High-resolution spectroscopy of cation-helium complexes

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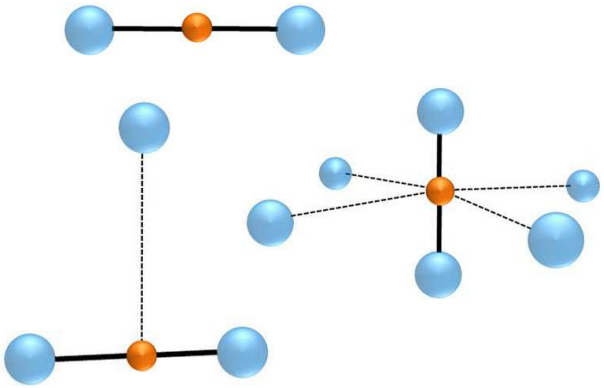
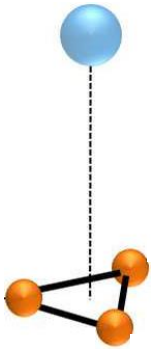
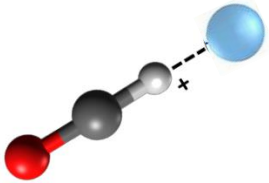
Universität zu Köln



H^+-He_n

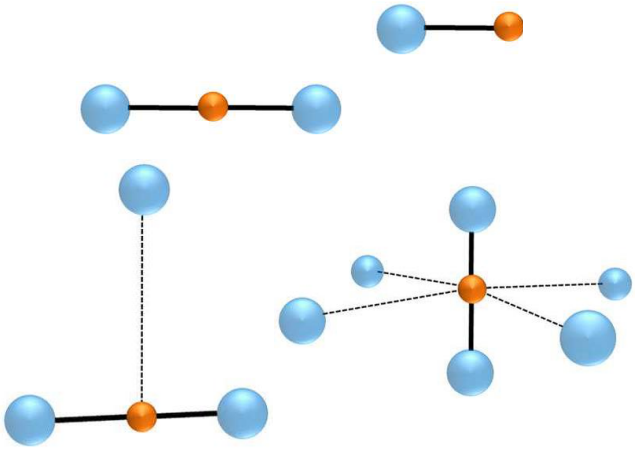


H_3^+-He_n



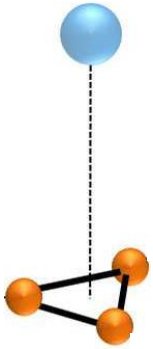
HCO^+-He

virtual SPIG 2020, August 24-28, 2020



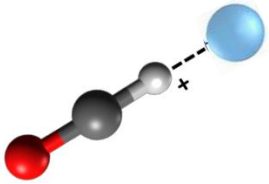
JPCL **10**, 5325 (2019)
Front. Chem. **8**, 462 (2020)

H^+-He_n



Mol. Phys. **113**, 2320 (2015)

H_3^+-He_n

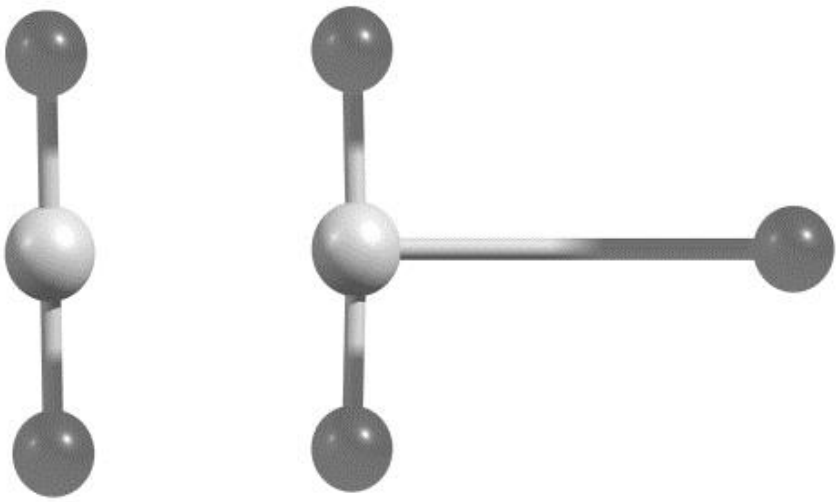


PCCP **21**, 3440 (2018)
JPC **103**, 1297 (1995)

HCO^+-He

- typically weak van-der-Waals bonds
- challenging due to large amplitude motions
- some are of astrophysical importance

IR spectroscopy of H^+-He_n



HHe_2^+ HHe_3^+ HHe_6^+

short story of HHe^+

mass spectr. detection

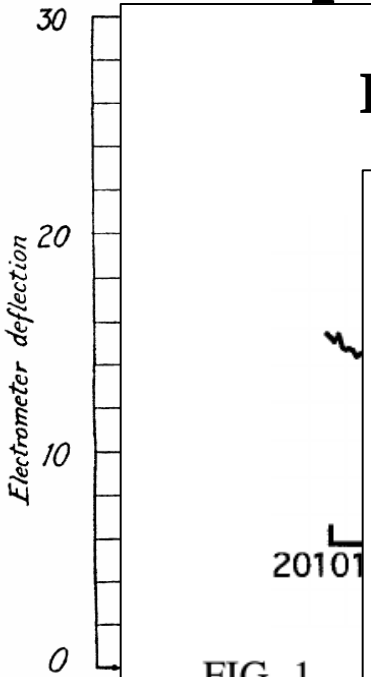


FIG. 1.
One min
accumula

rotational detection

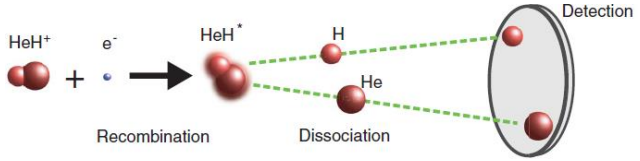
Phys. Rev. Lett. **78**, 1664 (1997)

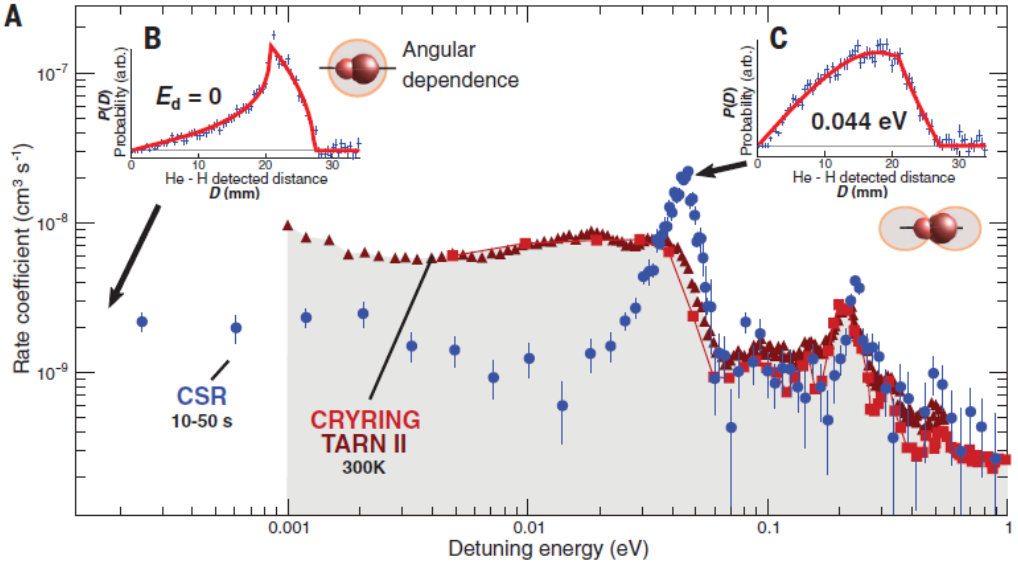
detection in space

Nature **568**, 357 (2019)

