Laser Spectroscopy of Stable and Radioactive Negative Ions

DAG HANSTORP

CompAS 2025, Lund, Sweden

12-14 June 2025


new scientist
14 June 1973
Vol 58 No 850
Weekly 15p
Australia 35 cents/
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Are negative ions good for you?


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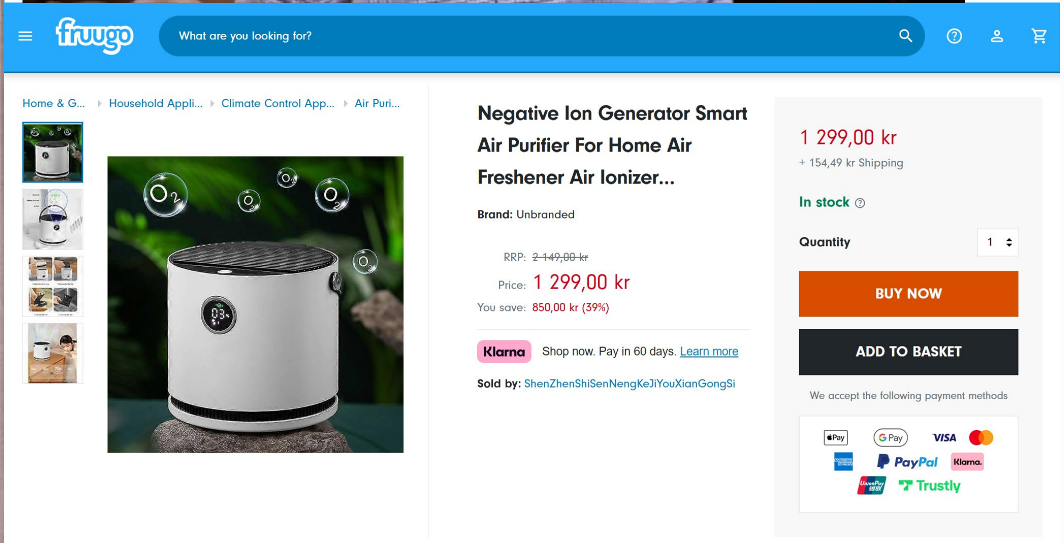
Are negative ions good for you?


Eric Berg


fruugo
What are you looking for?
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Negative Ion Generator Smart Air Purifier For Home Air Freshener Air Ionizer...
Brand: Unbranded
RRP: 2 149,00 kr
Price: 1 299,00 kr
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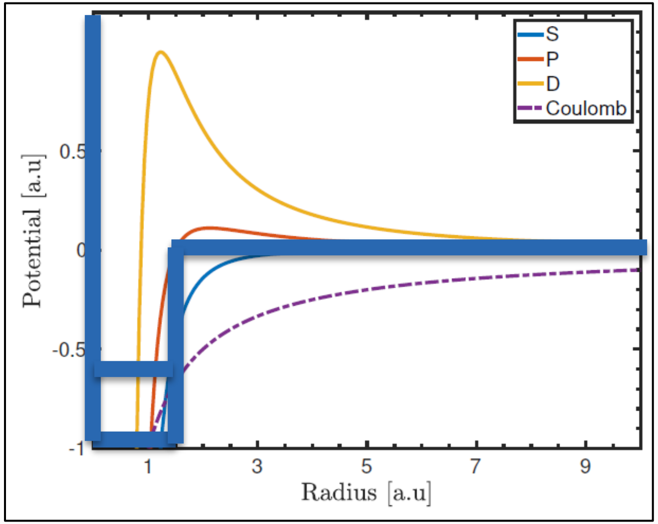
Negative ions

$$H = H_e + H_{ee} + V(r_i) = -\frac{\hbar^2}{2m_e}\sum_i \Delta_i + \sum_{i,j,i\neq j} \frac{e^2}{4\pi\epsilon_0 r_{ij}} - \frac{Ze^2}{4\pi\epsilon_0 r_i}$$



For an atom:

$$V_C(\boldsymbol{r}) = -\frac{e^2}{4\pi\varepsilon_0 r}$$

For a negative ion:

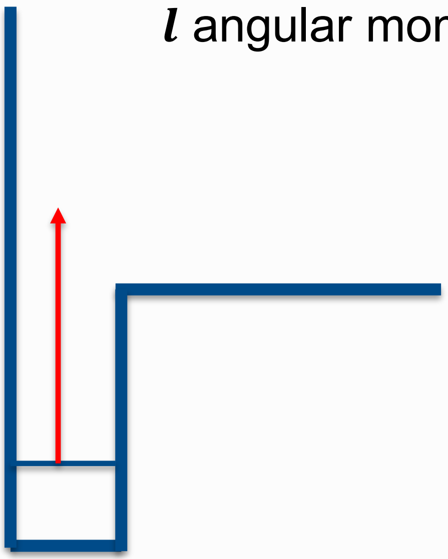
$$V(r) = \frac{l(l+1)}{2r^2} - \frac{\alpha_D}{2r^4}$$

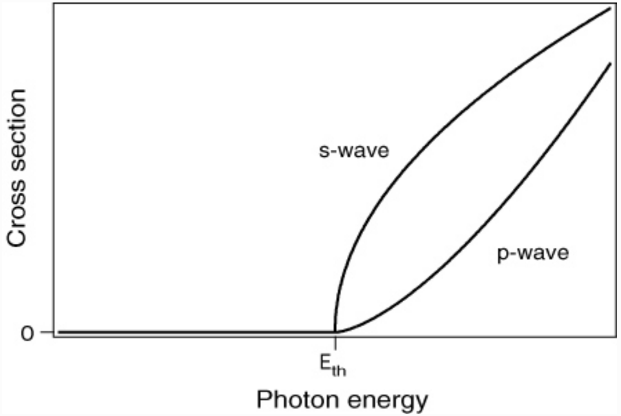
Photdetachment: $hf + A^{-} \rightarrow A + e^{-}$

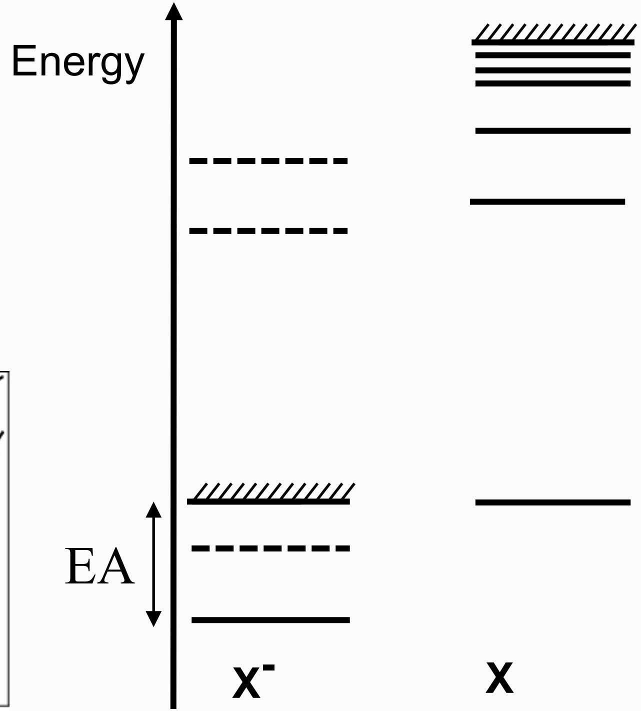
Wigner threshold law:

$$\sigma(E) = k\,(E_{\gamma} - E_{th})^{l+\frac{1}{2}}$$

l angular momentum of emitted electron



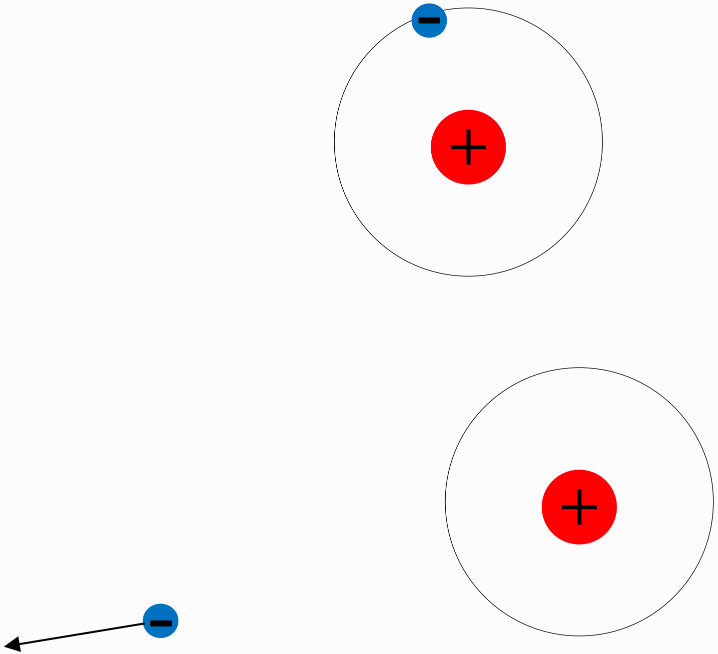




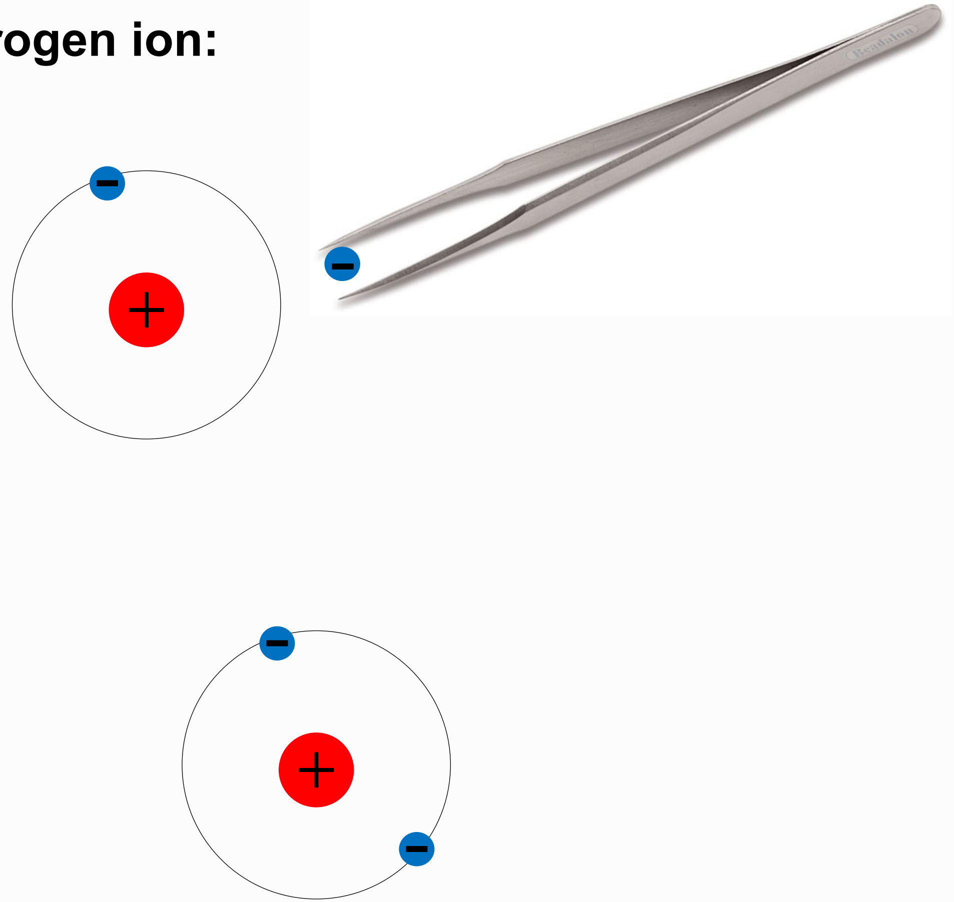
Why study negative ions?

