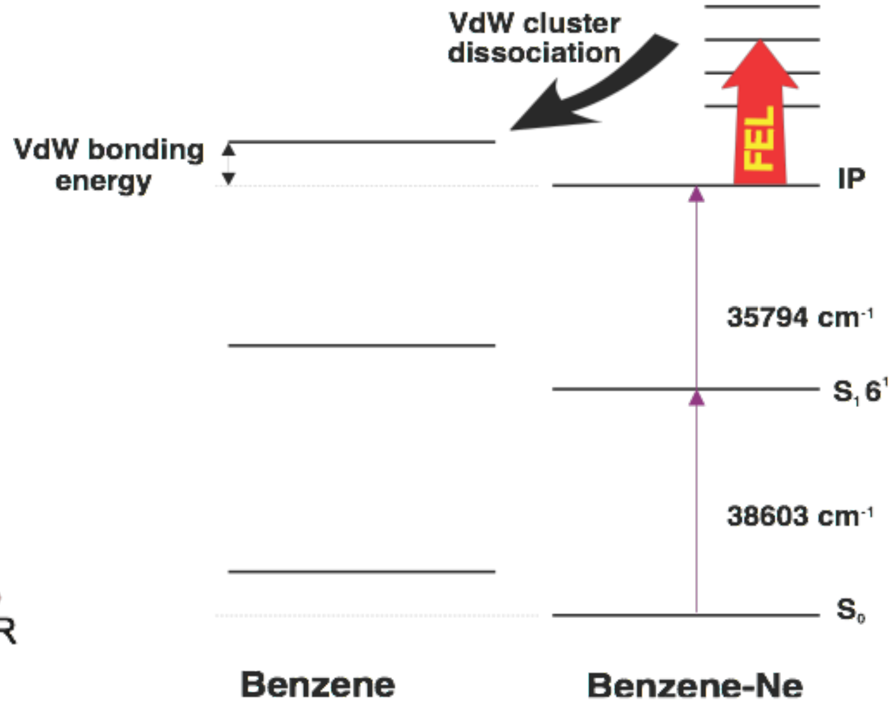




- Tuning range: 40-2000 cm^{-1}
- Lasing on 3^{rd} harmonic: 2000-3500 cm^{-1}
- Macropulse energy: 150 mJ
- Bandwidth: Fourier transform limited

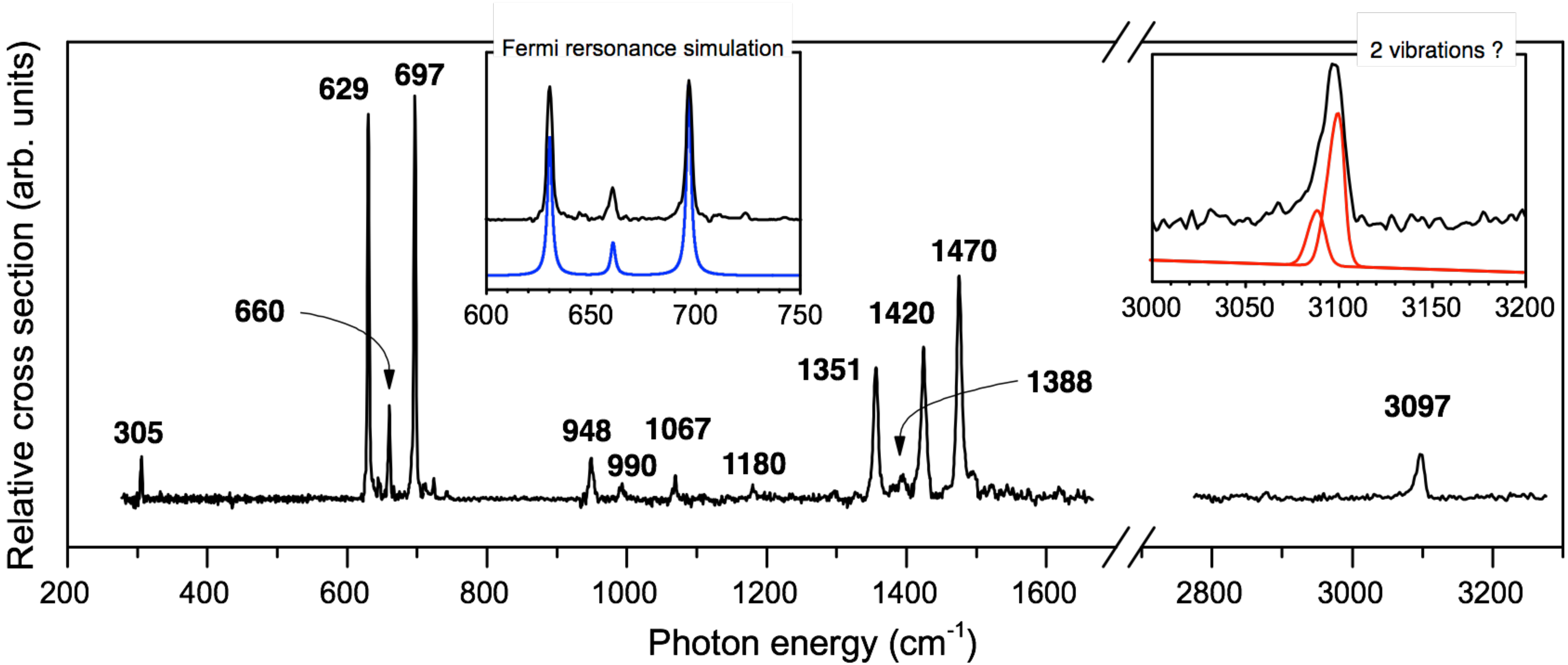
The IR absorption spectrum of the benzene cation





- Benzene molecules are seeded in a rare gas (Ne) and expanded into vacuum. Clusters with rare gas atoms form.
- Benzene-Ne is selectively ionized between the plates of a mass spectrometer.
- Upon absorption of an IR photon, the weakly bonded cluster-ions can dissociate.
- Appearance of bare benzene cations as a function of IR wavelength yields the IR absorption spectrum (of the benzene-Ne cation).

The IR absorption spectrum of the benzene cation



- Neutral C_6H_6 has only 4 IR active fundamental modes.
- $C_6H_6^+$ has a very rich IR spectrum.
- IR spectrum can be used to search for $C_6H_6^+$ in space (*ApJ 546 (2001) L123*).

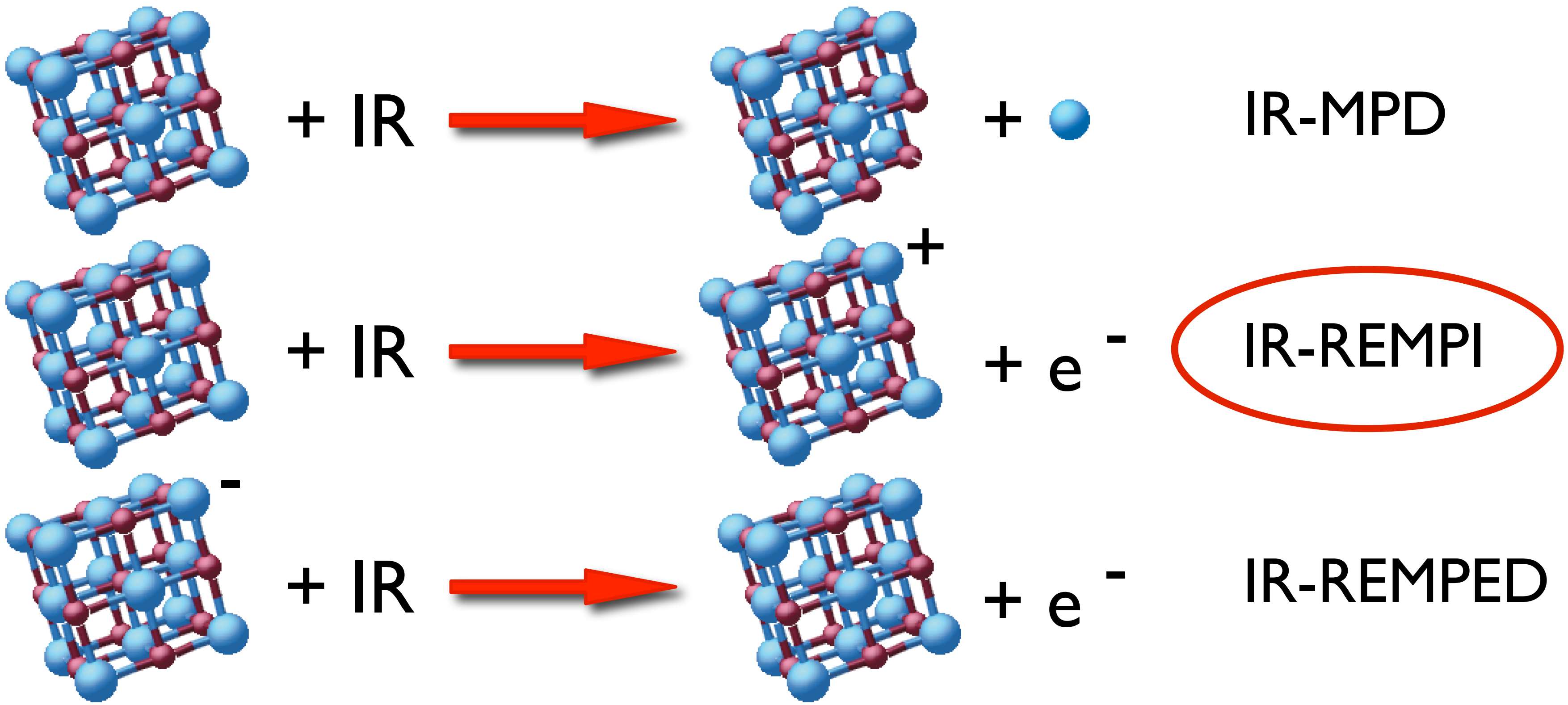
J.M. Bakker, R.G. Satink, G. von Helden & G. Meijer, *Phys. Chem. Chem . Phys. 4 (2002) 24*

IR-resonance enhanced Multiple Photon Dissociation
Ionization
Electron Detachment

"Resonant heating" with IR light:

Very many photons (hundreds) need to be absorbed by a single cluster.