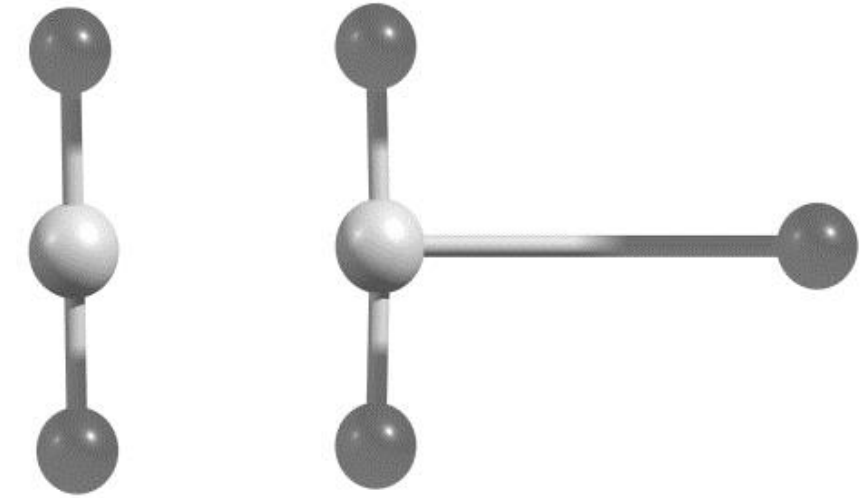
dissociative recombination

Science **365**, 676 (2019)





What about HHe_n^+, n>1 ?



HHe_2^+ HHe_3^+ HHe_6^+

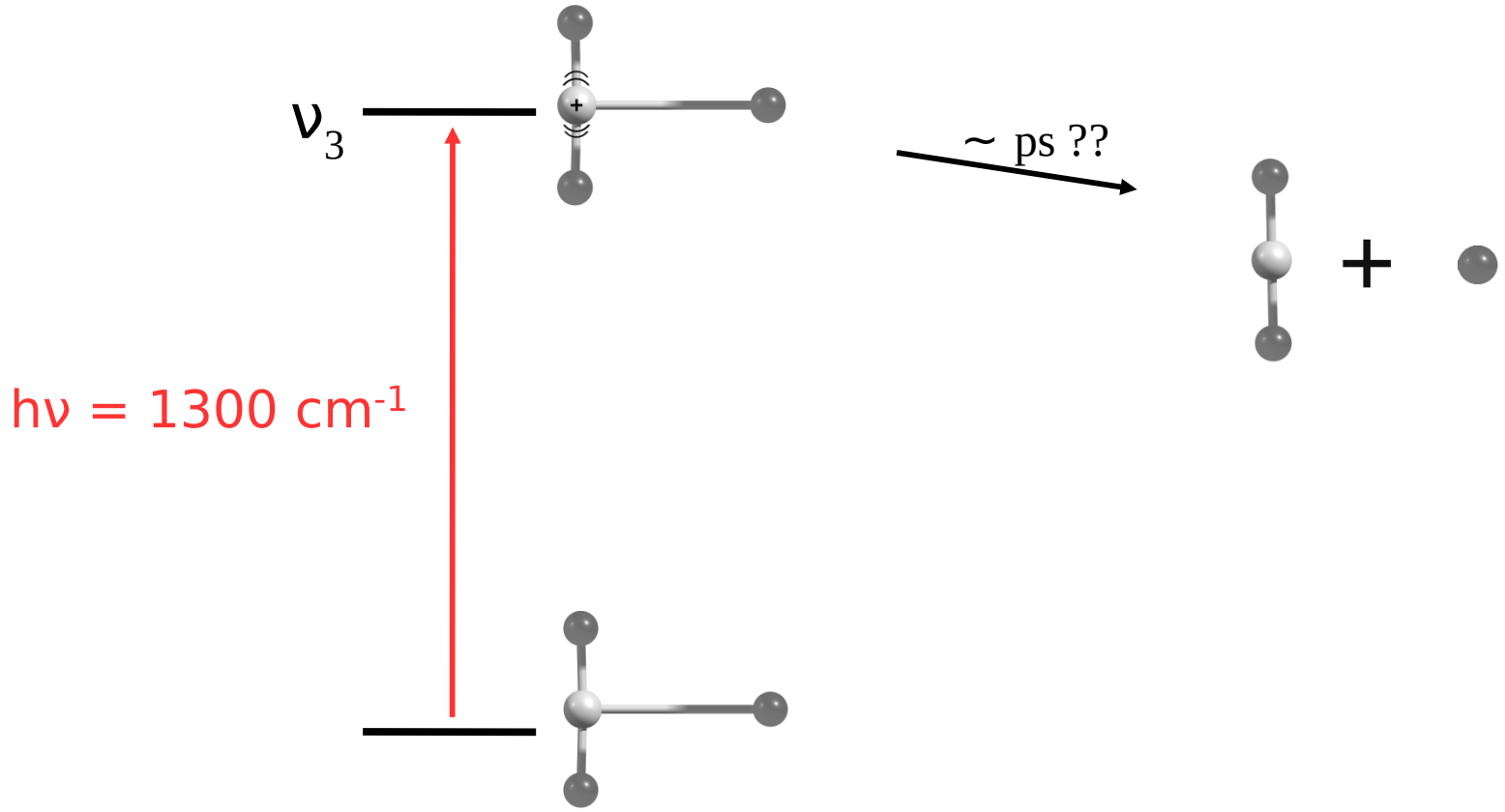
mass spectra reveal special stability for n=2, 6, 13

Z. Phys. D **23**, 181 (1992)
Chem Phys Chem **14**, 227 (2013)
Mol. Phys. **117**, 1559 (2019)

but no spectroscopic data available ...

.. except HAr_n^+: JCP **145**, 231101 (2016)