- Benchmark for electron correlation theory
- Model system in physics
- Appears in many environments and used applications

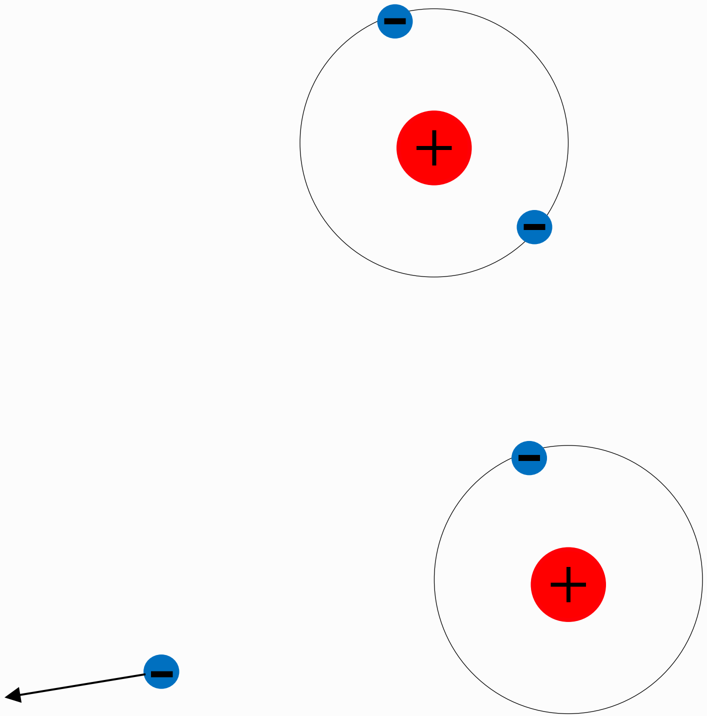
Producing a positive hydrogen ion:



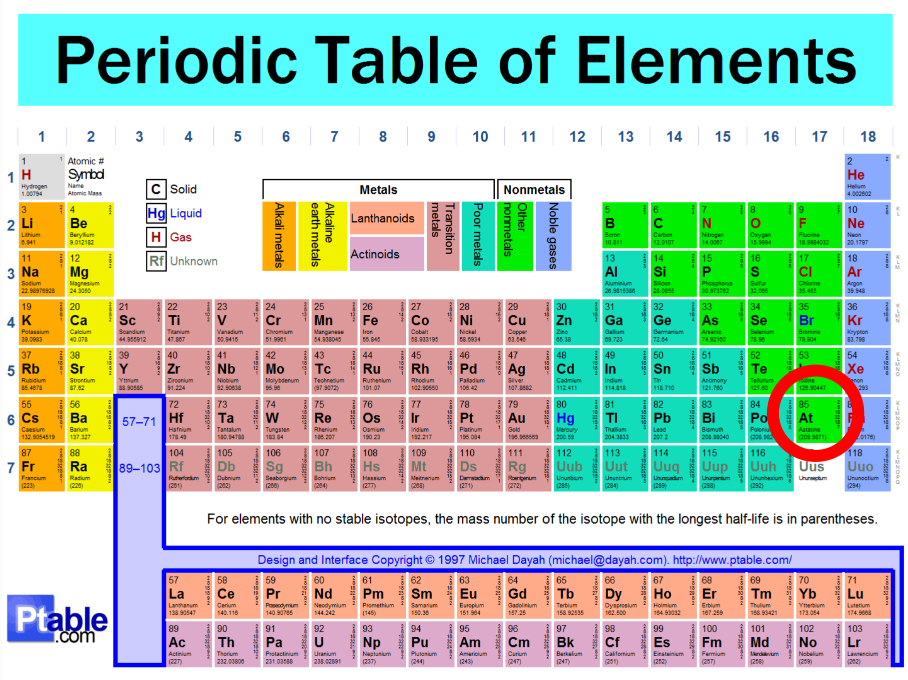
Producing a negative hydrogen ion:



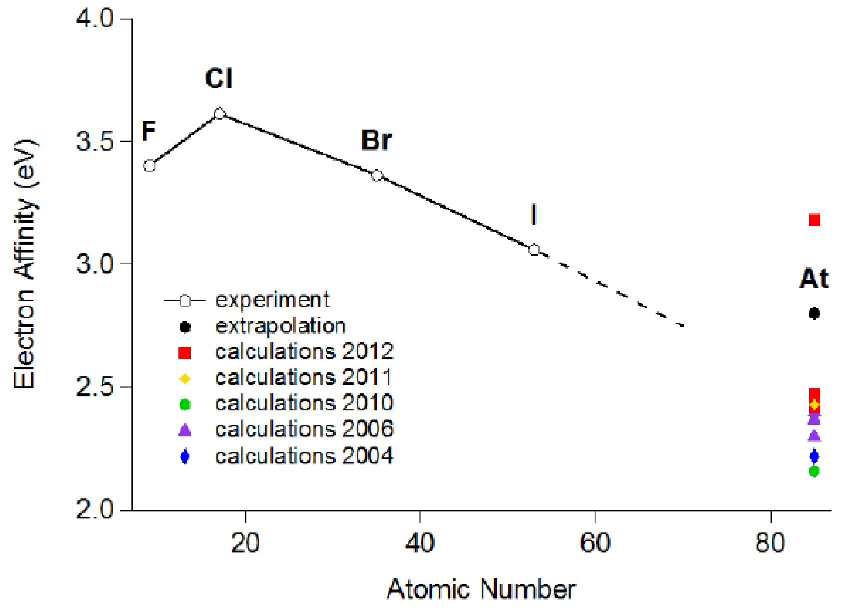
Study negative ions:

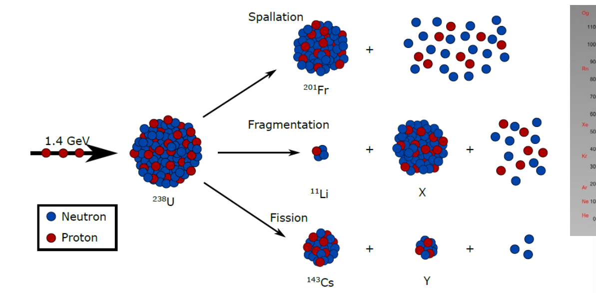


The electron affinity of Astatine

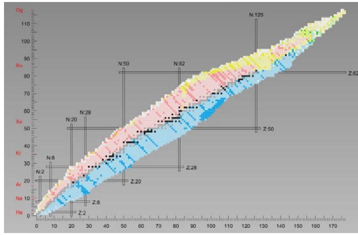


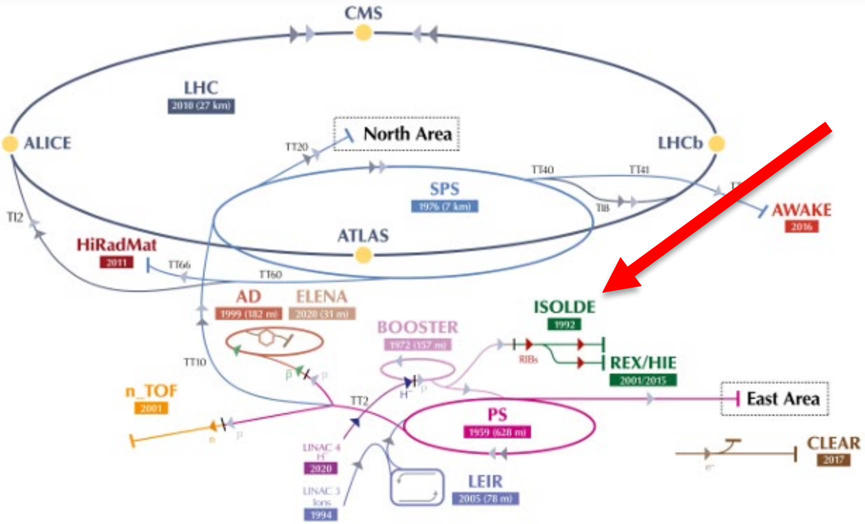
- Least abundant element on earth
- 70 mg in the crust of the earth (1 atom per 100 kg mass)
- Decays through α-decay
- Used in cancer treatment Targeted Alfa Therapy (TAT) (suitable lifetime and energy, non-toxic, non-radioactive daughters)
- Small knowledge about its chemical and physical properties


4.0
3.5
3.0
2.5
2.0
Electron Affinity (eV)
20
40
60
80
Atomic Number
F
Cl
Br
I
At
experiment
extrapolation
calculations 2012
calculations 2011
calculations 2010
calculations 2006
calculations 2004

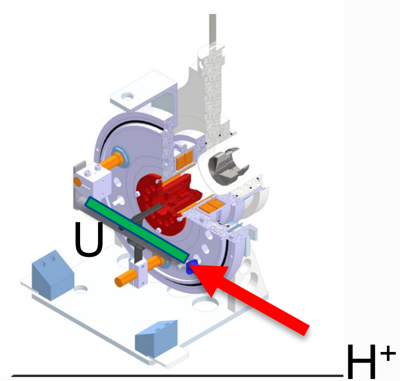


1.4 GeV
238U
Spallation
201Fr
Fragmentation
11Li
X
Fission
143Cs
Y
Neutron
Proton





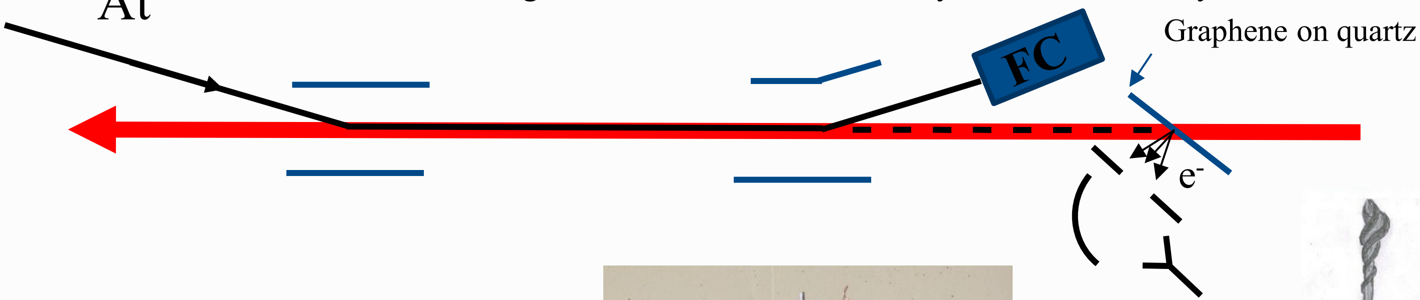
CMS
LHC
2010 (27 km)
ALICE
North Area
LHCb
TT20
TT40
TT41
SPS
1976 (7 km)
AWAKE
2016
TI2
TI8
ATLAS
HiRadMat
2011
TT66
TT60
AD
1999 (182 m)
ELENA
2020 (31 m)
ISOLDE
1992
BOOSTER
1972 (157 m)
RIBs
REX/HIE
2001/2015
TT10
n_TOF
2001
TT2
East Area
PS
1959 (628 m)
CLEAR
2017
LINAC 4
2020
LEIR
2005 (78 m)
LINAC 3
Ions
1994



U
H+

GANDALPH

Gothenburg **AN**ion **D**etector for **A**ffinity measurements by **L**aser **PH**otodetachment



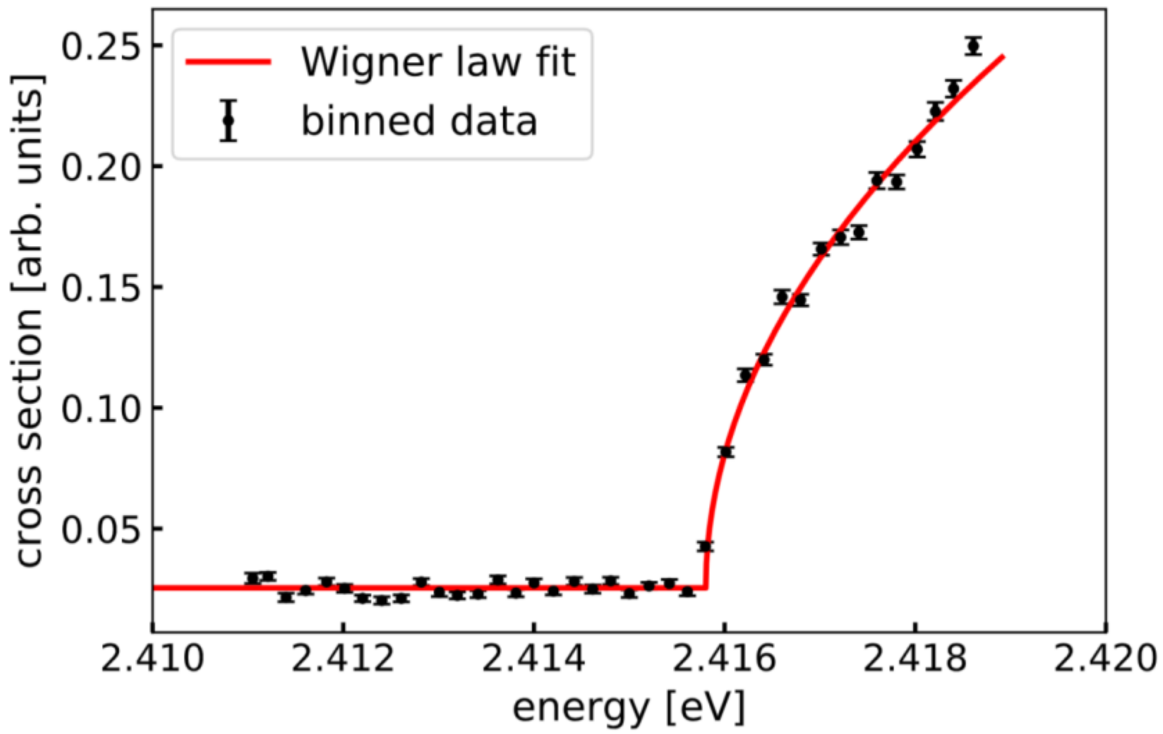
For each laserpuls:

Signal:
0.01 atom

Background:
10^{14} photons

Drawing: Annie Ringvall -Moberg

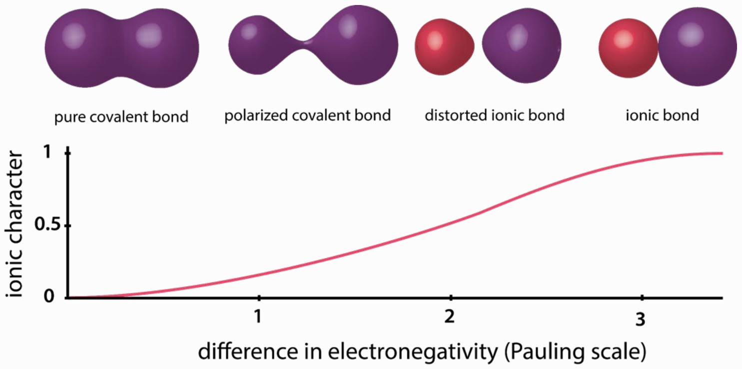
RESUTLS



Experiment: EA= 2.415 78 (5) eV

Method	Author	Year	EA
Experiment			2.41578(5)
CBS-DC-CCSDT(Q)+Breit+QED			2.414(16)
MCDHF+SE corr.	Chang et al	2010	2.38(2)
MCDHF	Zhao et al	2012	2.416
DC-CCSD(T)+Breit+QED	Broschevsky et al	2015	2.412
MCDHF+Extrap.+Breit+QED	Si and Fischer	2018	2.3729(46)
CBS-DC-CCSD(T)+Gaunt+QED	Finney and Peterson	2019	2.423(13)

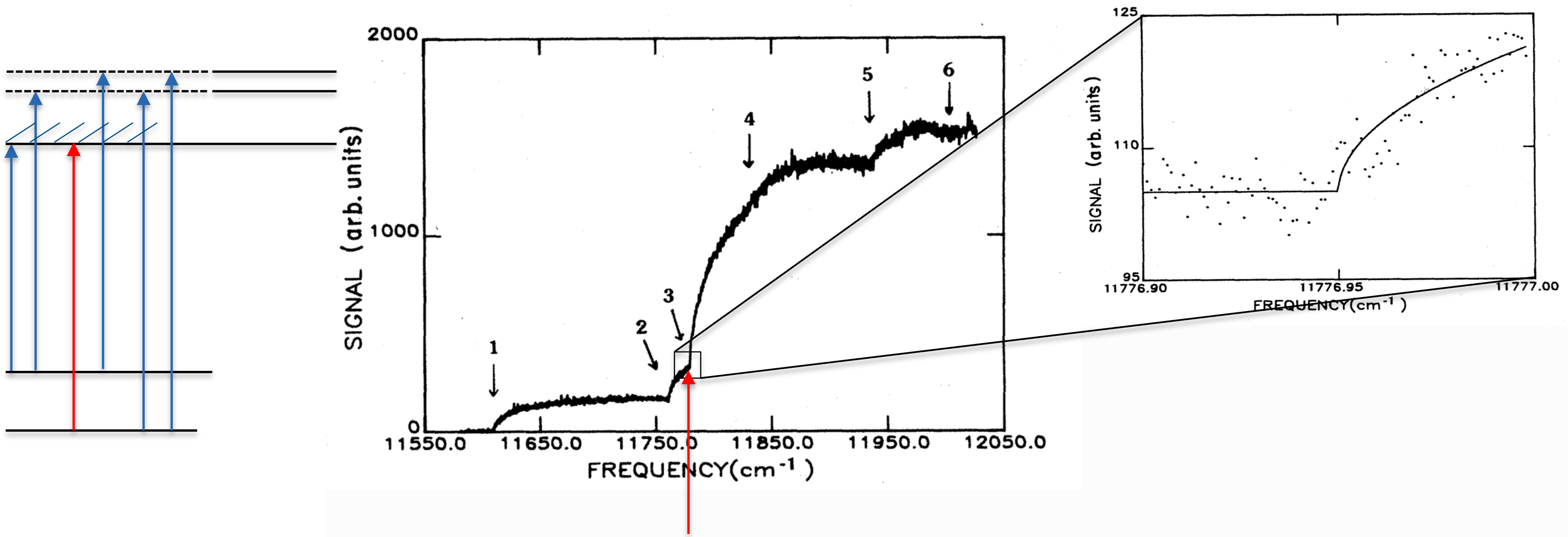
Property	Definition	Value
Electron affinity	EA	$2.415\,78(5)\,\mathrm{eV}$
Ionization energy	IE	$9.317\,51(8)\,\mathrm{eV}$[20]
Electronegativity	$\chi_M = \frac{IP+EA}{2}$	$5.866\,65\,\mathrm{eV}$
Hardness	$\eta = IE - EA$	$6.901\,72(13)\,\mathrm{eV}$
Softness	$S = \frac{1}{\eta}$	$0.144\,89(2)\,\mathrm{eV}^{-1}$
Electrophilicity	$\omega = \frac{\chi^2}{2\eta}$	$2.493\,41(8)\,\mathrm{eV}$



The At-H molecule should be called **astatine hydride** (not hydrogen astatide)

Leimbach *et al.* Nature Communications, 11 (2020) 3824

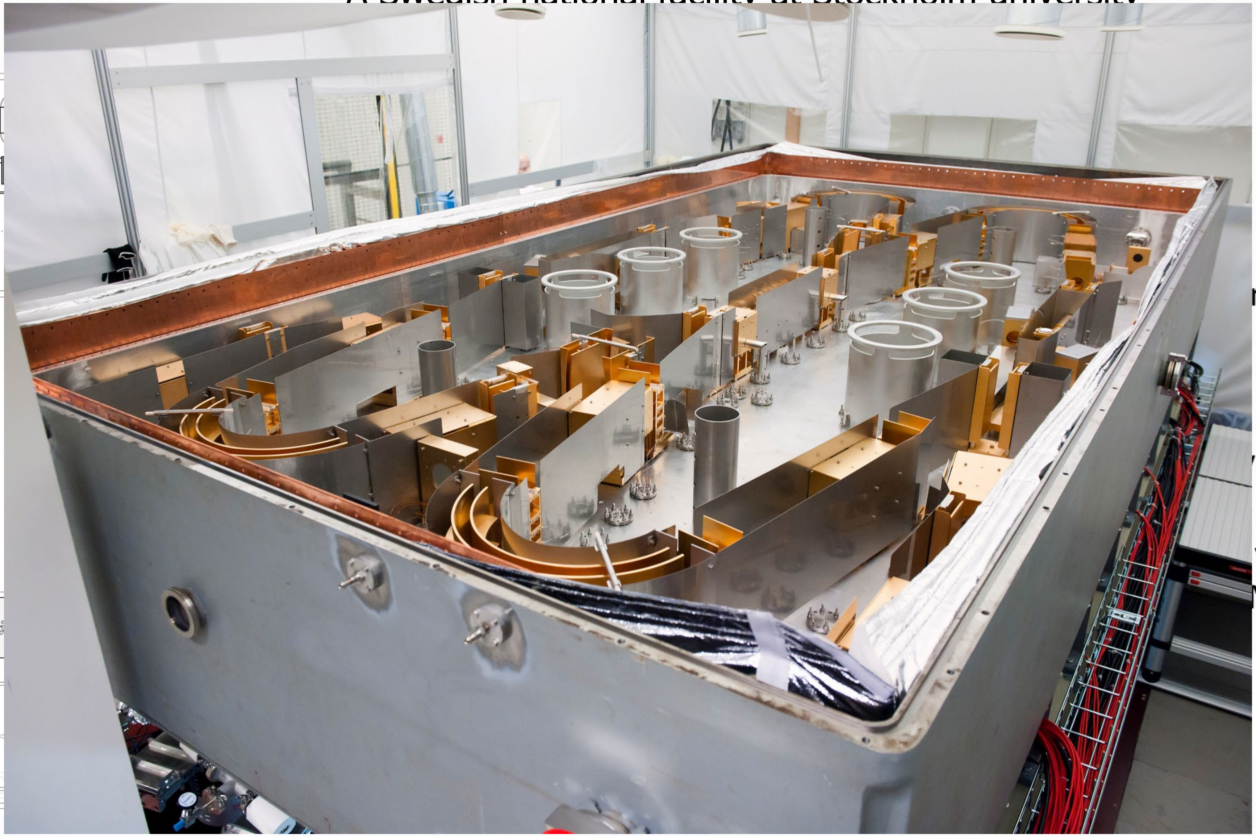
Precision measurement of the EA of O^-



Neumark, D. M., et al. Physical Review A 32.3 (1985): 1890

DESIREE – Double Electrostatic Ion Ring Experiment

A Swedish national facility at Stockholm university



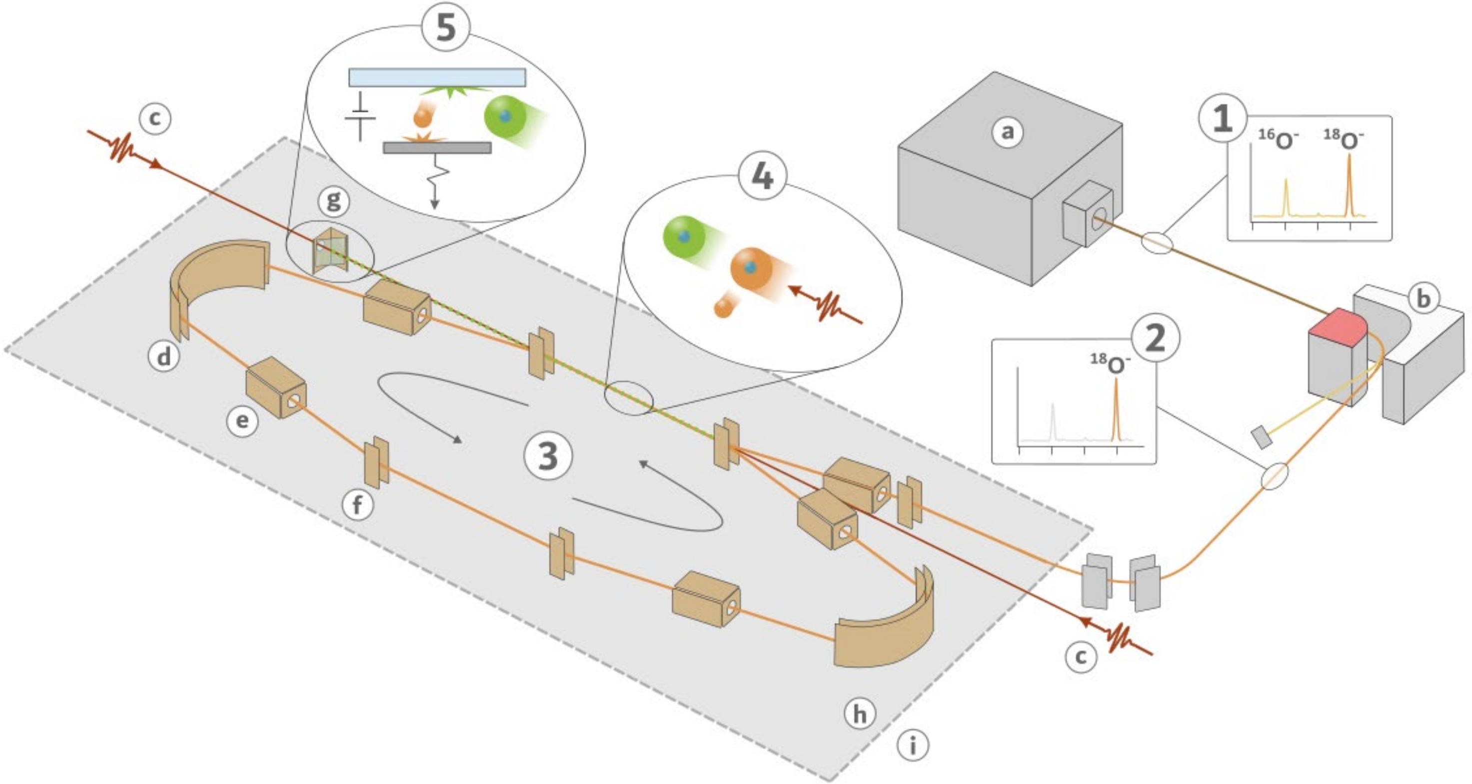
nds amu

' - keV

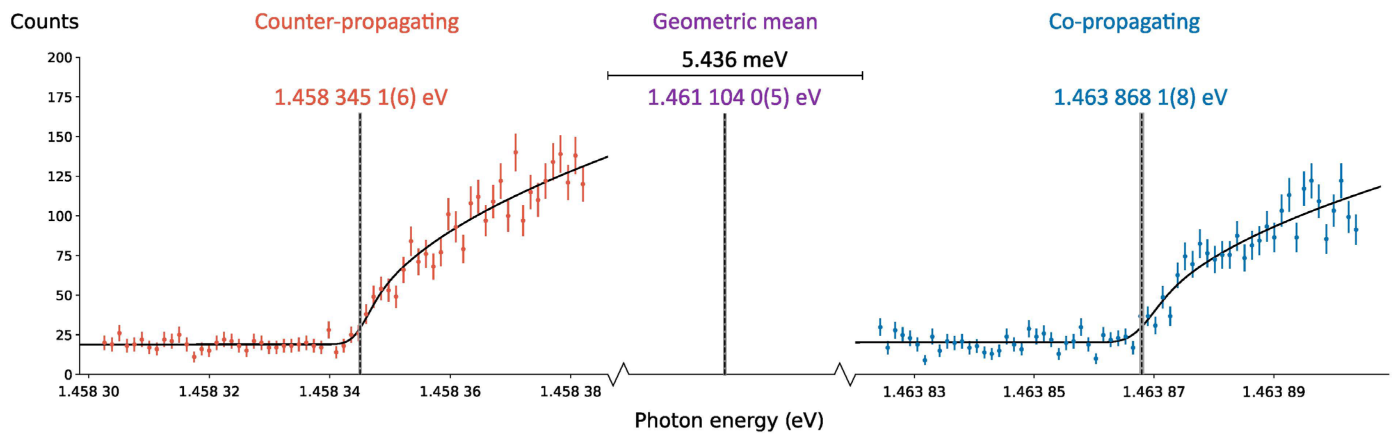
years

MEURO

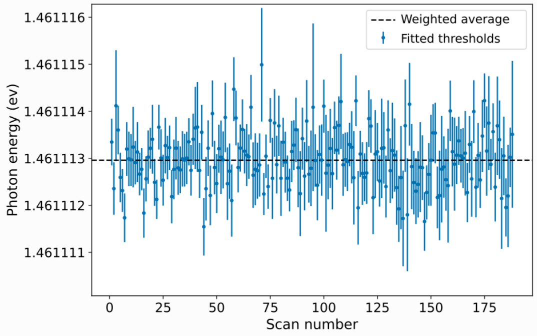
→ ***Physics at conditions of the interstellar media***