Monitoring the dissociation-, ionization-, or electron detachment-yield as a function of wavelength gives (information on) the IR absorption spectrum.



Delayed Ionization of C_{60} and C_{70}

E. E. B. Campbell, G. Ulmer, and I. V. Hertel

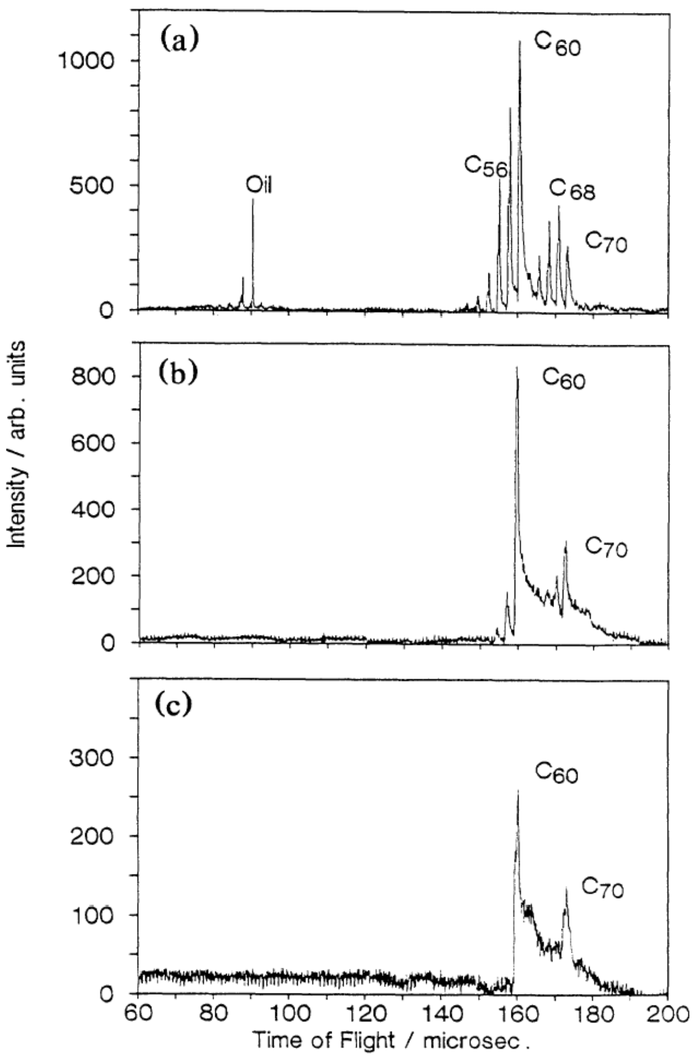
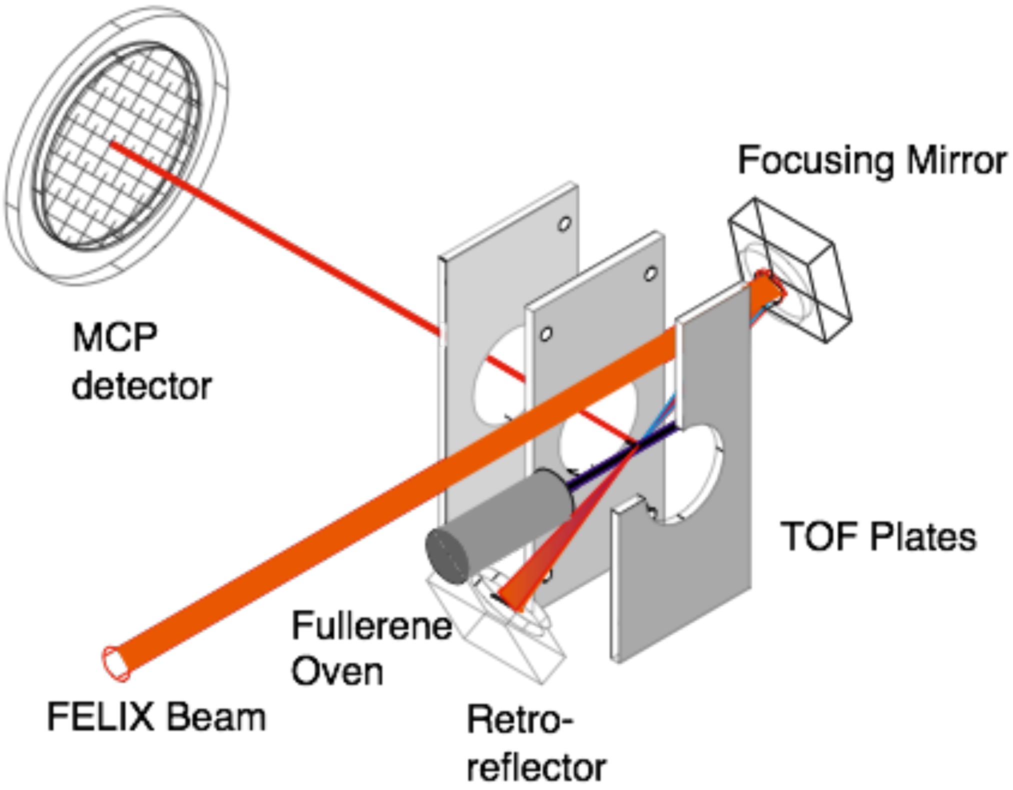


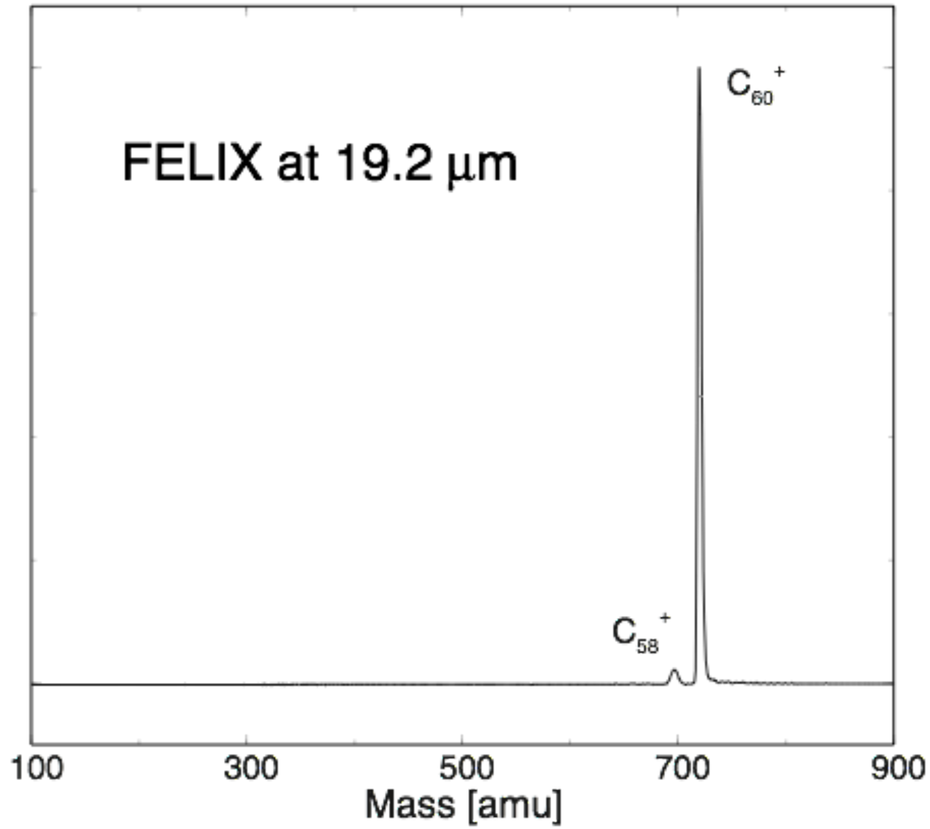
FIG. 2. Mass spectra produced from ionization with a 20-mJ cm $^{-2}$, 308-nm excimer laser with a delay between laser and pulsed extraction field of (a) 0, (b) 2, and (c) 8 μsec.