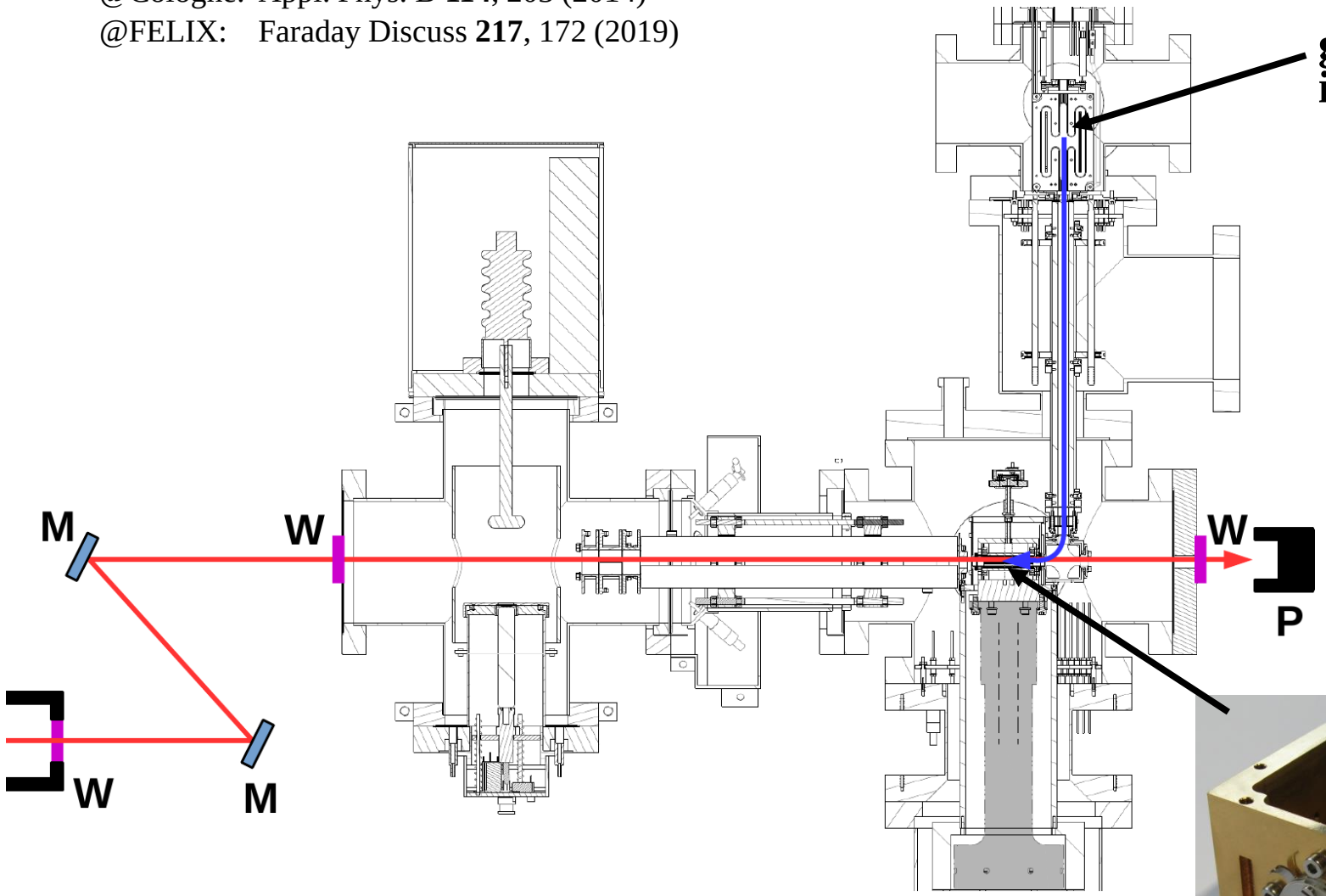
IR predissociation spectroscopy of HHe_n^+ , n>2



HHe_2^+ is strongly bound chromophore, all outer He atoms loosely bound

use 4 K trap machines

@Cologne: Appl. Phys. B **114**, 203 (2014)
@FELIX: Faraday Discuss **217**, 172 (2019)

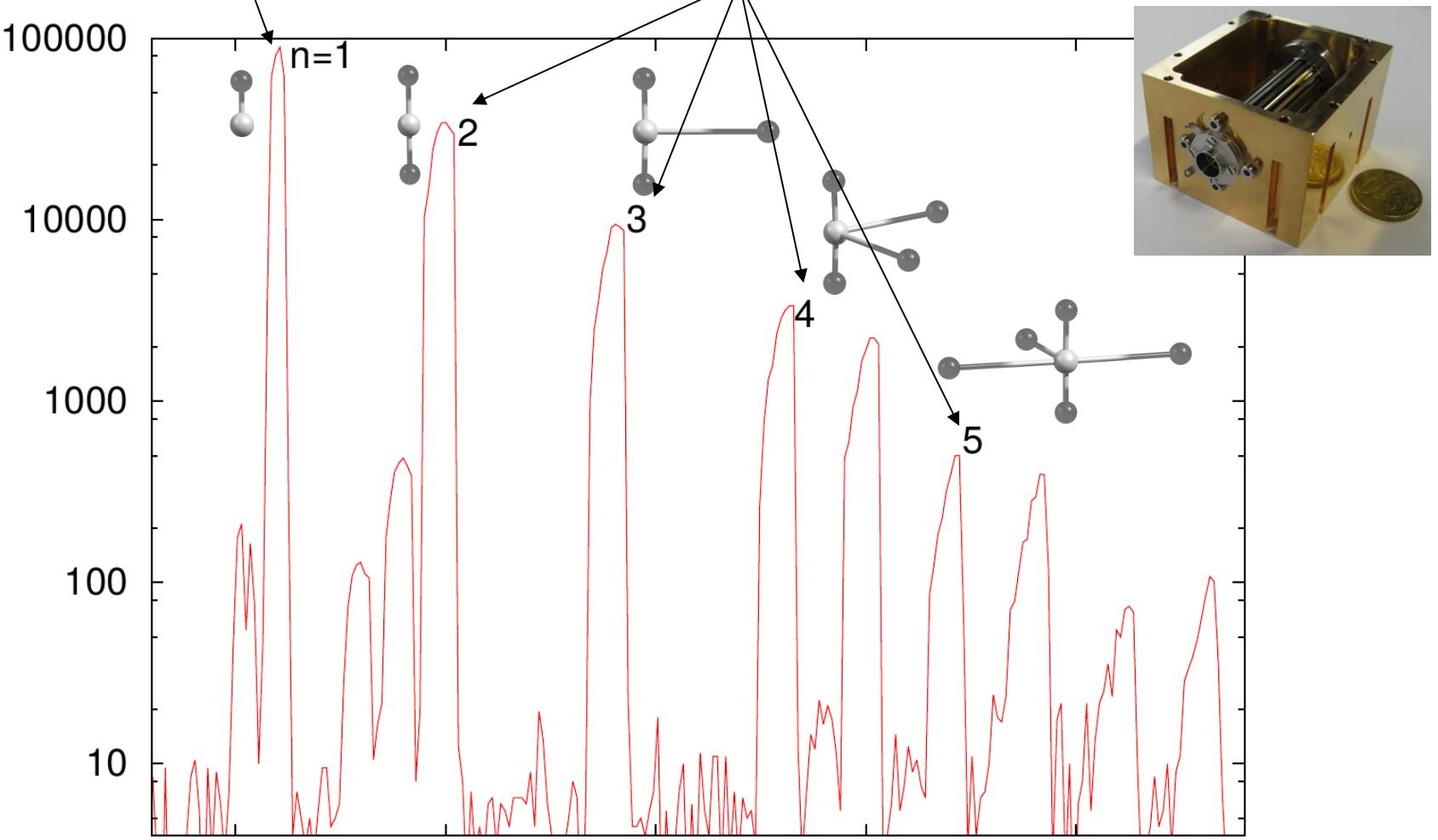


Rev. Sci. Instr. **81**, 076102 (2010)