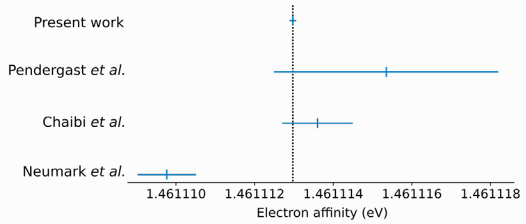


5
c
g
4
a
1
$^{16}O^-$
$^{18}O^-$
b
2
$^{18}O^-$
d
e
3
f
c
h
i



$$\sqrt{E^p_{EA}E^a_{EA}} = \sqrt{\frac{1+v/c}{\sqrt{1-v^2/c^2}}E_{EA}\frac{1-v/c}{\sqrt{1-v^2/c^2}}E_{EA}} = \sqrt{E_{EA}E_{EA}} = E_{EA}$$





Final result: E_{EA} = 1.461 112 972 (87) eV

Kristiansson, *et al.* Nature Communications **13** (2022) 5906

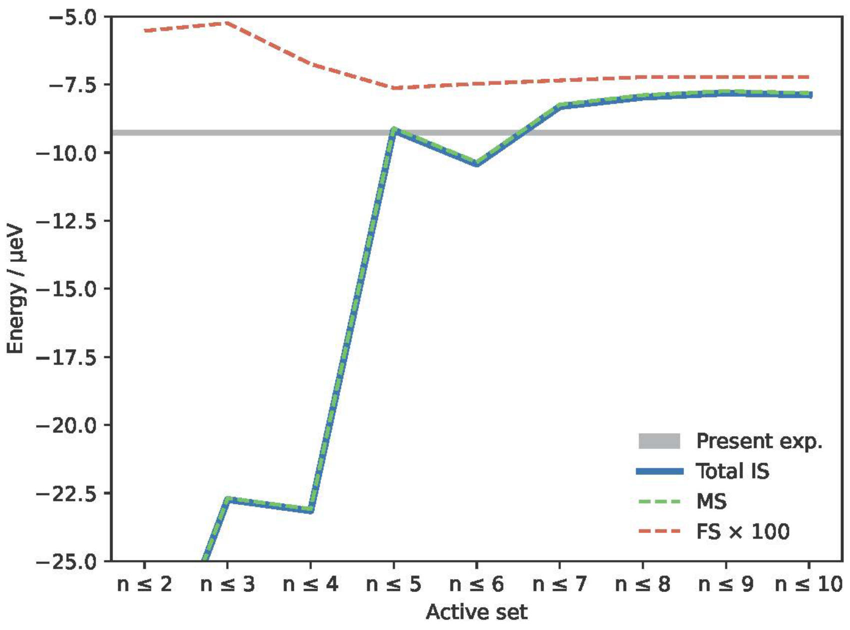
$^{18\text{-}16}$O isotope shift

E_{EA} (^{16}O)= 1.461 112 972 (87) eV

E_{EA} (^{18}O)= 1.461 103 706 (67) eV

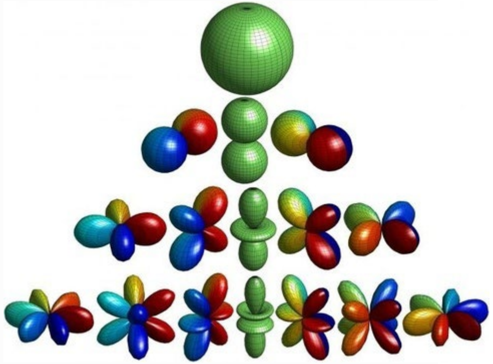
IS **= -0.000 009 267(11) eV**

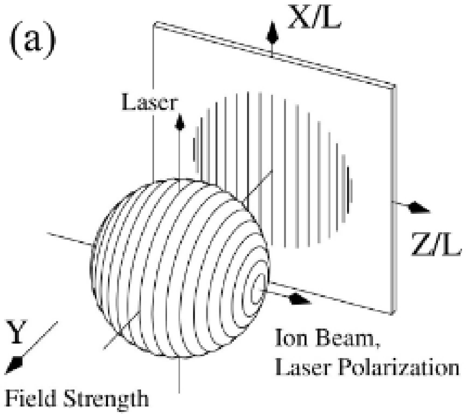
Multi-configurational Dirac-Hartree-Fock (MCDHF) and relativistic configuration-interaction (RCI) methods, as implemented in thecurrent development version of GRASP2018 (Jon Grumer)

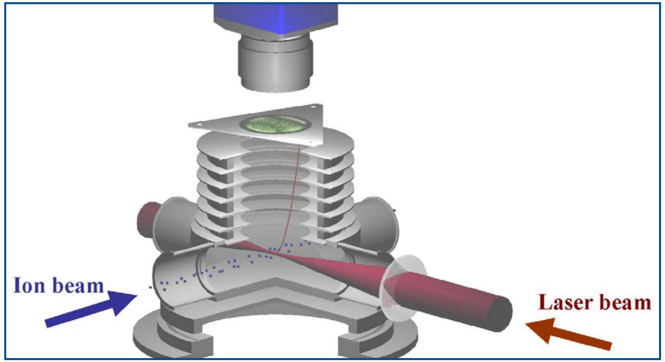


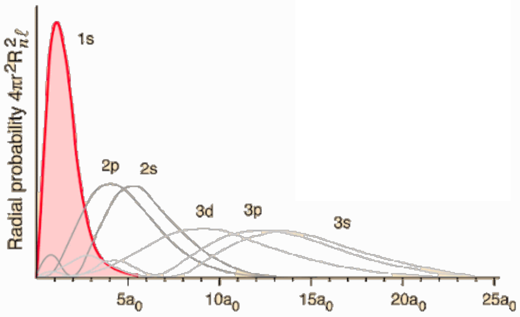
New experimental value	-9.27(0.09) μeV
Previous IS experimental value: C. Blondel, Physical Review A 64, 052504 (2001).	-9.2(2.2) μeV
New theoretical value:	-7.884 μeV
Previous Theoretical value: Godefroid and C. F. Fischer, Phys. Rev. A 60, R2637 (1999).	-7.104 μeV

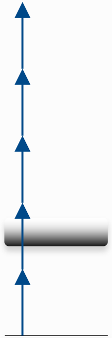
Probing wavefunctions: Velocity map imaging (VMI)