„speculatively attributed to thermionic electron emission“

C_{60}:
ionization potential: 7.6 eV
lowest dissociation limit: 10 eV

The fullerene experiment

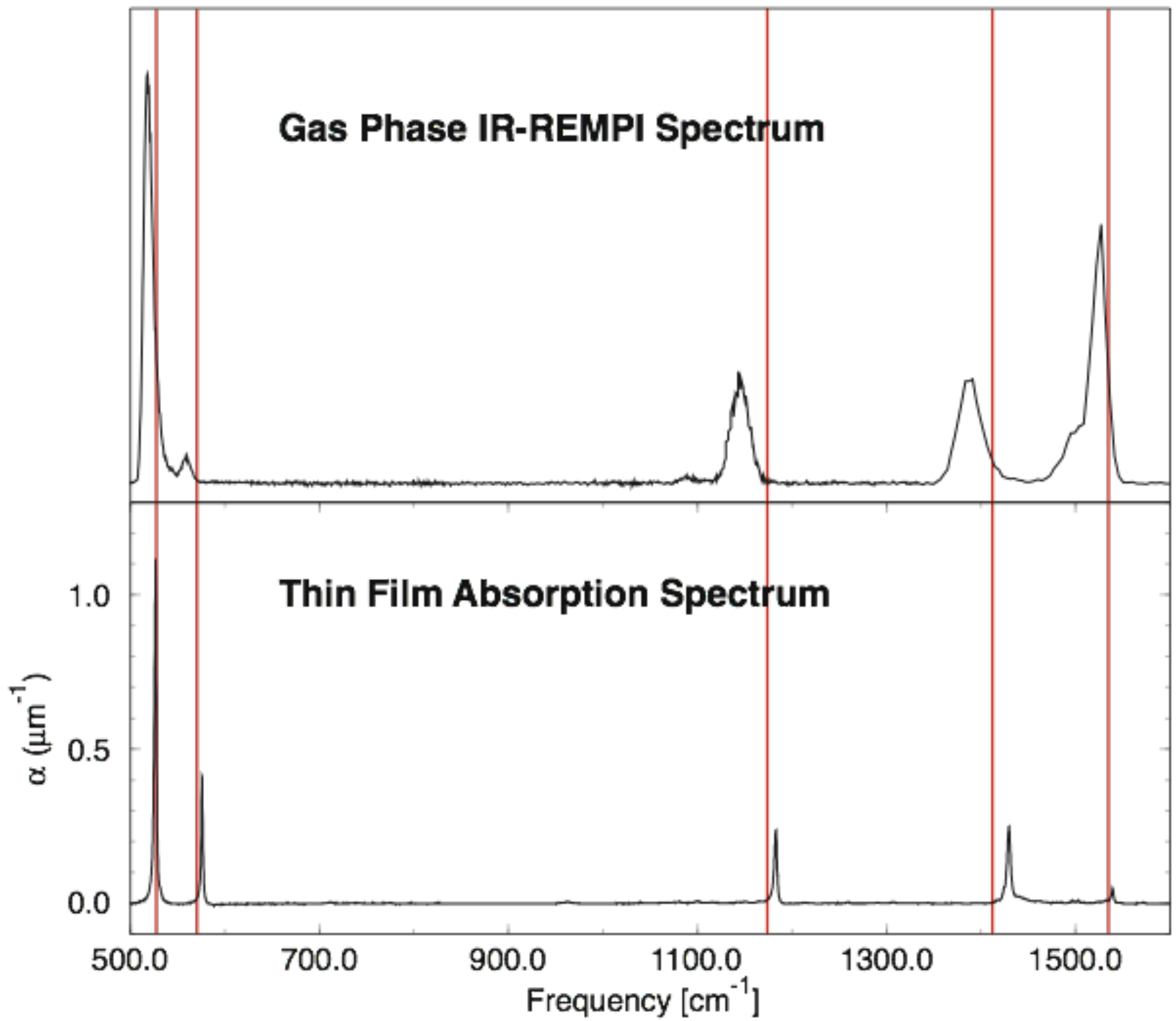




Ionization of C_{60} with pulsed IR radiation indeed works

Unexpectedly clean mass-spectrum; hardly any fragmentation

C_{60} IR-REMPI spectrum



All resonances from the linear absorption spectrum appear in the IR-REMPI spectrum.

All IR-REMPI peaks are red shifted.

Small red shift ⟶ high IR-REMPI intensity.

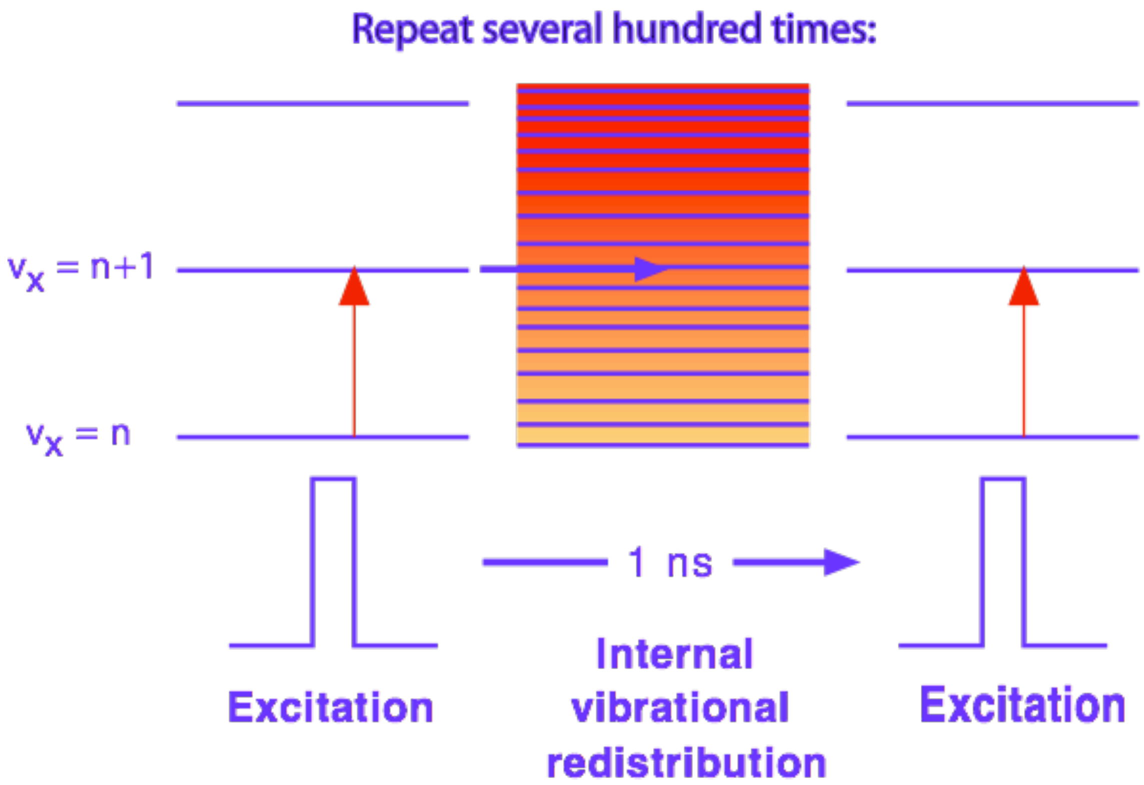
G. von Helden, I. Holleman, G.M.H. Knippels, A.F.G. van der Meer & G. Meijer, *Phys. Rev. Lett. 79 (1997) 5234*

(Simplified scheme of the) Excitation mechanism

For efficient thermionic emission of C_{60}:

Internal energies of about 40 eV (≈ 3300 K) need to be reached !

> 600 photons at 500 cm^{-1} need to be absorbed in a single molecule.