production of HHe_n^+ in the 4K cold ion trap

HHe^+ produced in source, injected into trap

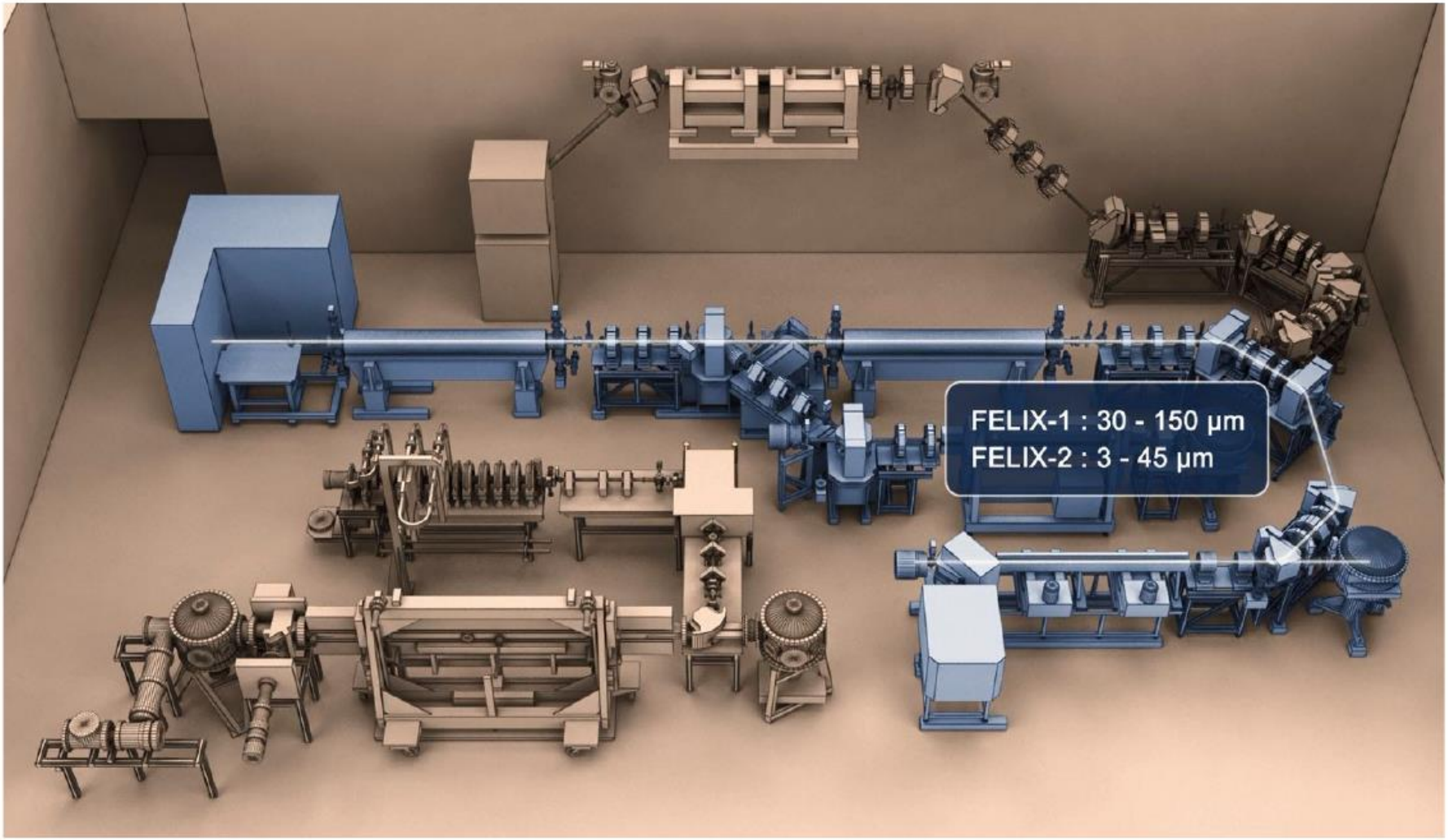
generated in trap by attaching He at 4 K



actually spectrum is for DHe_n^+

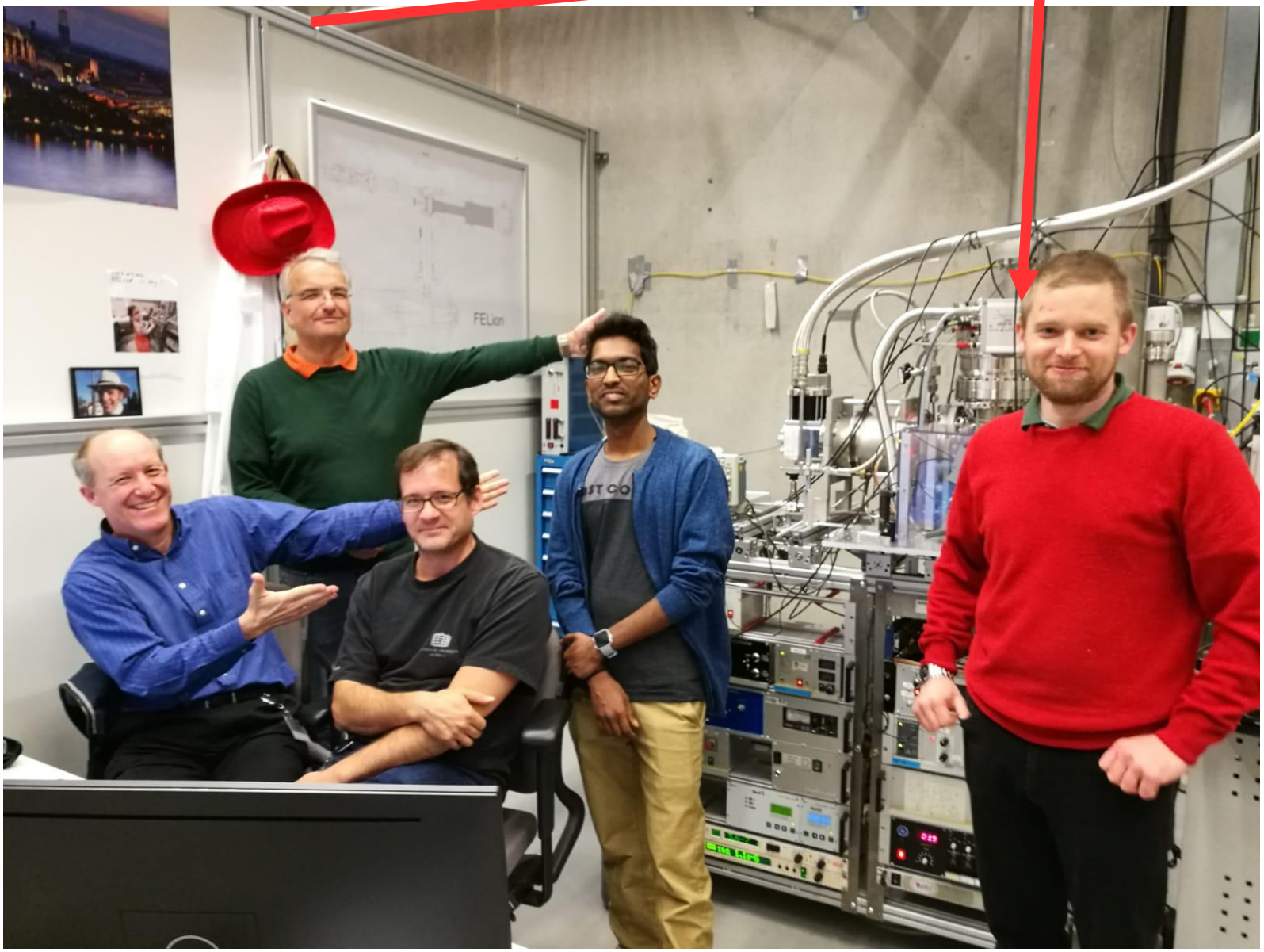
FELIX free electron laser: ~ 67 – 3300 cm^{-1}