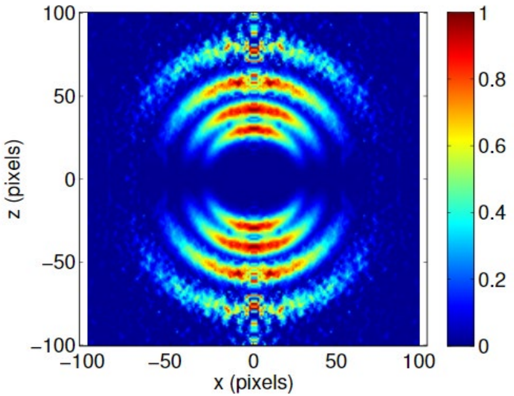




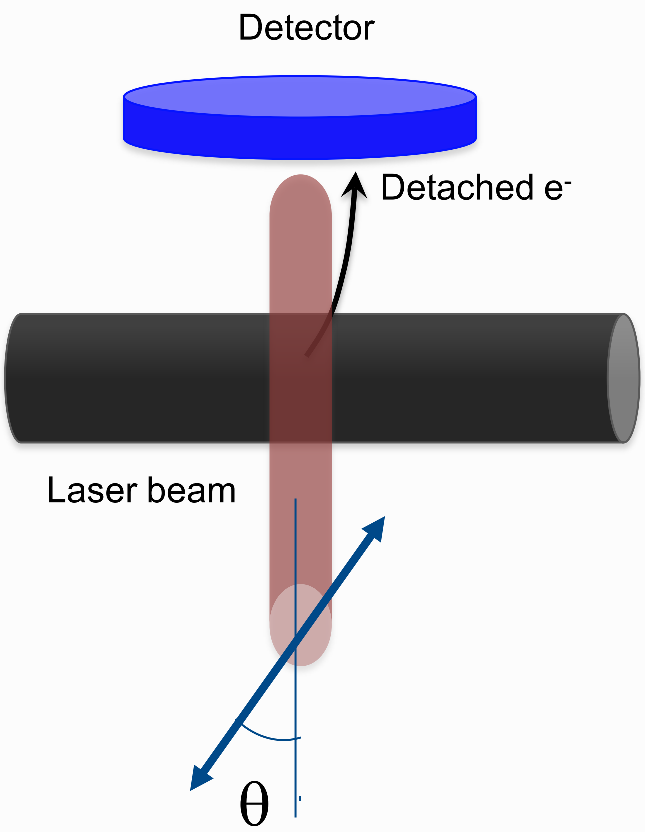


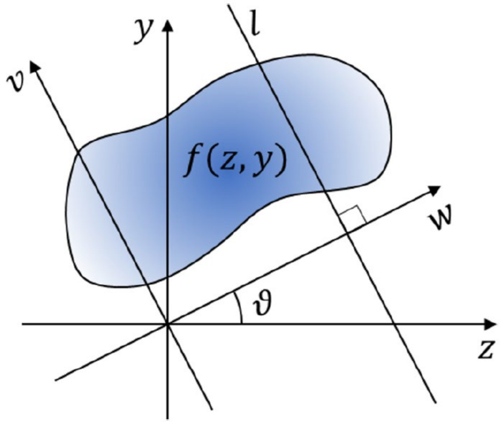


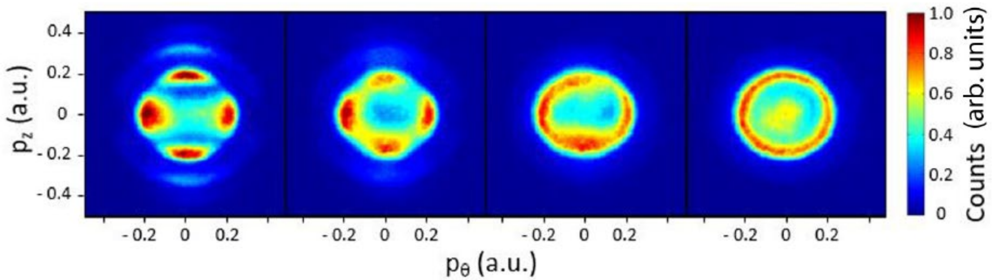




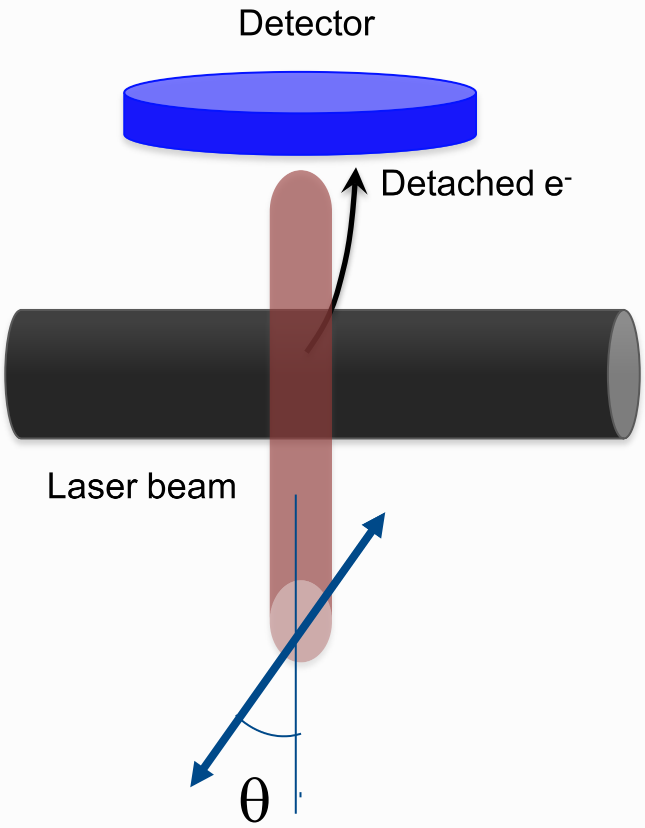
Optical tomography

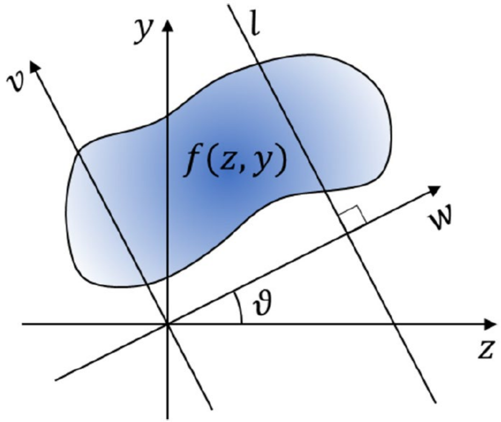


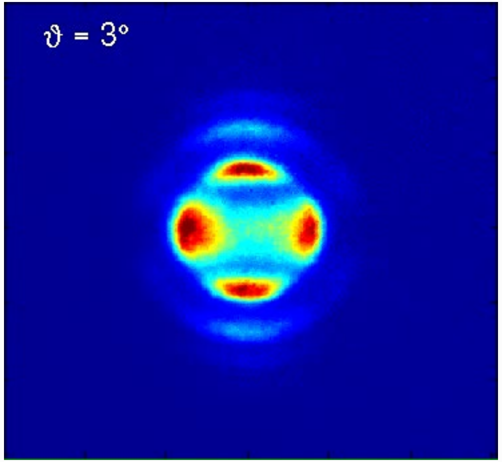


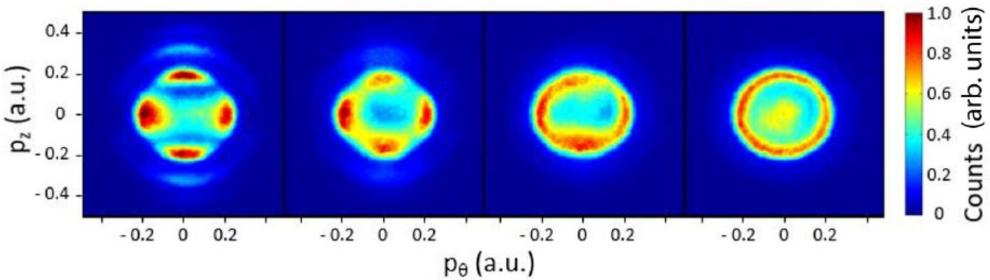


Optical tomography

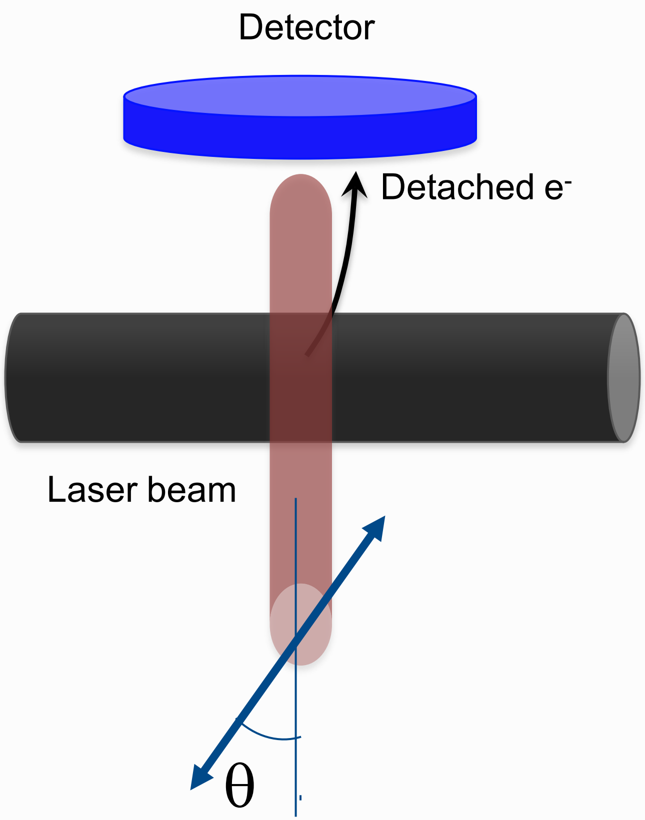


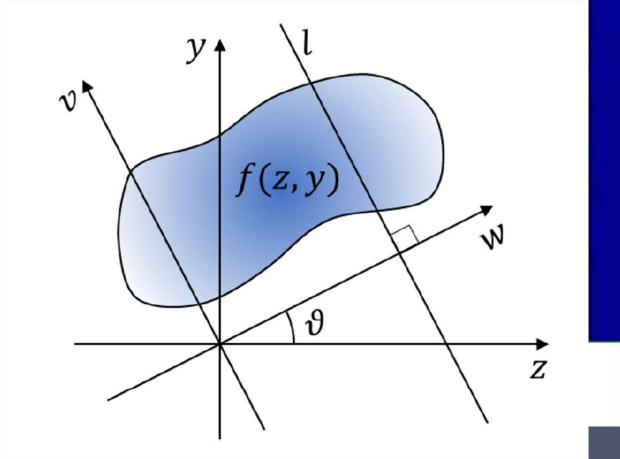


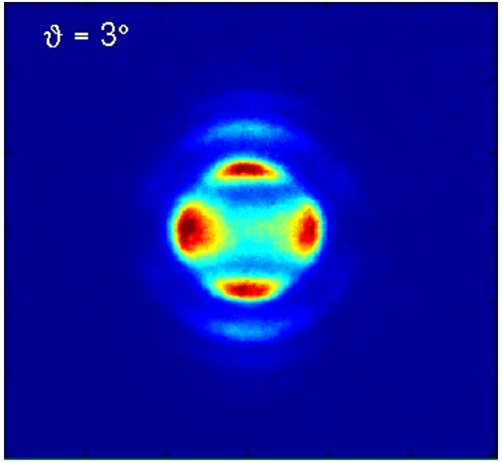


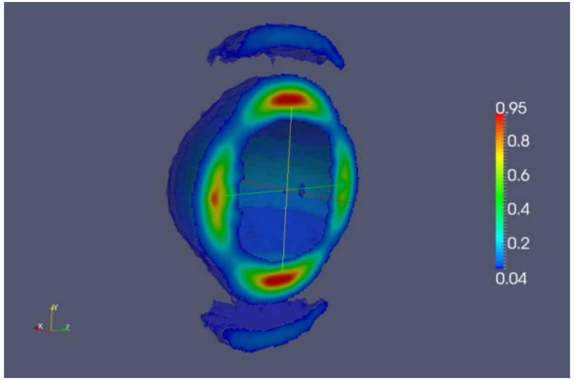


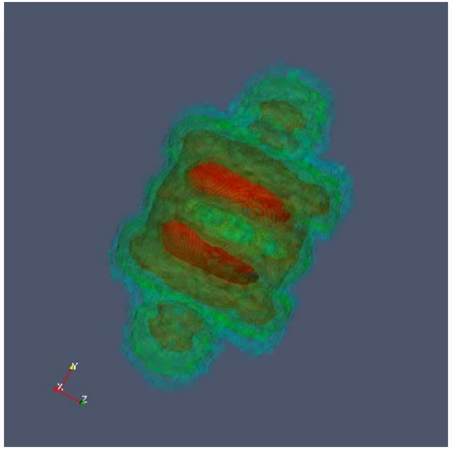
Optical tomography





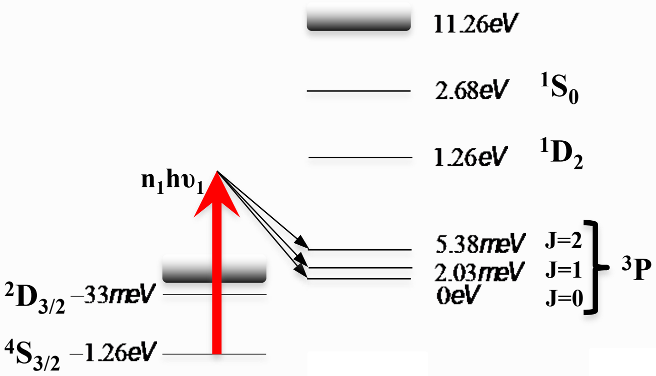


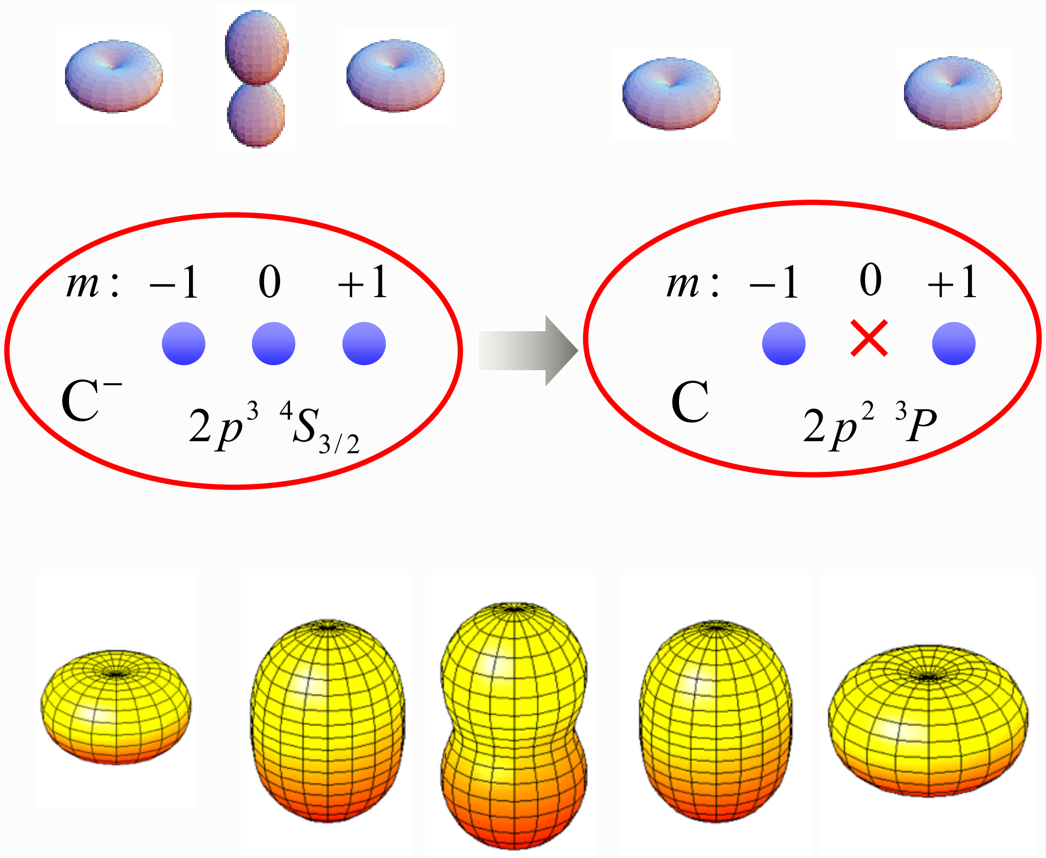


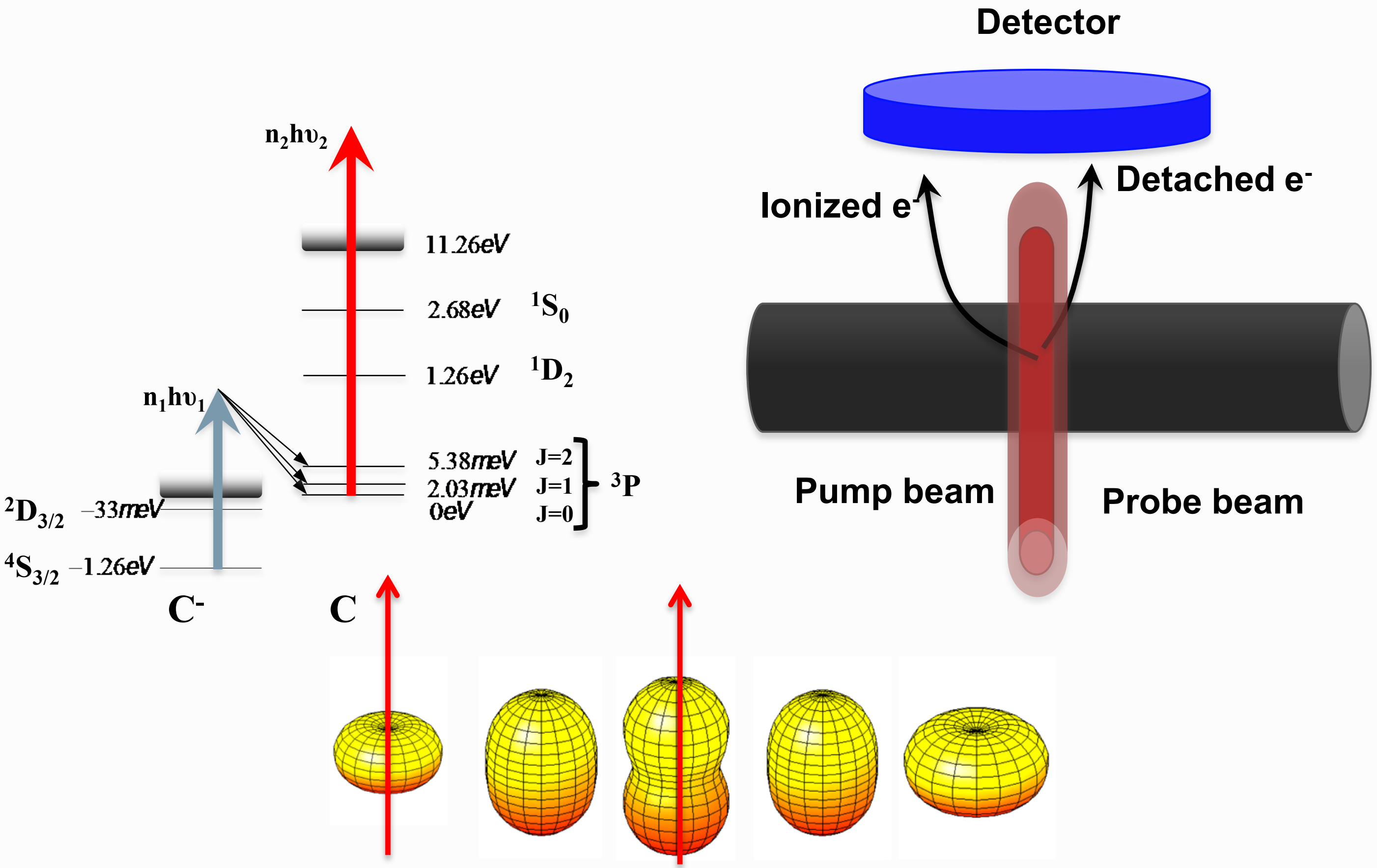


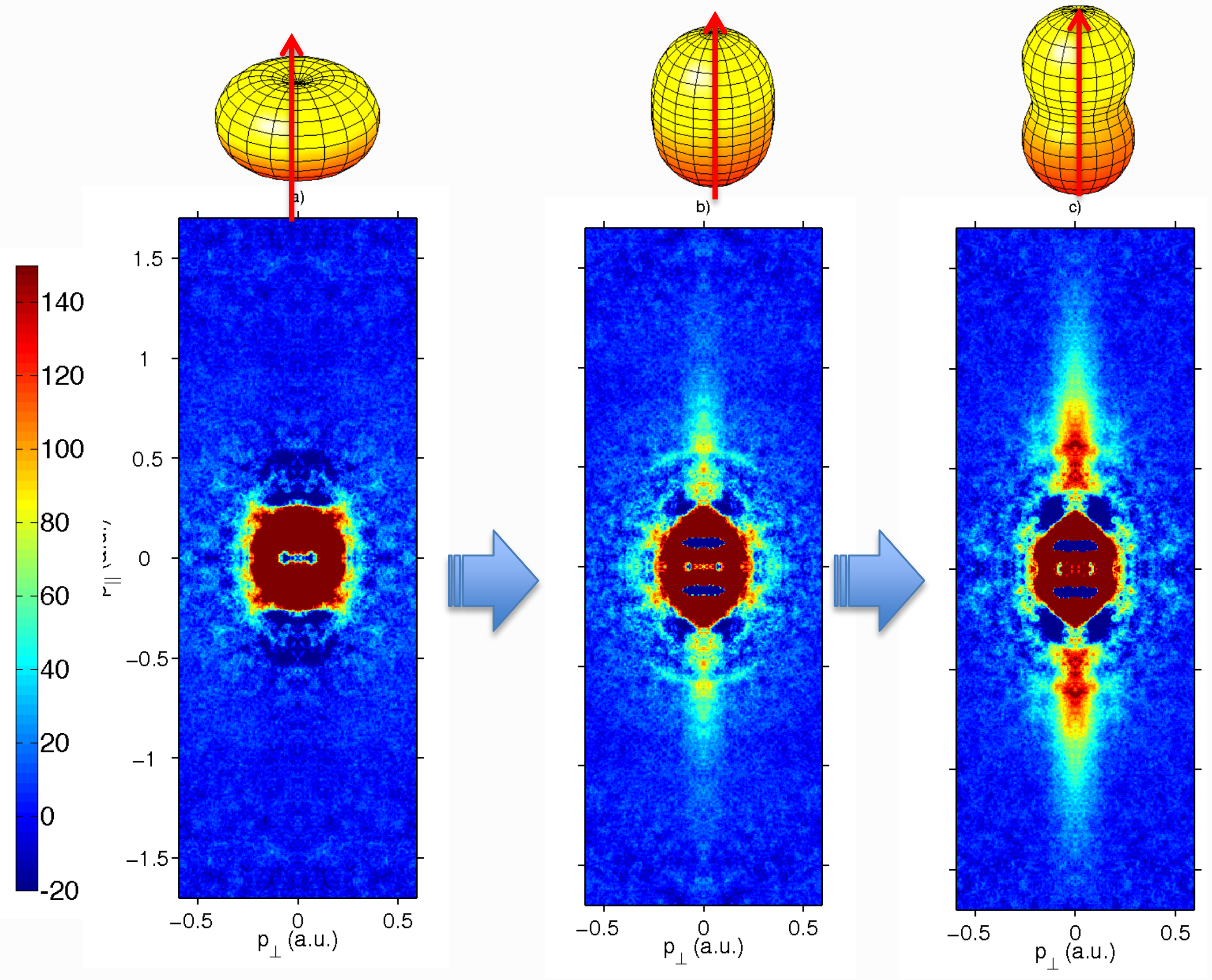
Eklund *et al.* PRA 102 023114 (2020)

Photodetachment in a strong field:

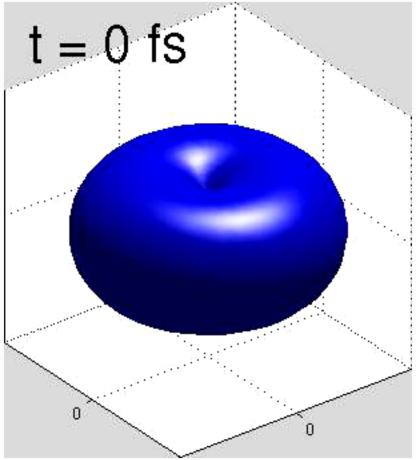


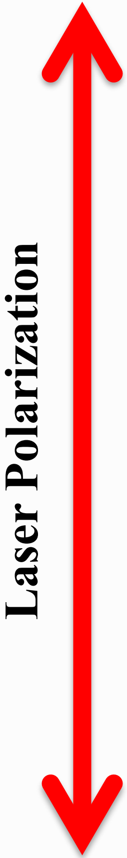


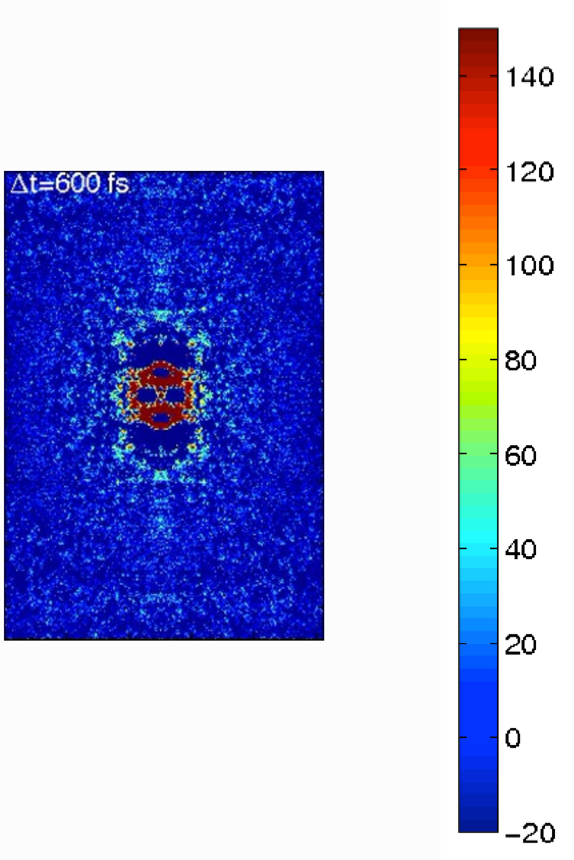

$n_2h\upsilon_2$
11.26eV
2.68eV $^1S_0$
1.26eV $^1D_2$
$n_1h\upsilon_1$
5.38meV J=2
2.03meV J=1
0eV J=0
^3P
$^2D_{3/2}$ −33meV
$^4S_{3/2}$ −1.26eV
C^-
C
Detector
Ionized e^-
Detached e^-
Pump beam
Probe beam



a)
b)
c)
140
120
100
80
60
40
20
0
-20
1.5
1
0.5
0
−0.5
−1
−1.5
−0.5
0
0.5
$p_\perp$ (a.u.)