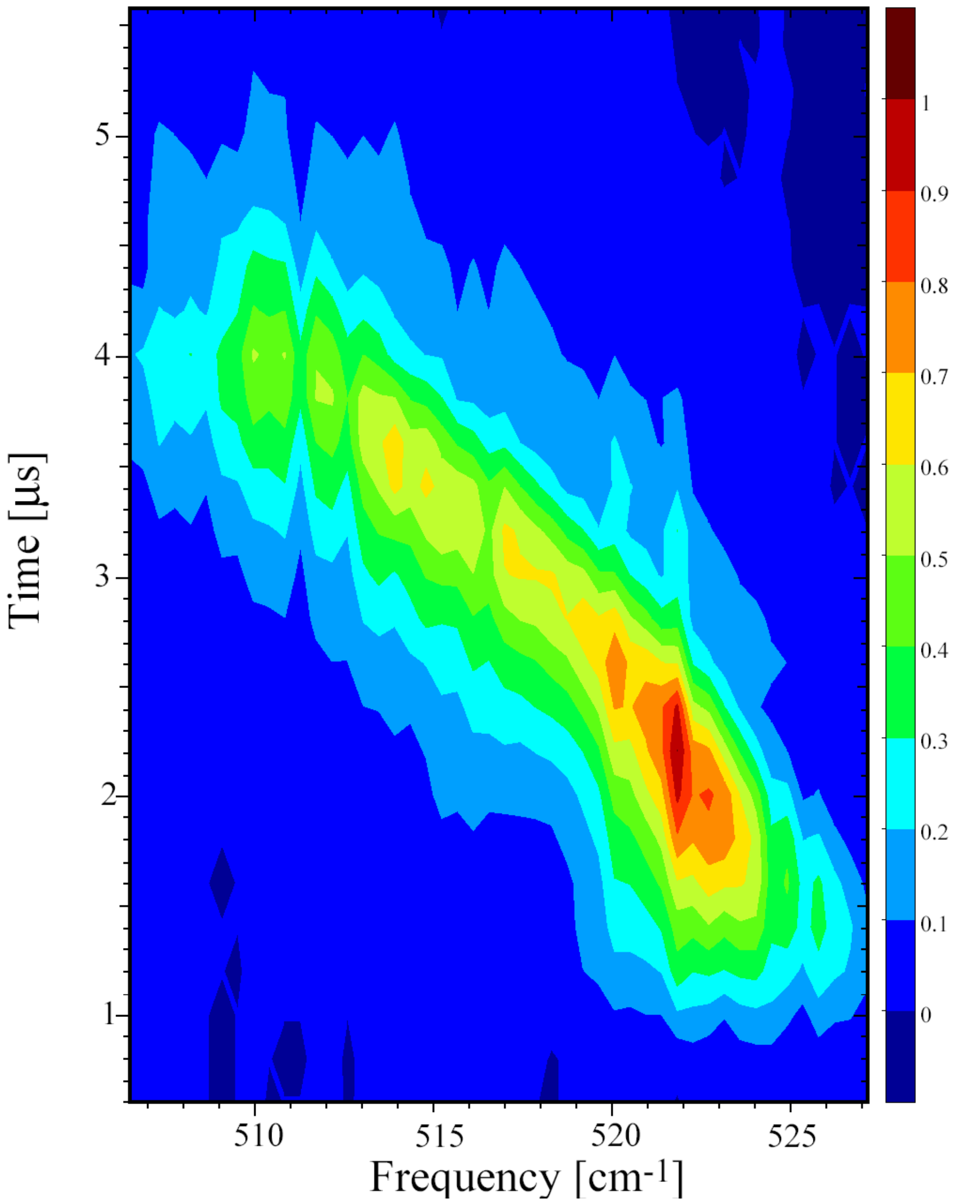


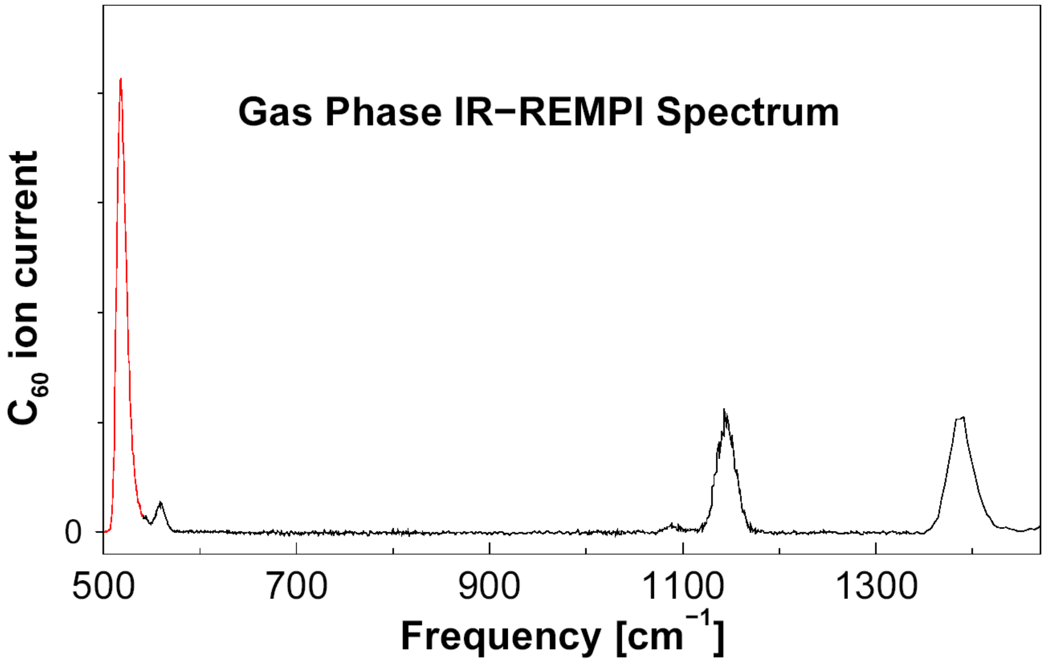
Sequential single photon absorption.

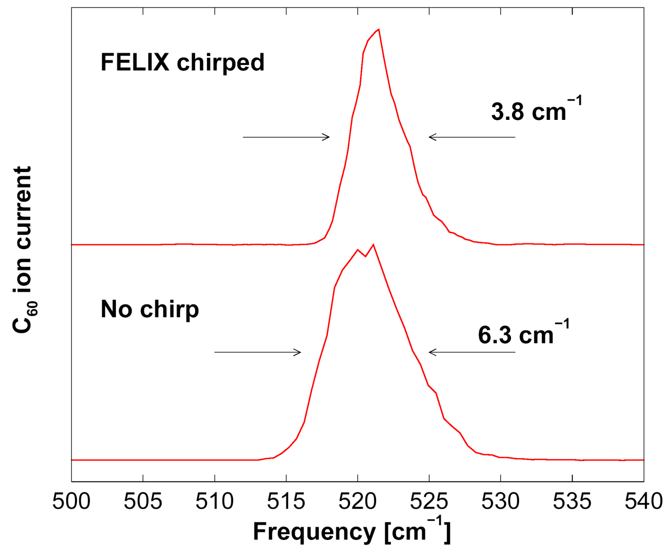
Relaxation in between micropulses.

Redshift due to anharmonicities.

Compensating for anharmonicity: Chirped excitation of C_{60}







G. von Helden, I. Holleman, G. Meijer & B. Sartakov, *Optics Express 4 (1999) 46*

IR-REMPI has been demonstrated for various systems:

- Fullerenes (C_{60}, C_{70}, C_{84})
- Titanium-, vanadium-, niobium-, and tantalum-carbide clusters
- Zirconium-, magnesium-, and aluminum-oxide clusters

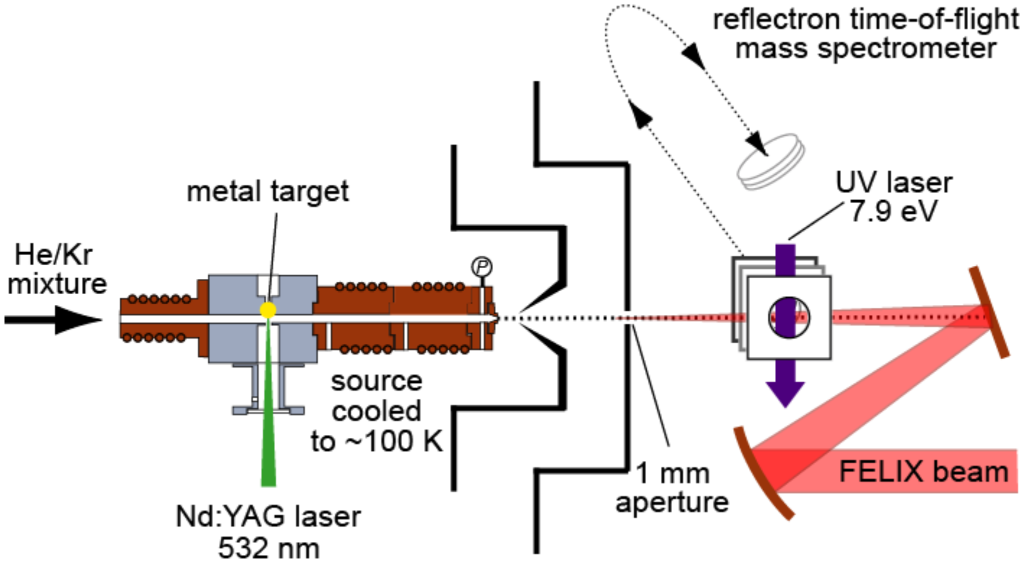
IR-ionization yields very clean mass-spectra:
only species that undergo thermionic emission are observed

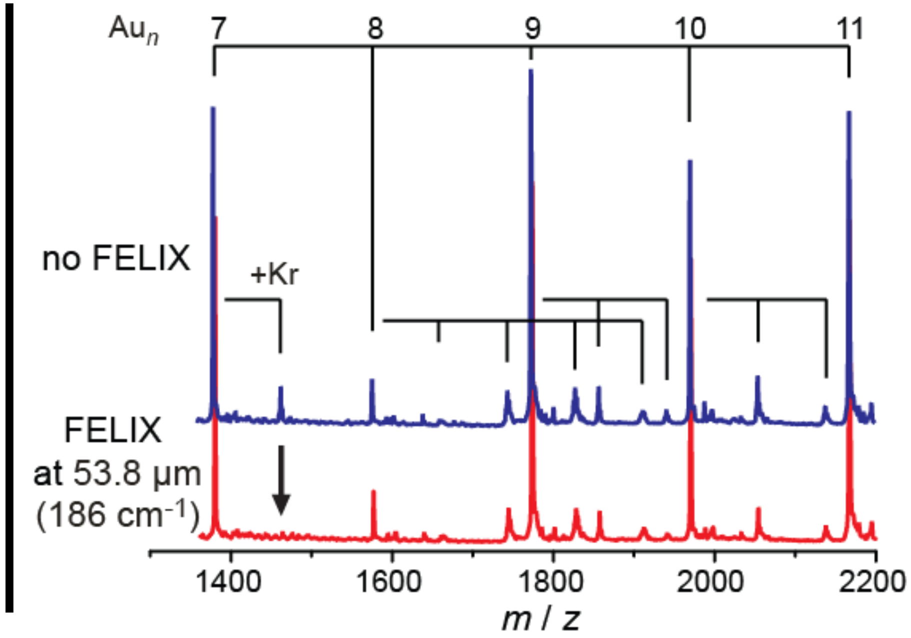
Although the amount of IR spectroscopic information that can be obtained via this method is limited, it often is the only information of its kind that is available for these systems.

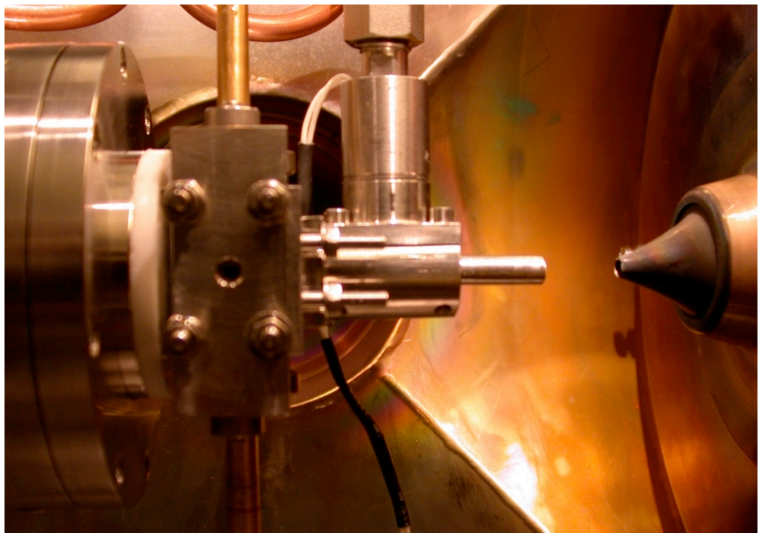
Gert von Helden

Review: „Resonant ionization using IR light: A new tool to study the spectroscopy and dynamics of gas-phase molecules and clusters", G. von Helden, D. van Heijnsbergen & G. Meijer, *J. Phys. Chem., 107 (2003) 1671*