FWHM ~ 0.5%

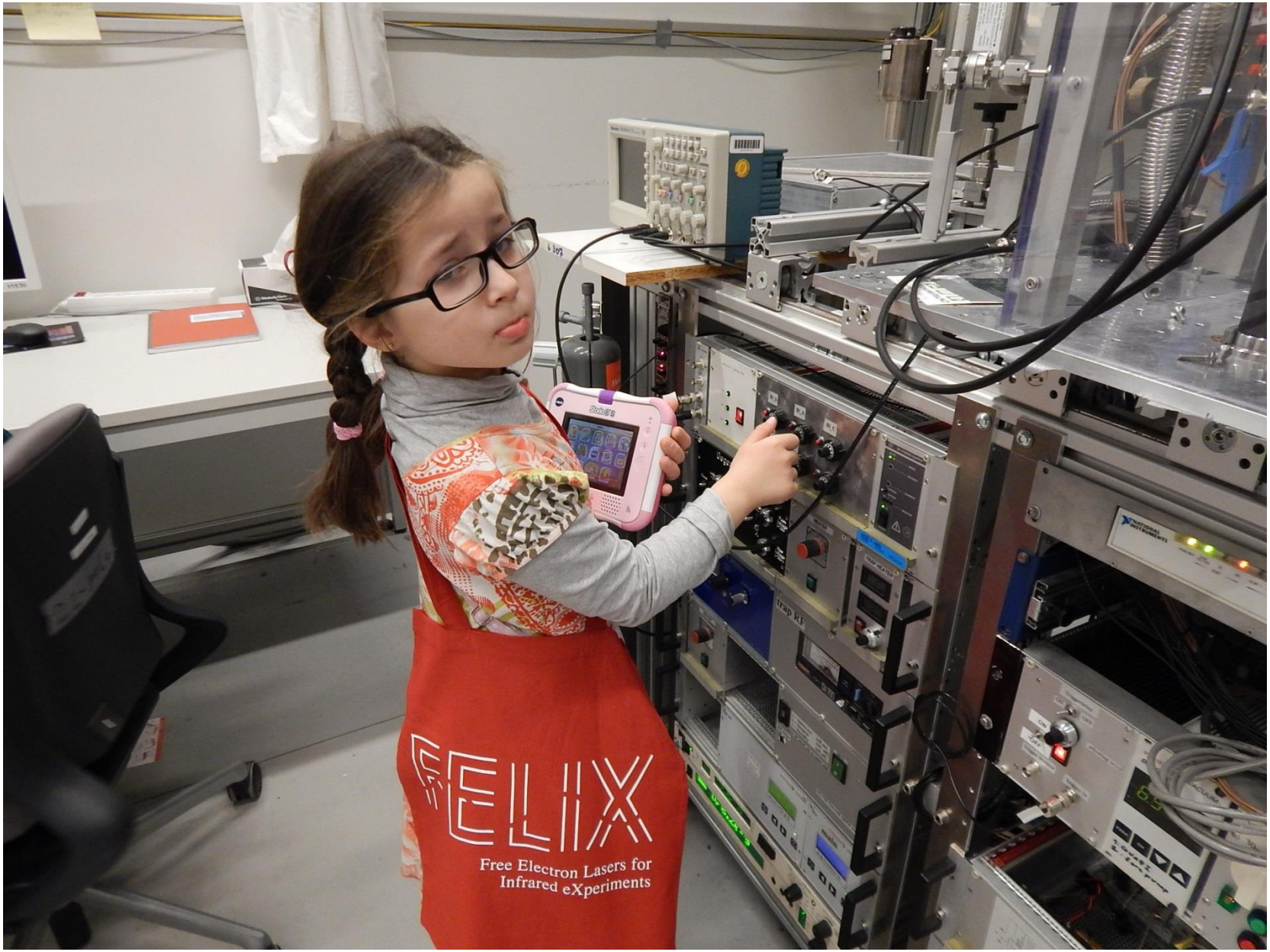


Nijmegen, the Netherlands

4 K trap machine FELion



ion trap is easy to operate ….