Hultgren, Mikael Eklund, Dag Hanstorp, and Igor Yu. Kiyan,
Phys. Rev. A 87, (2013) 031404.

Detection of photoemitted electrons

$X^- + h\nu \rightarrow X + e^-$

Energy → structure of the ion

Angular distrubution → relative phases of emitted electron waves the symmetry of the negative ion

$$\frac{d\sigma}{d\Omega} = \left[\frac{\sigma}{4\pi}\right][1+\beta P_2(\cos\theta)]$$

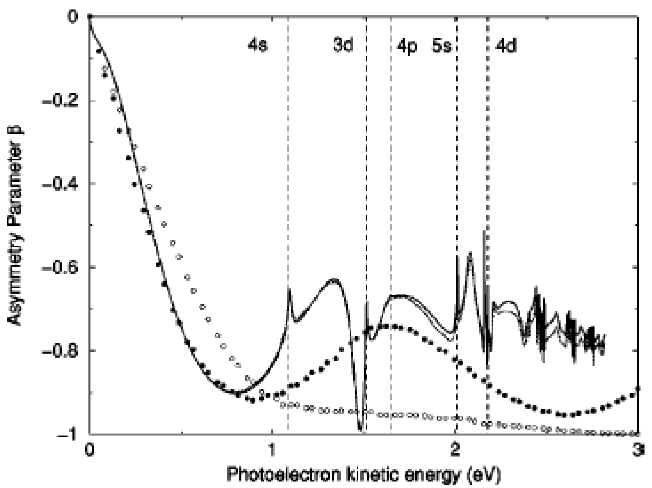
$$P_2(\cos\theta)=(3\cos^2\theta-1)/2,$$

$$-1 < \beta < 2$$

$\beta = -1$ $\sin^2(\theta)$

$\beta = 0$ isotropic

$\beta = 2$ $\cos^2(\theta)$



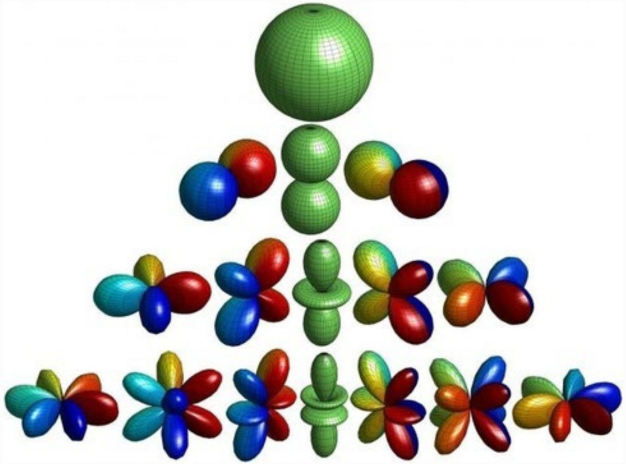
Photodetachment of $Na^- + h\nu \rightarrow Na(3p) + e$

Liu and Starace PRA, 59 (1999) 3643

$X^-(ns) + h\nu \rightarrow X + e^- (\varepsilon p)$ $(\beta = 2)$

$X^-(np) + h\nu \rightarrow X + e^- (\varepsilon s)$ $(\beta = 0)$

$\rightarrow X + e^- (\varepsilon d)$ $(\beta = +)$



Two waves → Interference

Cooper and Zare, J. Chem. Phys. 48 (1968) 942:

$$\beta = \frac{l(l-1)R_{l-1}^2 + (l+1)(l+2)R_{l+1}^2 - 6l(l+1)R_{l+1}R_{l-1}\cos(\delta_{l+1} - \delta_{l-1})}{(2l+1)[lR_{l-1}^2 + (l+1)R_{l+1}^2]},$$

$$\beta = \frac{l(l-1)R_{l-1}^2 + (l+1)(l+2)R_{l+1}^2 - 6l(l+1)R_{l+1}R_{l-1}\cos(\delta_{l+1}-\delta_{l-1})}{(2l+1)[lR_{l-1}^2 + (l+1)R_{l+1}^2]} ,$$

Photodetachment of P^-

Windelius *et al.* Rev. A. **103** (2021) 033108.