Far-infrared spectroscopy of (Krypton tagged) gold clusters







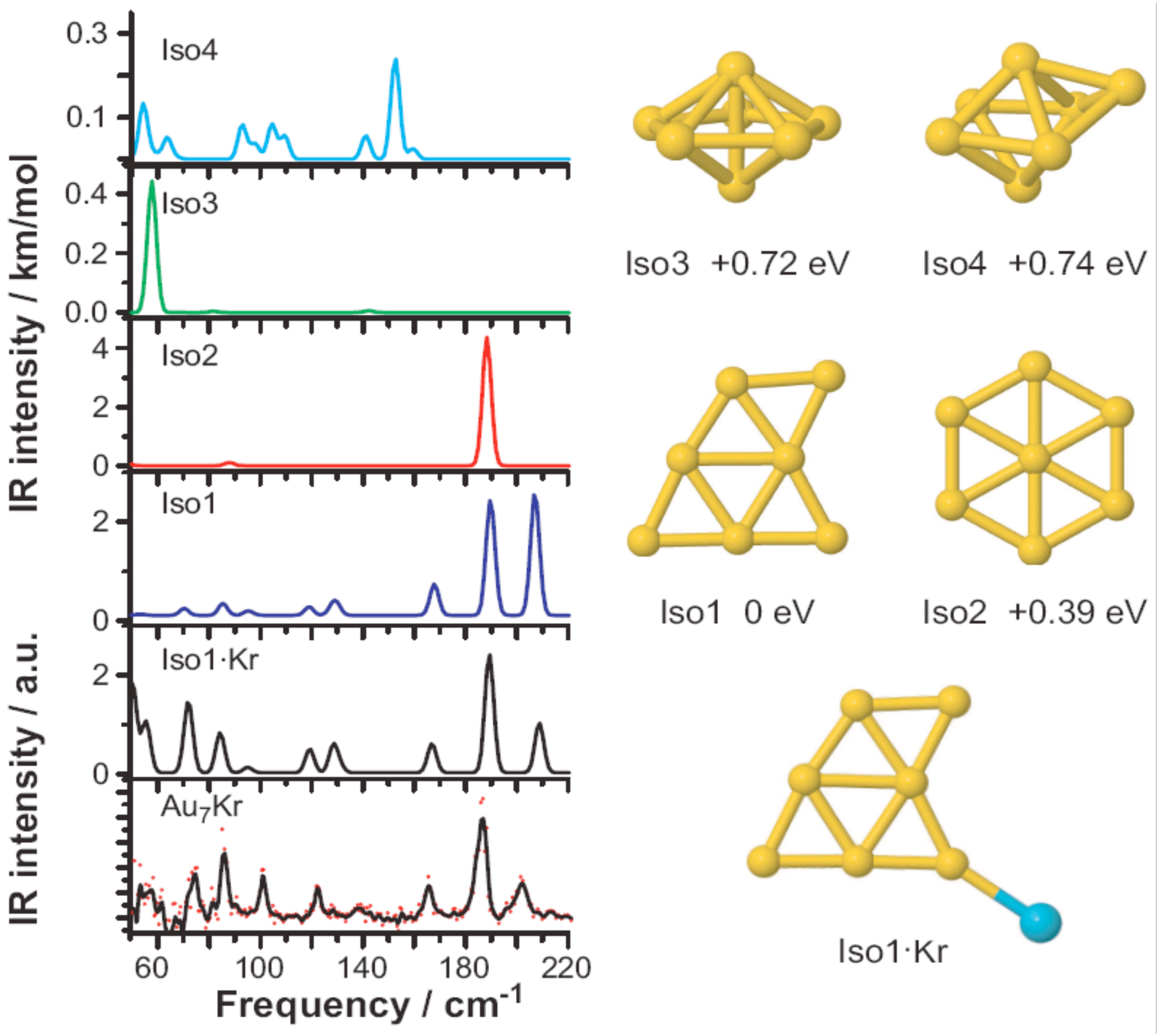
Clusters are generated by laser vaporization.

The cluster beam is overlapped with the FELIX beam.

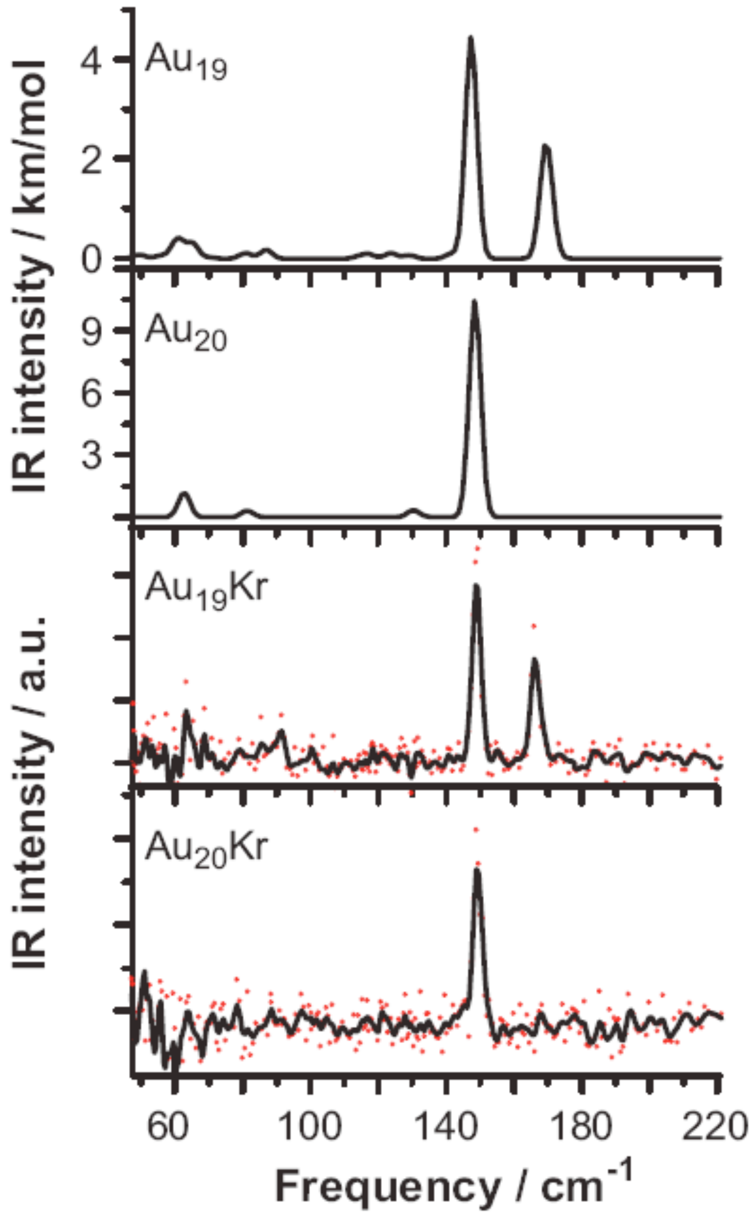
Mass spectra are recorded with and without FELIX.

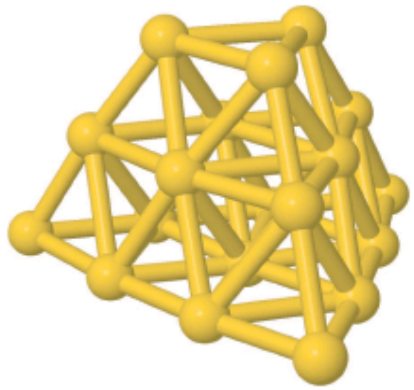
Monitoring the fragmentation yield as a function of IR frequency gives the IR spectrum of the cluster.