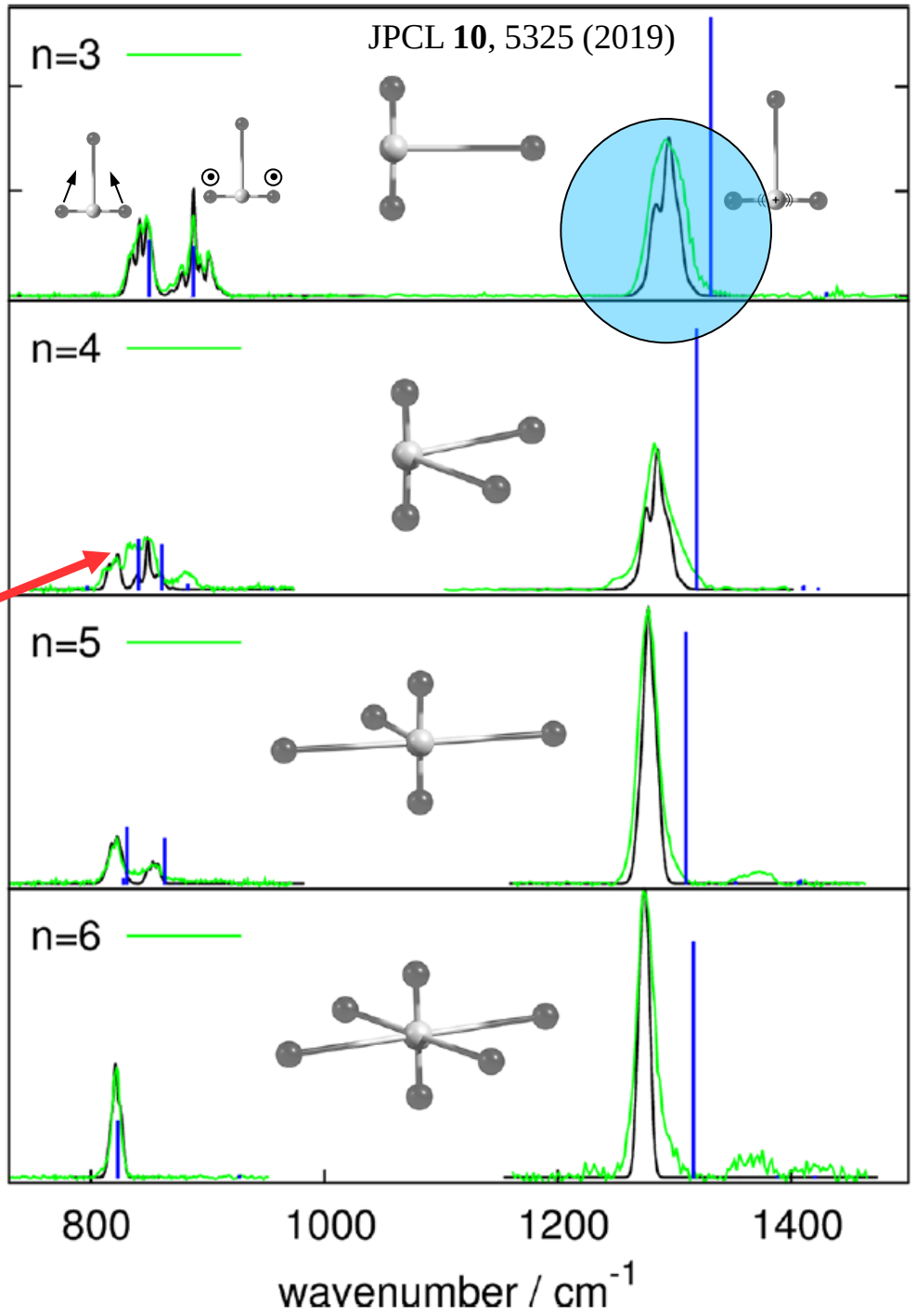


IR overview spectra of HHe_n^+ @ FELIX

observation of stretching and bending mode of HHe_2^+ chromophore

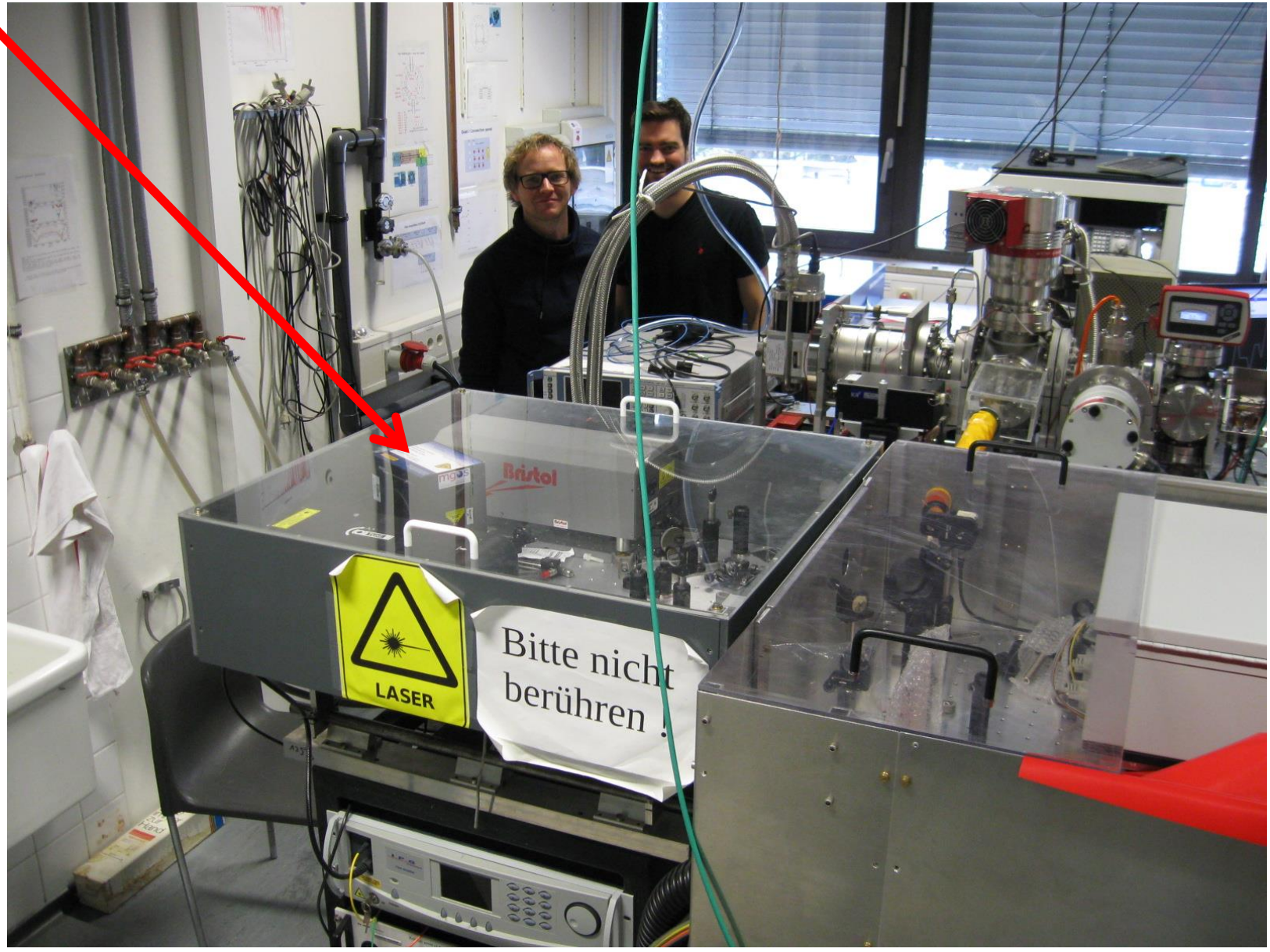
large amplitude motion ?!

--- measurement FELIX
--- simulation with PGOPHER
--- ab initio (Budapest)