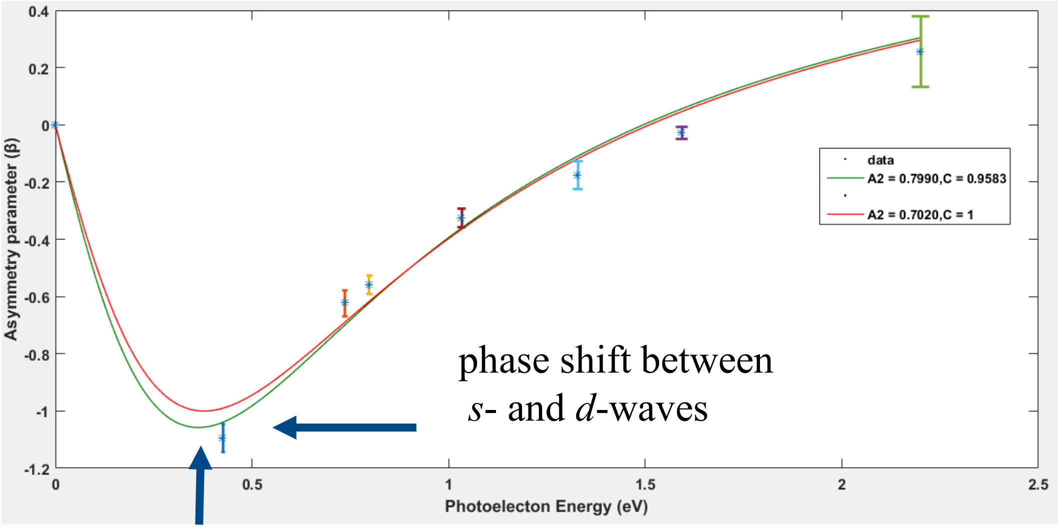
Wigner law:

$$R_{l\pm1} \sim k^{l\pm1}$$

$$R_2/R_0 = \frac{k^{l+1}}{k^{l-1}} = k^2 = A_2\varepsilon$$

$$c = (\delta_{l+1} - \delta_{l-1})$$

$$\beta = 2A_2\varepsilon(A_2\varepsilon - 2c)/(1 + 2A_2^2\varepsilon^2)$$



Amplitude of
s- and *d*-waves are equal

THE JOURNAL OF CHEMICAL PHYSICS **141**, 124312 (2014)

Photoelectron angular distributions for states of any mixed character: An experiment-friendly model for atomic, molecular, and cluster anions

Dmitry Khuseynov, Christopher C. Blackstone, Lori M. Culberson,[a)] and Andrei Sanov[b)]
Department of Chemistry and Biochemistry, University of Arizona, Tucson, Arizona 85721, USA

(Received 25 March 2014; accepted 11 September 2014; published online 30 September 2014)

We present a model for laboratory-frame photoelectron angular distributions in direct photodetachment from (in principle) any molecular orbital using linearly polarized light. A transparent mathematical approach is used to generalize the Cooper-Zare central-potential model to anionic states of any mixed character. In the limit of atomic-anion photodetachment, the model reproduces the Cooper-Zare formula. In the case of an initial orbital described as a superposition of s and p-type functions, the model yields the previously obtained s-p mixing formula. The formalism is further advanced using the Hanstorp approximation, whereas the relative scaling of the partial-wave cross-sections is assumed to follow the Wigner threshold law. The resulting model describes the energy dependence of photoelectron anisotropy for any atomic, molecular, or cluster anions, usually without requiring a direct calculation of the transition dipole matrix elements. As a benchmark case, we apply the p-d variant of the model to the experimental results for NO^- photodetachment and show that the observed anisotropy trend is described well using physically meaningful values of the model parameters. Overall, the presented formalism delivers insight into the photodetachment process and affords a new quantitative strategy for analyzing the photoelectron angular distributions and characterizing mixed-character molecular orbitals using photoelectron imaging spectroscopy of negative ions. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4896241]

C. Examples of binary mixing curves

As discussed previously,[3,24] the s-p mixing equation with the Hanstorp coefficients, Eq. (33), can be rearranged as follows:

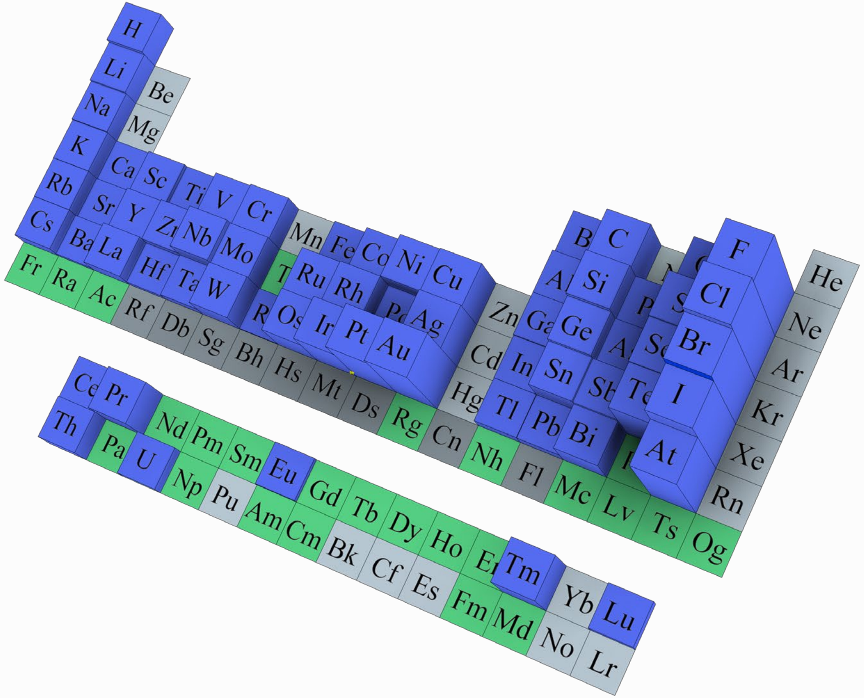
$$\beta_{sp}(\varepsilon) = \frac{2Z_1(A_1\varepsilon) + 2(A_1\varepsilon)^2 - 4(A_1\varepsilon)\cos\delta_{2,0}}{Z_1(A_1\varepsilon) + 1 + 2(A_1\varepsilon)^2}, \qquad (40)$$

What do we know about negative ions?

Many EAs determined

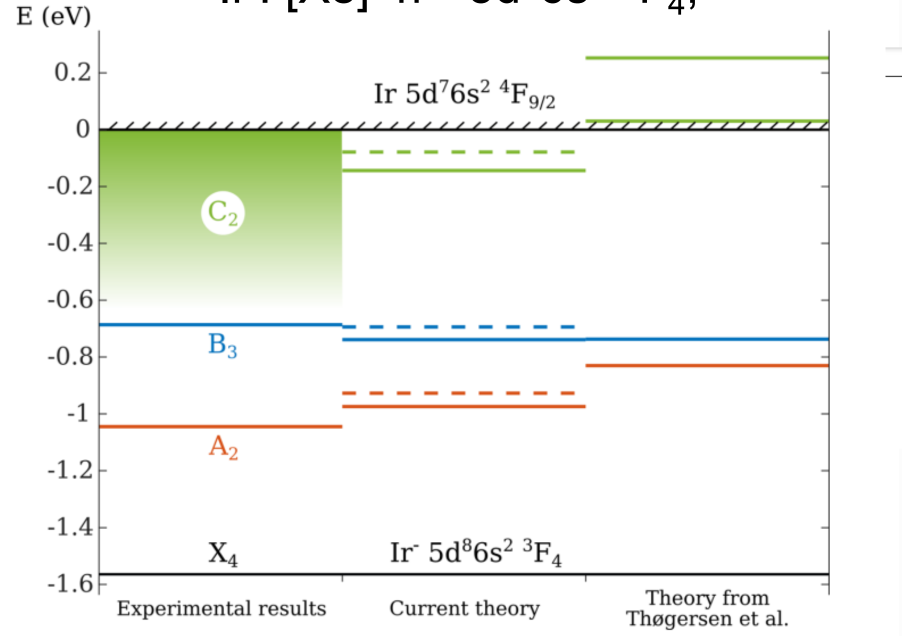
Five elements with allowed transitions found

Some lifetimes of metastable states have been determined



Essentially no traditional optical spectroscopy!

Ir⁻: [Xe] $4f^{14}\,5d^{8}6s^{2}\ {}^{3}F_{4}$,

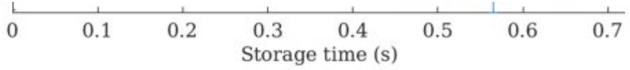


PHYSICAL REVIEW A **103**, 062806 (2021)

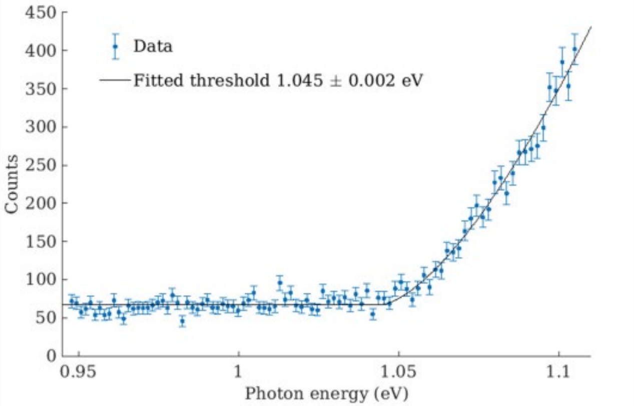
Experimental and theoretical studies of excited states in Ir⁻

M. K. Kristiansson,[1,*] S. Schiffmann,[2,3] J. Grumer,[4] J. Karls,[5] N. de Ruette,[1,6] G. Eklund,[1] V. Ideböhn,[5] N. D. Gibson,[7] T. Brage,[2] H. Zettergren,[1] D. Hanstorp,[5] and H. T. Schmidt[1]
[1]*Department of Physics, Stockholm University, AlbaNova, SE-106 91 Stockholm, Sweden*
[2]*Department of Physics, Division of Mathematical Physics, Lund University, Box 118, SE-221 00 Lund, Sweden*
[3]*Spectroscopy, Quantum Chemistry and Atmospheric Remote Sensing (SQUARES), CP160/09, Université Libre de Bruxelles (ULB), B 1050 Bruxelles, Belgium*
[4]*Department of Physics and Astronomy, Theoretical Astrophysics, Uppsala University, Box 516, SE-751 20 Uppsala, Sweden*
[5]*Department of Physics, University of Gothenburg, SE-412 96 Gothenburg, Sweden*
[6]*European Spallation Source ERIC (ESS), SE-221 00 Lund, Sweden*
[7]*Department of Physics and Astronomy, Denison University, Granville, Ohio 43023, USA*

(Received 13 February 2021; accepted 20 May 2021; published 10 June 2021)



State	τ_{MCDHF}	τ_{expt}
A_2	> 2500 s	> 1200 s
B_3	112(11) ms	133(10) ms
C_2	161(8) ms	172(35) ms



PHYSICAL REVIEW A **103**, 062806 (2021)

Experimental and theoretical studies of excited states in Ir^-

M. K. Kristiansson,[1,*] S. Schiffmann,[2,3] J. Grumer,[4] J. Karls,[5] N. de Ruette,[1,6] G. Eklund,[1] V. Ideböhn,[5]
N. D. Gibson,[7] T. Brage,[2] H. Zettergren,[1] D. Hanstorp,[5] and H. T. Schmidt[1]
[1] *Department of Physics, Stockholm University, AlbaNova, SE-106 91 Stockholm, Sweden*
[2] *Department of Physics, Division of Mathematical Physics, Lund University, Box 118, SE-221 00 Lund, Sweden*
[3] *Spectroscopy, Quantum Chemistry and Atmospheric Remote Sensing (SQUARES), CP160/09, Université Libre de Bruxelles (ULB), B 1050 Bruxelles, Belgium*
[4] *Department of Physics and Astronomy, Theoretical Astrophysics, Uppsala University, Box 516, SE-751 20 Uppsala, Sweden*
[5] *Department of Physics, University of Gothenburg, SE-412 96 Gothenburg, Sweden*
[6] *European Spallation Source ERIC (ESS), SE-221 00 Lund, Sweden*
[7] *Department of Physics and Astronomy, Denison University, Granville, Ohio 43023, USA*