On the structures of neutral gold clusters: Au_7

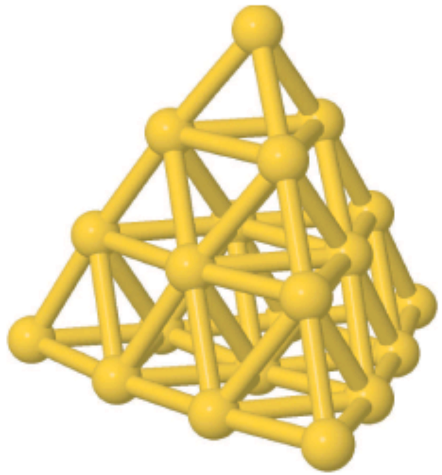


On the structures of neutral gold clusters: Au_{19} & Au_{20}



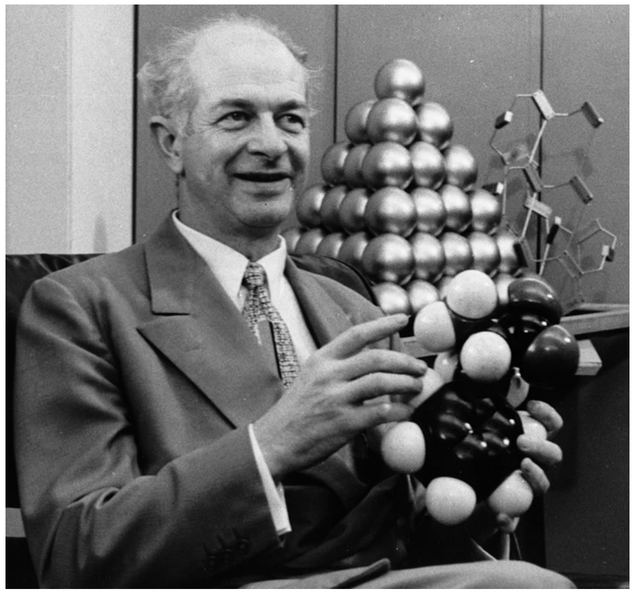


Au_{19}



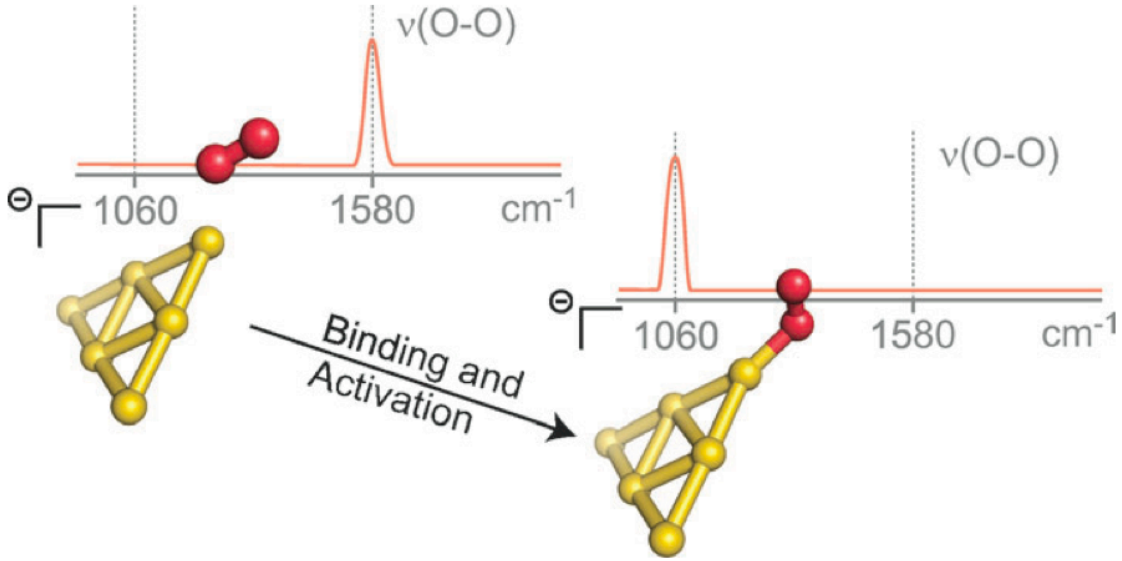
Au_{20}

André Fielicke

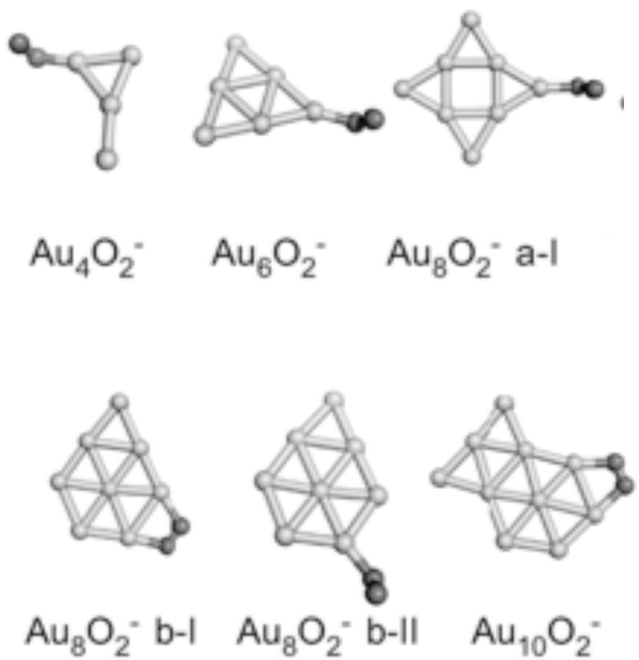


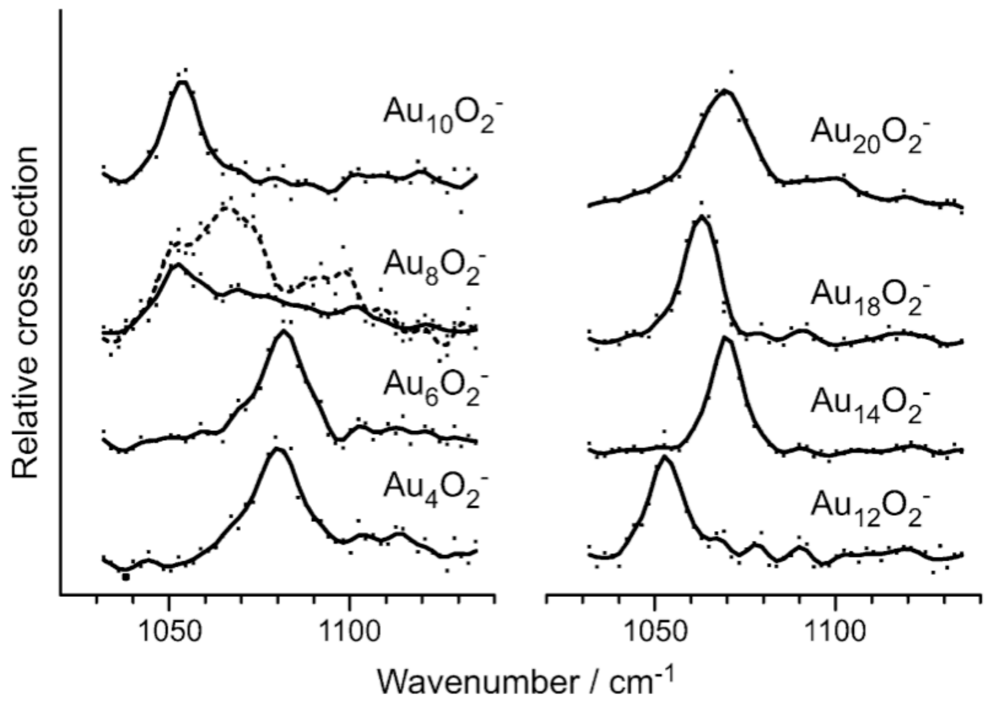
P. Gruene, D.M. Rayner, B. Redlich, A.F.G. van der Meer, J.T. Lyon, G. Meijer & A. Fielicke, *Science 321 (2008) 674*

Activation of molecular oxygen by anionic gold clusters



Molecular oxygen converts into a superoxo species (O_2^-) upon complexation to gold cluster anions containing an even number of Au atoms.



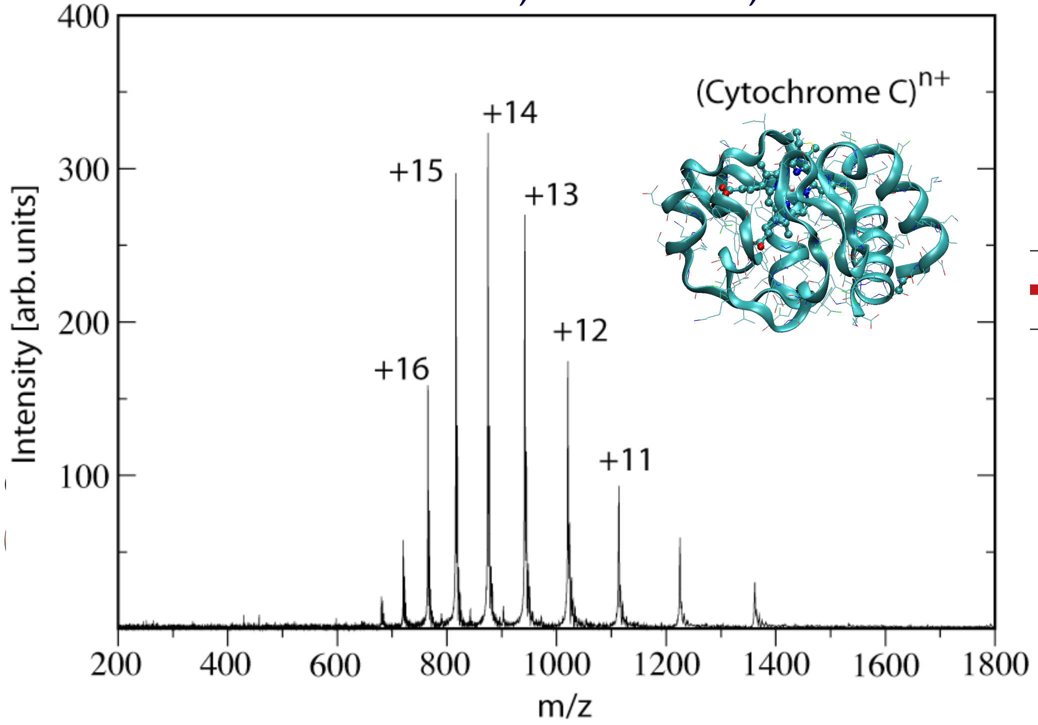


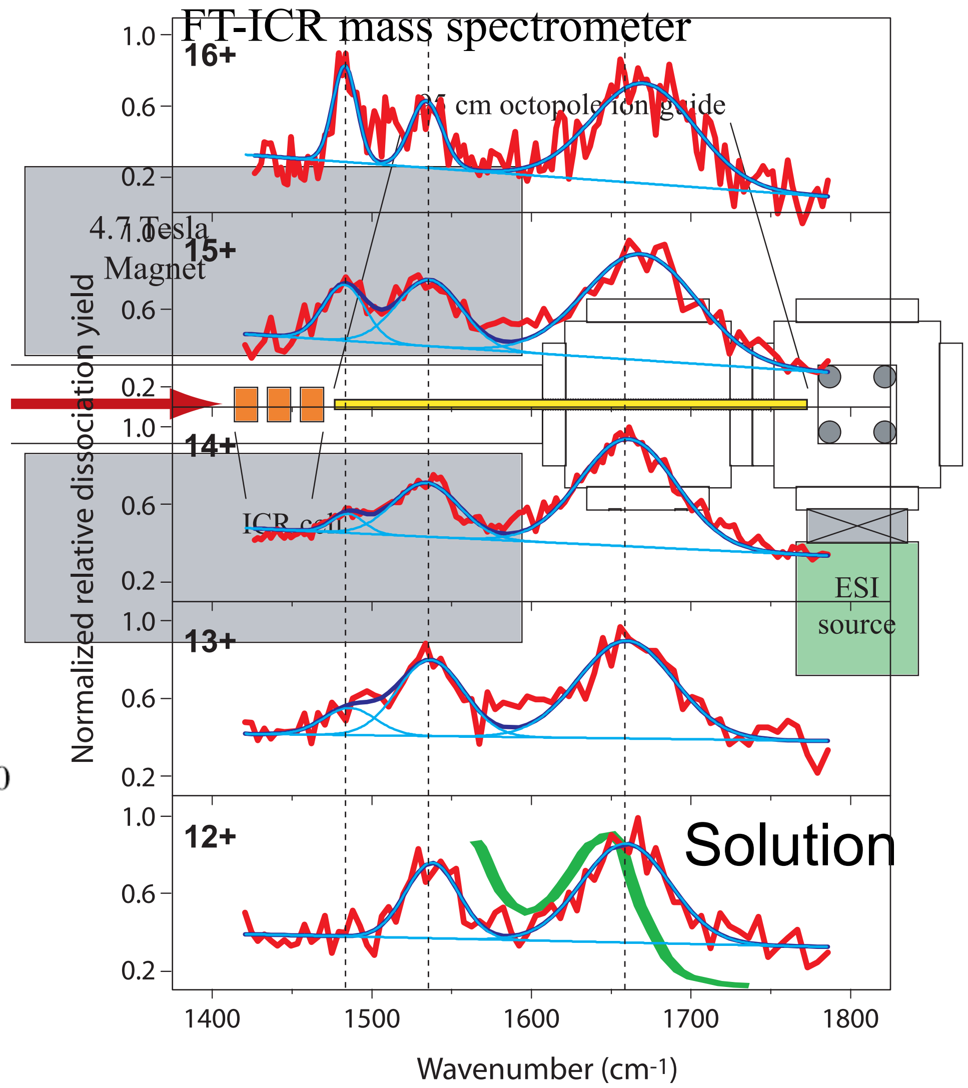
A.P. Woodham, G. Meijer & A. Fielicke, *Angew. Chem. Int. Ed. (in press)*