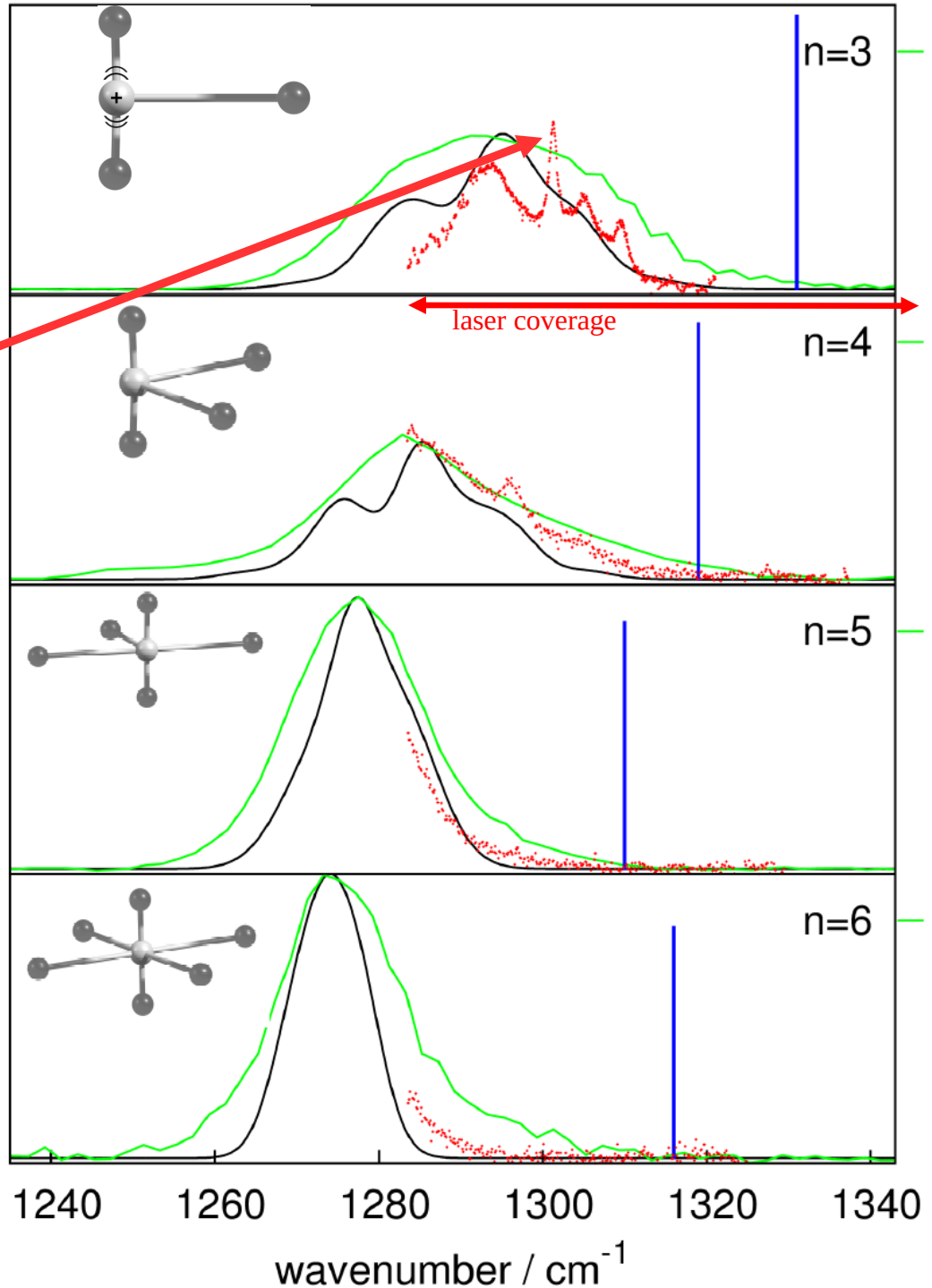


4 K trap machine COLTRAP @ Köln

high-resolution laser: QCL



IR spectra of HHe_n^+ with high-resolution laser (QCL)

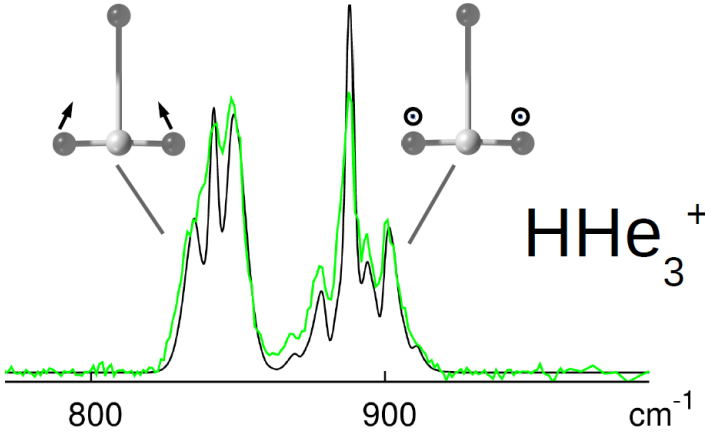


Short lifetime of ~ 5ps
leads to severe broadening

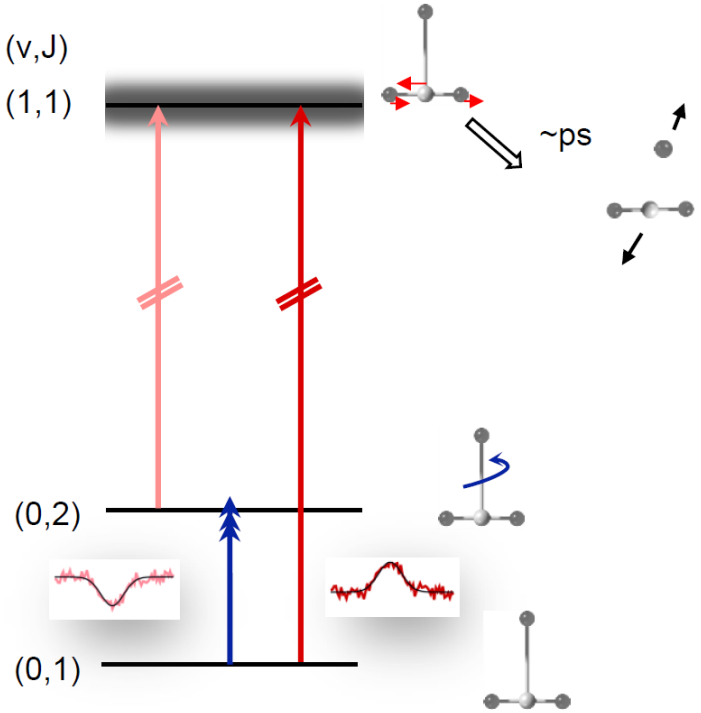
--- measurement FELIX
--- measurement high-res laser
--- simulation with PGOPHER
--- ab initio (Budapest)

Outlook for HHe_3^+

1) look at bending motion

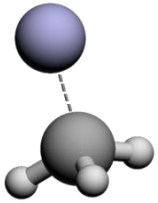


2) do rotational spectroscopy by double resonance

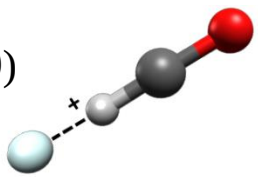


i) rotational transitions NOT affected by lifetime broadening!!

ii) we know it works!



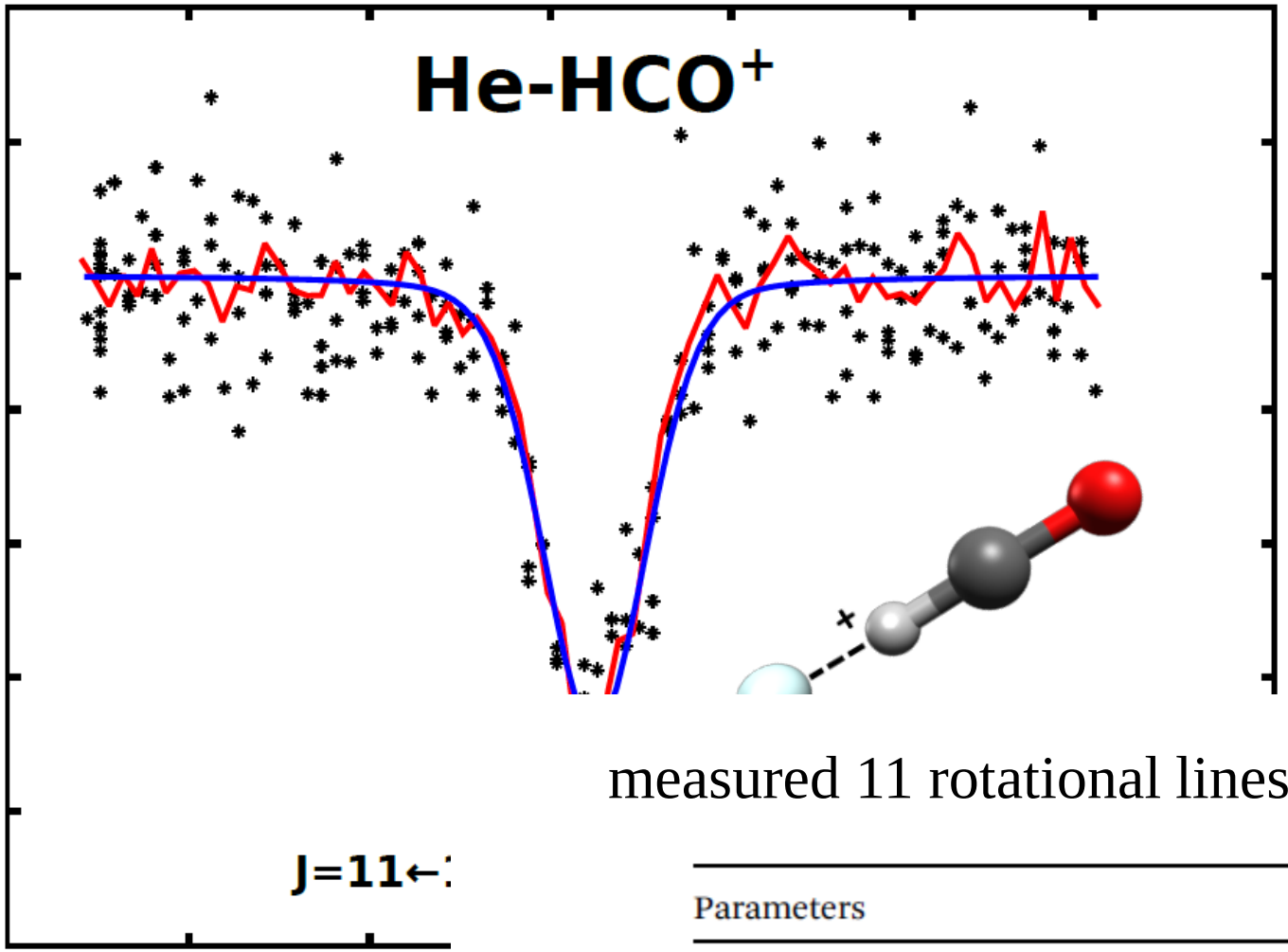
Phys. Rev. Lett. **121**, 143001 (2018)