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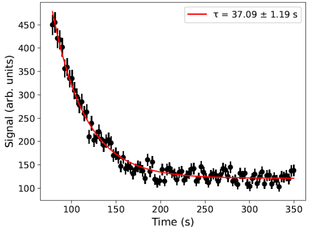
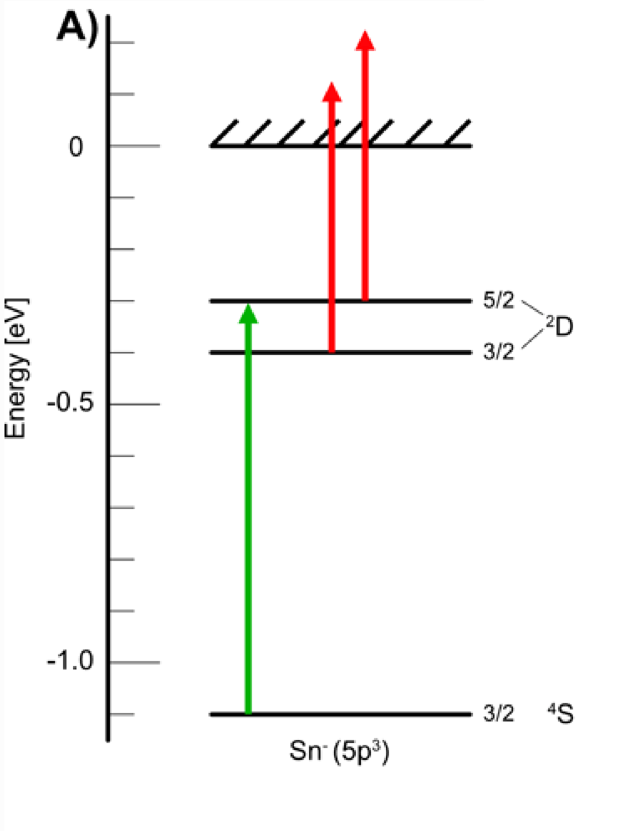
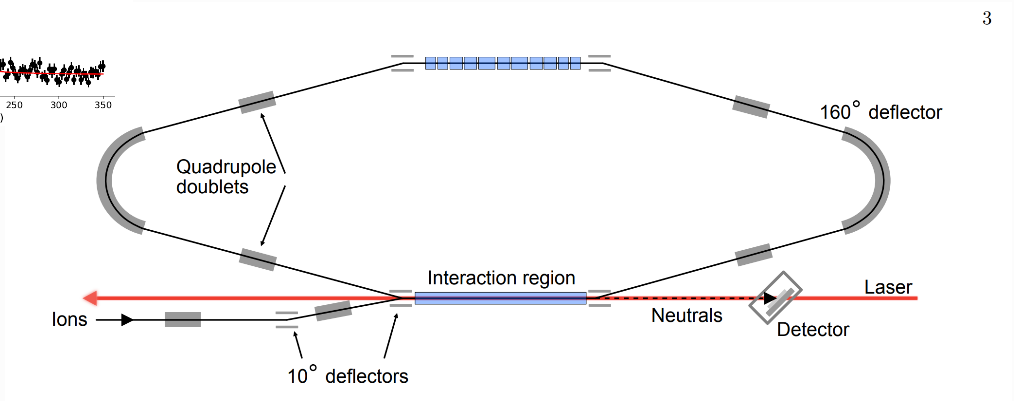
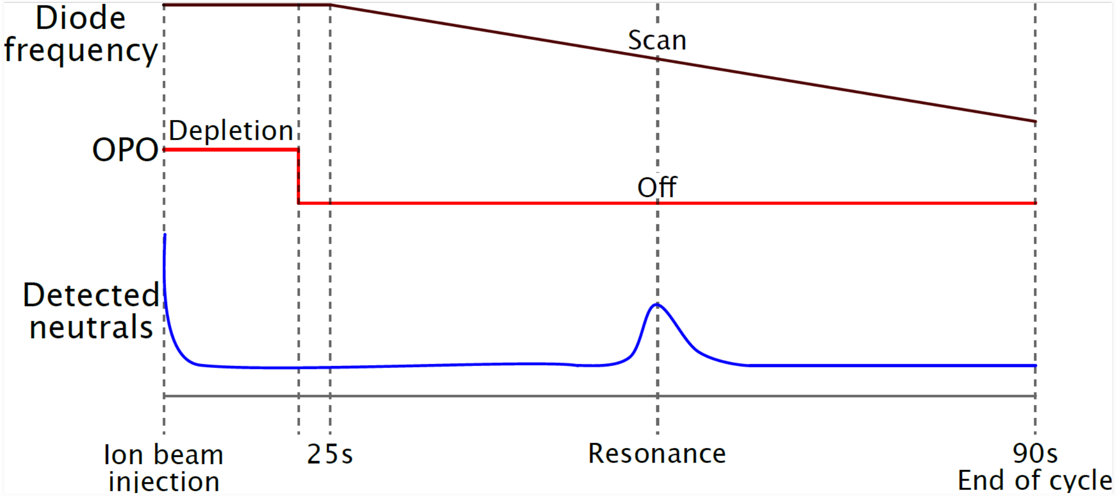
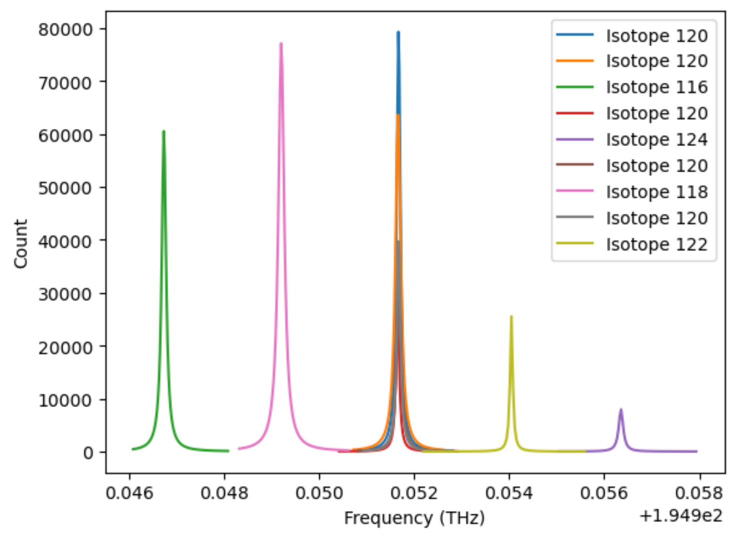
Sn^-

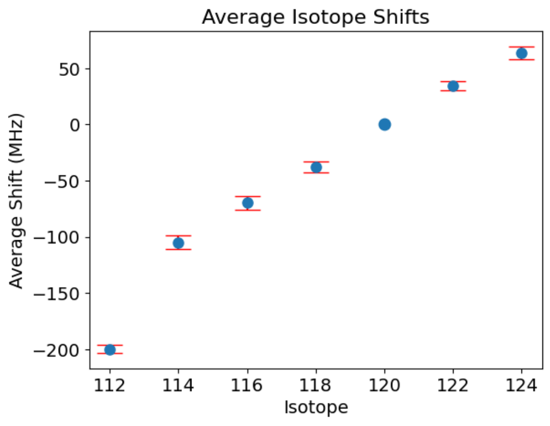

τ = 37.09 ± 1.19 s
Signal (arb. units)
Time (s)
100
150
200
250
300
350
400
450

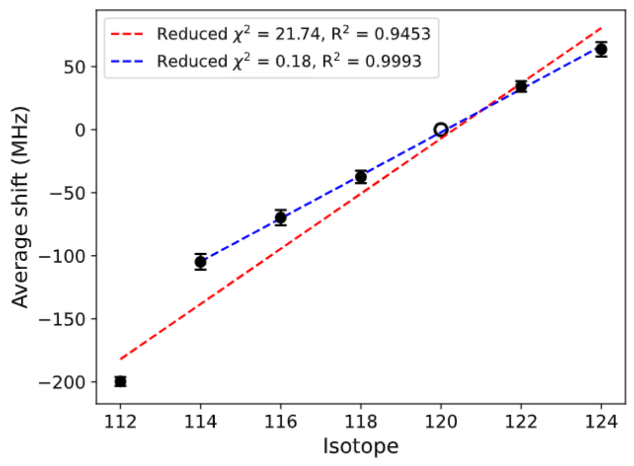

A)
Energy [eV]
0
-0.5
-1.0
5/2
3/2
^{2}D
3/2
^{4}S
Sn$^-$ (5p^3)


3
160° deflector
Quadrupole doublets
Interaction region
Laser
Ions
Neutrals
Detector
10° deflectors


Diode frequency
Scan
OPO
Depletion
Off
Detected neutrals
Ion beam injection
25s
Resonance
90s
End of cycle


Isotope 120
Isotope 120
Isotope 116
Isotope 120
Isotope 124
Isotope 120
Isotope 118
Isotope 120
Isotope 122
Count
Frequency (THz)
+1.949e2


Average Isotope Shifts
Average Shift (MHz)
Isotope


Reduced χ^2 = 21.74, R^2 = 0.9453
Reduced χ^2 = 0.18, R^2 = 0.9993
Average shift (MHz)
Isotope

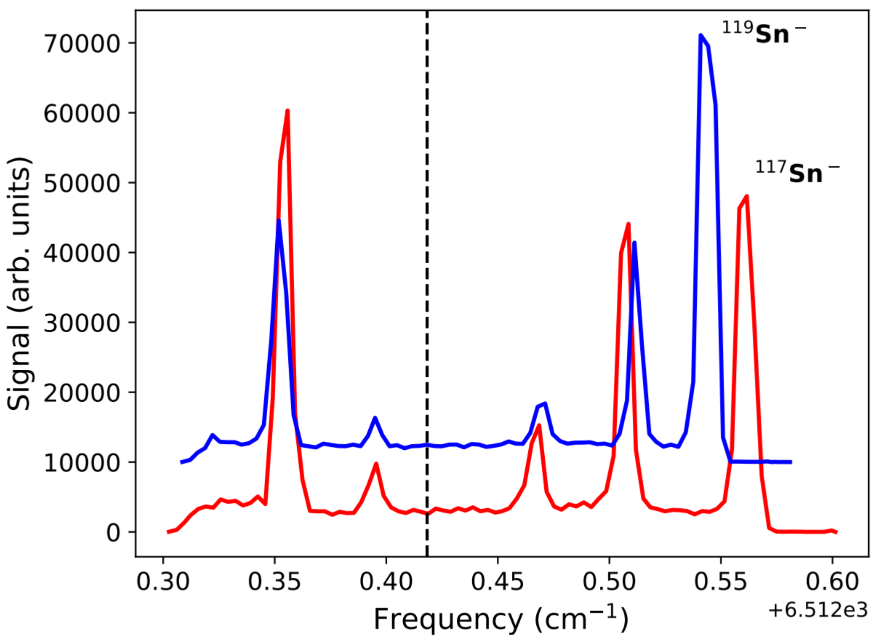
$$\Delta\nu^{A,A'} = \nu^{A'} - \nu^{A} = k_{\rm MS}\frac{m_{A'} - m_A}{m_{A'} m_A} + F\delta\langle r^2\rangle^{A,A'}$$

Transition	F	$F_{\rm exp.}$	$k_{\rm NMS}$	$k_{\rm SMS}$	$k_{\rm SMS,exp.}$	$k_{\rm MS}$	$k_{\rm MS,exp.}$
${}^4S_{3/2} \rightarrow {}^2D_{3/2}$	0.26	-	98.3	-181.3	-	-83.0	-
${}^4S_{3/2} \rightarrow {}^2D_{5/2}$	0.24	-0.03	107.5	-44.5	164.8	63.0	272.3

Theory made by A. Bondarev

[45] M. S. Safronova, M. G. Kozlov, W. R. Johnson, and D. Jiang, Phys. Rev. A 80, 012516 (2009).

Hyperfine structure



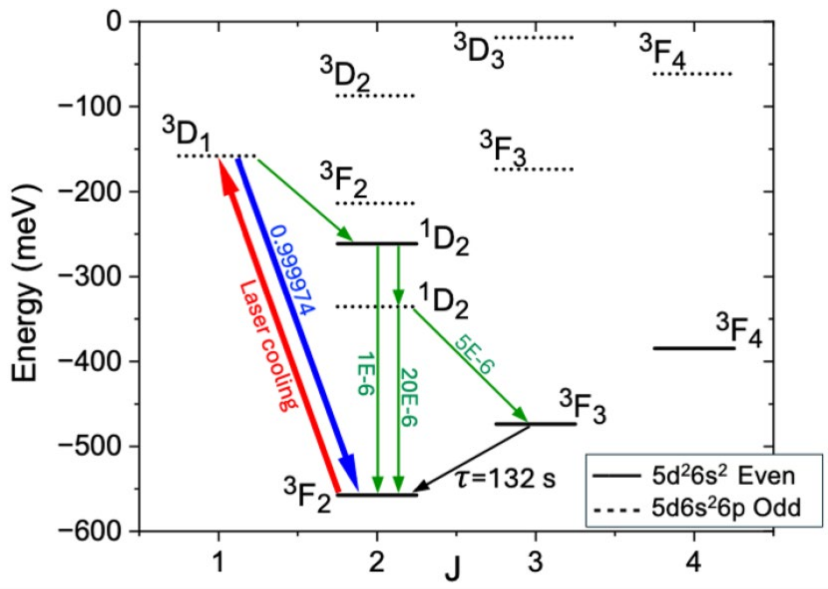
I = 1/2 for both ^{117}Sn and ^{119}Sn

→ Should have 4 HFS components

Magnetic moments for ^{117}Sn and ^{119}Sn are very similar

Forbidden transitions are not forbidden anymore!

La⁻



CI+all-order

[24] M. S. Safronova, M. G. Kozlov, W. R. Johnson, and D. Jiang, Phys. Rev. A **80**, 012516 (2009).

[25] C. Cheung, M. G. Kozlov, S. G. Porsev, M. S. Safronova, I. I. Tupitsyn, and A. I. Bondarev, Computer Physics Communications **308**, 109463 (2025).

TABLE I. Measured and calculated lifetimes of La^- excited states in seconds.

State	Present Experiment	Present Theory	O'Malley [14]	Cerchiari [11]
$^3F_3{}^e$	132(20)	131	132*	132
$^3F_4{}^e$	32(5)	135	134*	
Short-lived	0.22(3)			

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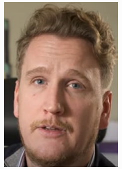
Aknowledgement









Next generation:



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