Spectroscopic studies on gas-phase proteins

Cytochrome C:

104 amino acids, mass ~ 12,000 amu





J. Oomens, N. Polfer, D.T. Moore, L. van der Meer, A.G. Marshall, J.R. Eyler, G. Meijer & G. von Helden, *Phys. Chem. Chem. Phys. 7 (2005) 1345*

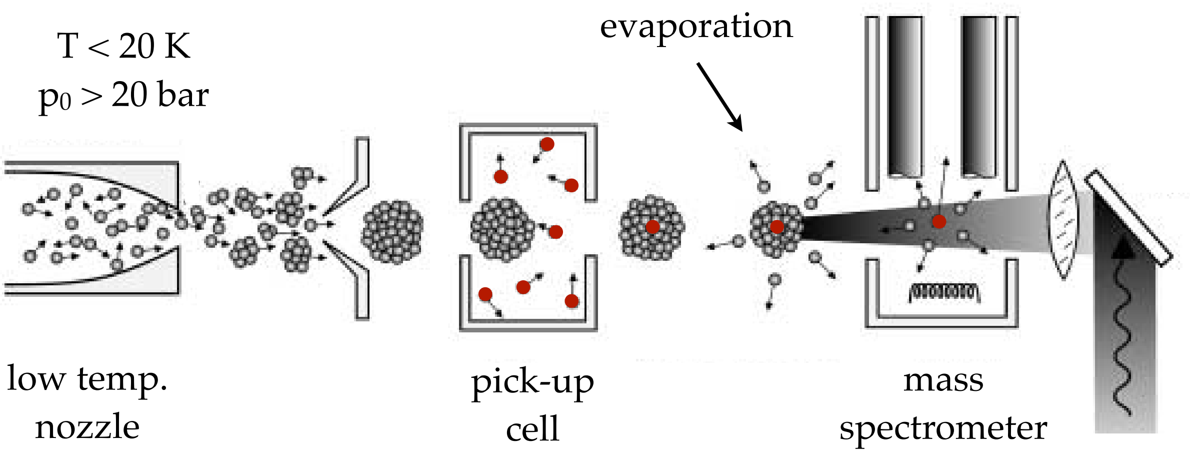
Spectroscopy in liquid Helium droplets

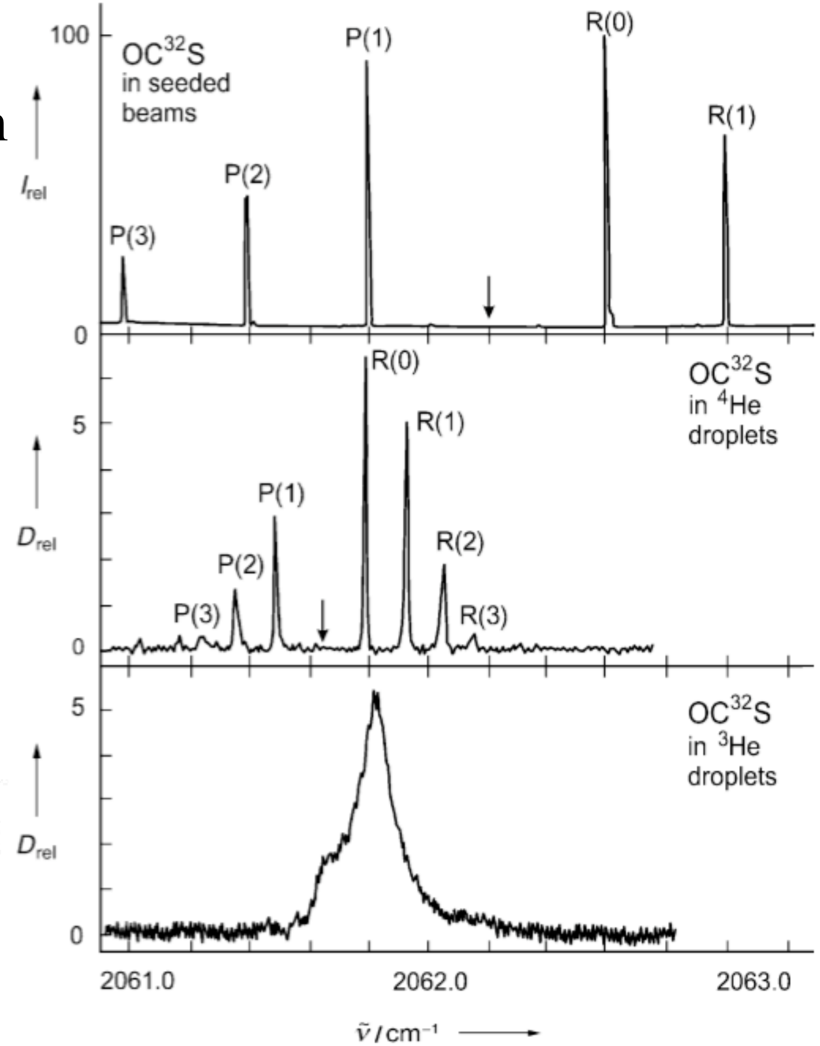
Droplets are liquid, superfluid, and maintain an equilibrium temperature of 0.38 K by evaporation