PCCP **21**, 3440 (2019)

rotational- predissociation spectroscopy

PCCP **21**, 3440 (2019)



measured 11 rotational lines in high resolution

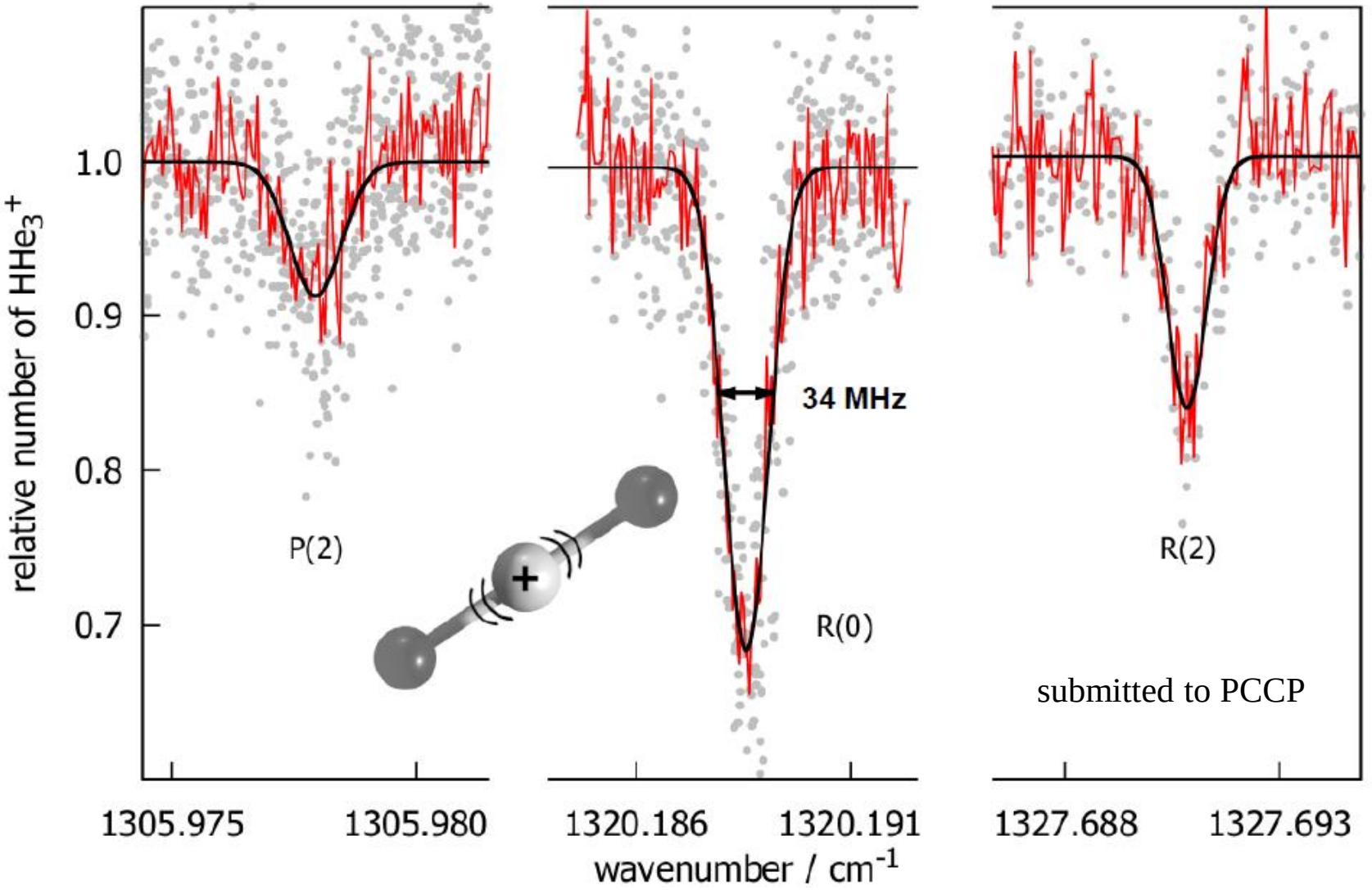
Parameters	$v_1 = 0$
B	8698.1947(16)
D	0.318741(46)
$H/10^{-5}$	10.03(6)
$L/10^{-7}$	−2.681(39)
$M/10^{-10}$	4.0(1)
$N/10^{-13}$	−3.2(1)

But what about HHe_2^+ ?

- HHe_2^+ is a fundamental three-nucleus-four-electron system
- it is similar to the CO_2 molecule: $^1\sum$ electronic ground state, only even-J states exist
- HHe_2^+ cannot be destroyed by its fundamental vibrations
- used another action spectroscopy method (so-called LIICG method) to record rovibrational transitions

LIICG method : Appl. Phys. B **114**, 203 (2014)

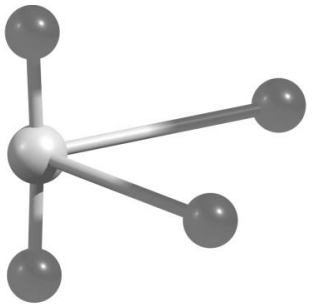
What about HHe_2^+ ?



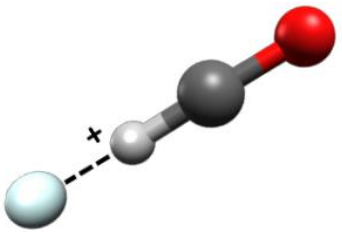
determined bond distance experimentally r_e = 0.924Å

Take home message

HHe_n^+ are interesting species for **IR spectroscopy**, potentially some exhibit large amplitude motion



High-resolution **rotational spectroscopy** of cation-helium complexes can be achieved via double resonance, and allow interesting discoveries



Cologne spectroscopy group

Stephan Schlemmer

Attila G. Császár

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