Weak interaction with dopant molecules

Optically transparent from deep UV to far IR

High resolution spectra can be obtained



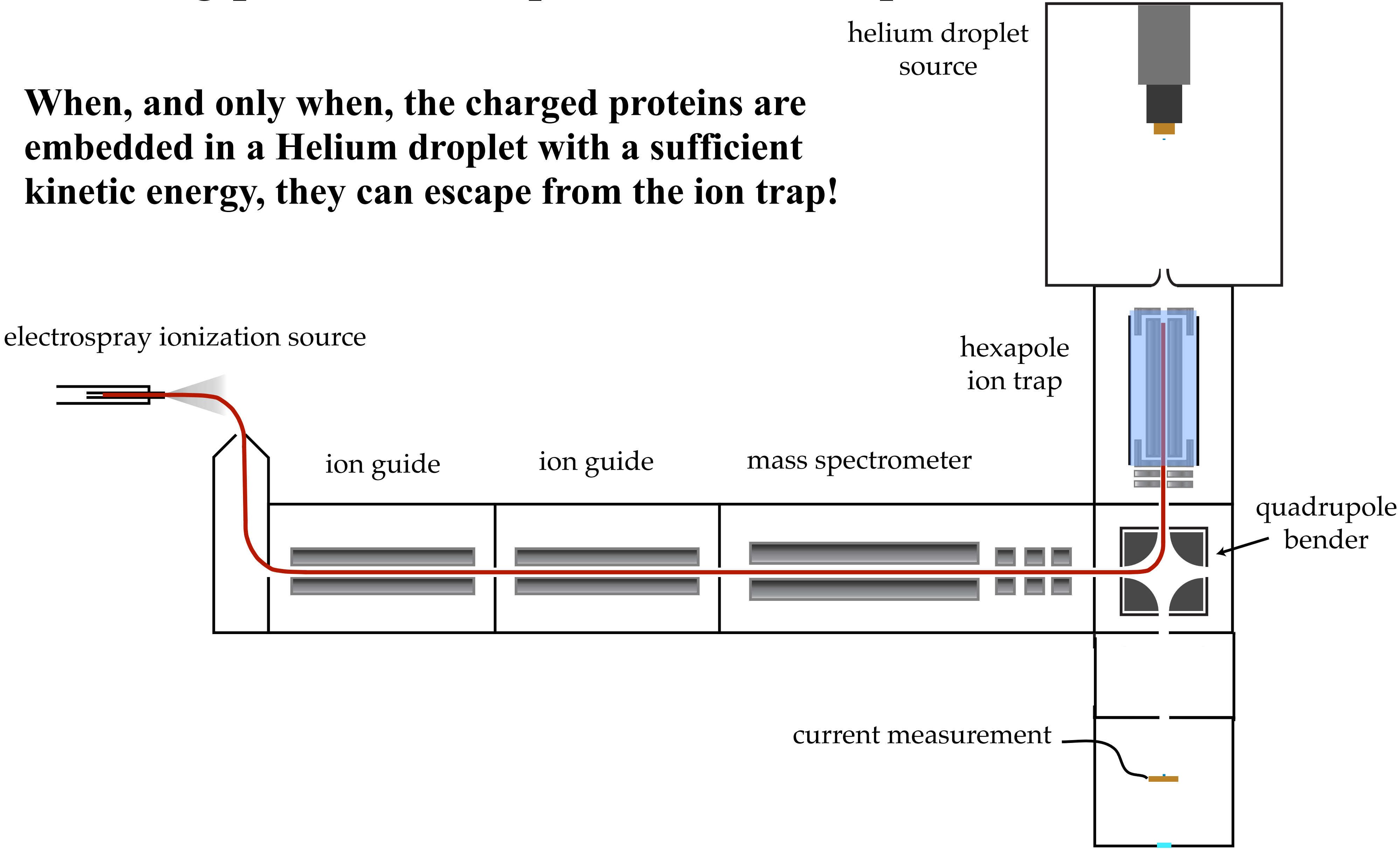


J.P. Toennies & A.F. Vilesov, *Angew. Chem. Int. Ed. 43 (2004) 2622*

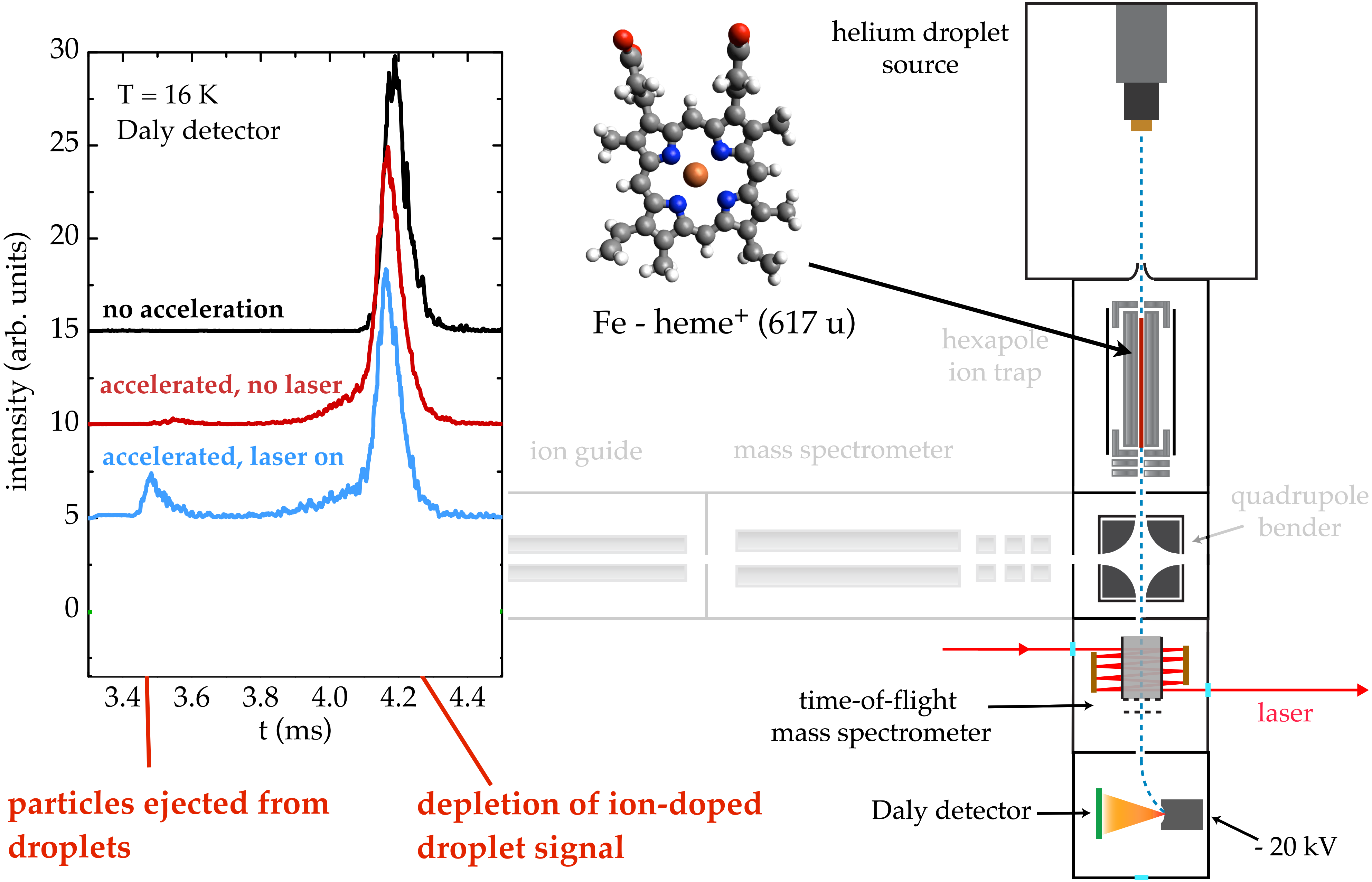
„Marriage“ between matrix isolation spectroscopy and molecular beams

Catching proteins in liquid Helium droplets

When, and only when, the charged proteins are embedded in a Helium droplet with a sufficient kinetic energy, they can escape from the ion trap!

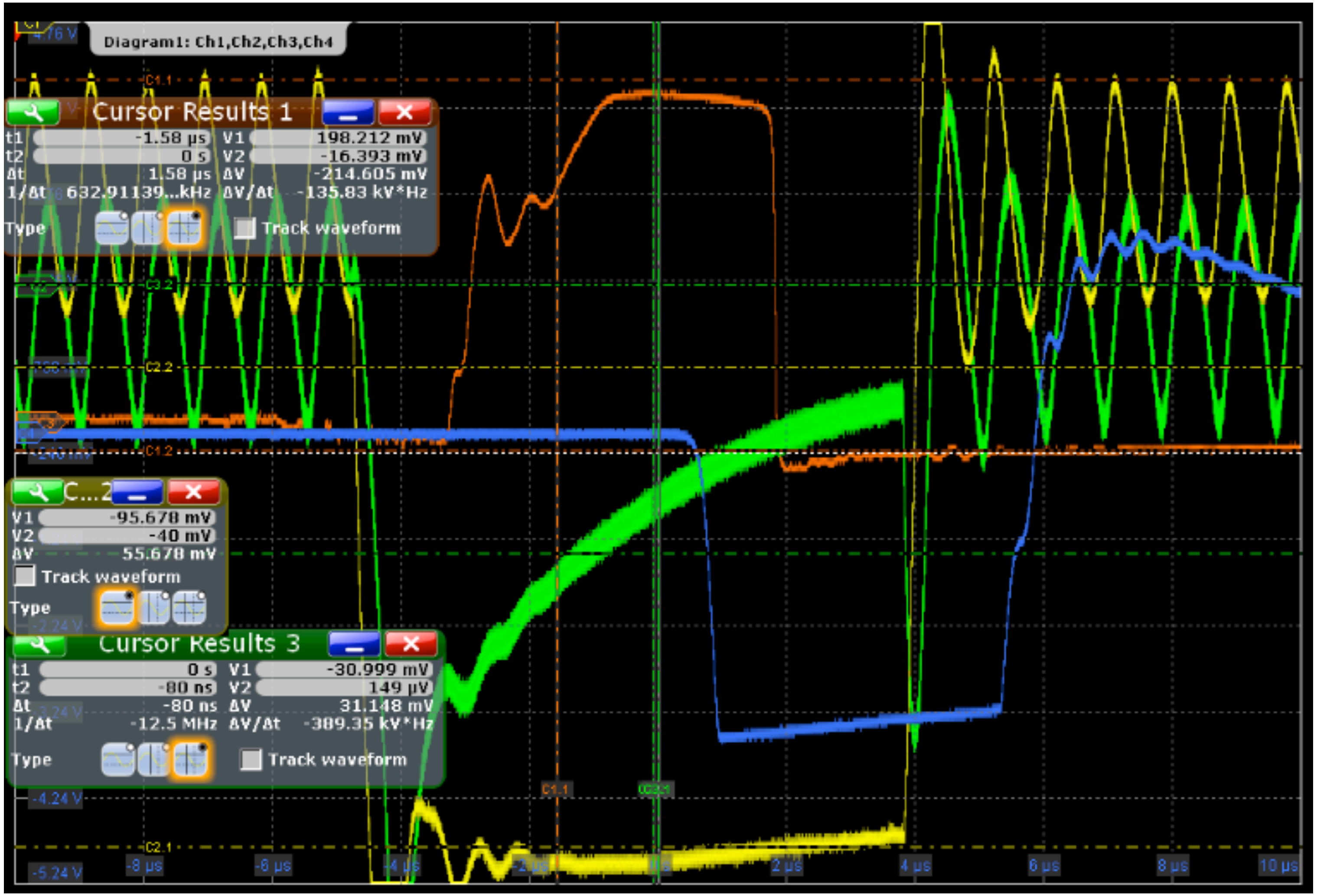


Spectroscopy in doped Helium droplets



First lasing of the IR-FEL at the Fritz Haber Institute

February 14, 2012 @ 19:45



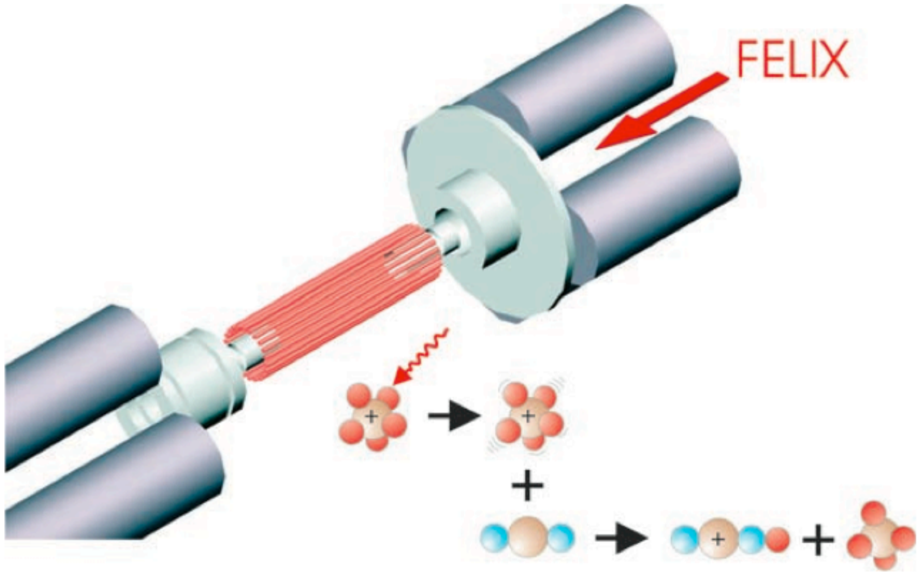
Orange: 5 microsecond duration 28 MeV electron beam; 200 mA beam current (@ 1 GHz, i.e. 200 pC bunch-charge)

Blue: Saturated MCT detector signal; IR-FEL radiation @ 18 micrometer produced

Conclusions

An IR-FEL provides unique opportunities for structure determination of gas-phase molecules and clusters using variants of "action spectroscopy".

Many other variants possible, e.g., Laser-Induced Reactions (LIR)



Understanding the Infrared Spectrum of Bare CH_5^+

Oskar Asvany,[1*] Padma Kumar P,[2*] Britta Redlich,[3] Ilka Hegemann,[2] Stephan Schlemmer,[1,4] Dominik Marx[2†]

SCIENCE VOL 309 19 AUGUST 2005 **1219**

By combining ever more sophisticated experimental setups with an IR-FEL, fully vibrationally resolved spectra of molecules and clusters of increasing complexity can be obtained.