Vacuum Ultraviolet (VUV) Photoabsorption Spectroscopy with Laser Induced Plasmas

John T. Costello
School of Physical Sciences & NCPST, DCU

11th EMSLIBS 2021, Gijon, Spain, Nov 29, 2021.

Talk Outline

- DCU Laser Plasma & AMO Group
- Dual Laser Plasma Photoabsorption (DLPP) - The Idea
- Why Do (Short Wavelength) Photoabsorption?
- Laser Plasma Continua – History & Physical Origin
- DLPP – Some History
- Some Recent VUV/EUV DLPP Results on Atoms and Molecules
- "For What's Next" – Perspectives for X-VUV….
- Acknowledgements

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LP & AMO Physics Group at DCU (PIs)

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John Costello (LP Spectroscopy & Free Electron Lasers)

Emr. Eugene Kennedy (LP Spectroscopy & Synchrotrons)

Jean-Paul Mosnier (Synchrotrons)

Lampros Nikolopoulos (AMO Theory)

Paul van Kampen (Synchrotrons/ Physics Education)

Current Postdoctoral and PhD students:
Lazaros Varvarezos, James Campbell, Séamus Cummins, Stephen Durkan, Andrew Foremski, Ross McGarry, Adam Prior and Sadaf Syedah Zehra.

Recent PhD Graduates:
2021: Muhammad Bilal Alli, Hu Lu & Tejaswi Katravulapally
2020: Ben Delaney, Stephen Davitt & Lazaros Varvarezos,

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Current Projects:

1. VUV & EUV Photoabsorption via the Dual Laser Plasma Technique
2. UV/VUV LIBS (Steel, Pharma & Wind Turbine Blades (SC))
3. Photoionization of Atoms and Molecules in EUV FEL Fields
4. Ultrafast FEL Pump – EUV Probes of Atoms and Molecules
5. Photoionization of Small Molecular Ions at Synchrotrons (ETK)
6. Development of an Ultrafast Laser Spectroscopy Laboratory

References

1. ***Near-Threshold Two-Photon Double Ionization of Kr in the Vacuum Ultraviolet***, L Varvarezos et al , *Physical Review A* **103** Art. No. 022832 (2021)
2. ***Time-integrated and time-resolved VUV LIBS: a comparative study***, S S Zehra, J T Costello, P Nicolosi and P Hayden, Proceedings of SPIE, **10674**, 106741H (2018)
3. ***Clocking Auger electrons***, D C Haynes et al, *Nature Physics* **17** pp.512–518 (2021)
4. ***The 5d → 6p EUV photoabsorption spectra of Pb II and Bi III: evidence of excited states***, H Lu, L Varvarezos, M Bilal Alli, P Nicolosi, J T Costello and P Hayden, *J. Phys. B: At. Mol. Opt. Phys.* **53** 115001 (2020)
5. ***Evolution of L-shell photoabsorption of the molecular-ion series SiH^{n+} (n=1,2,3): Experimental and theoretical studies***, E T Kennedy *et al* P*hys, Rev. A* **97** 043410 (2018)
6. https://www.dcu.ie/research/ultrafast-spectroscopy / http://uf-dynamics.org

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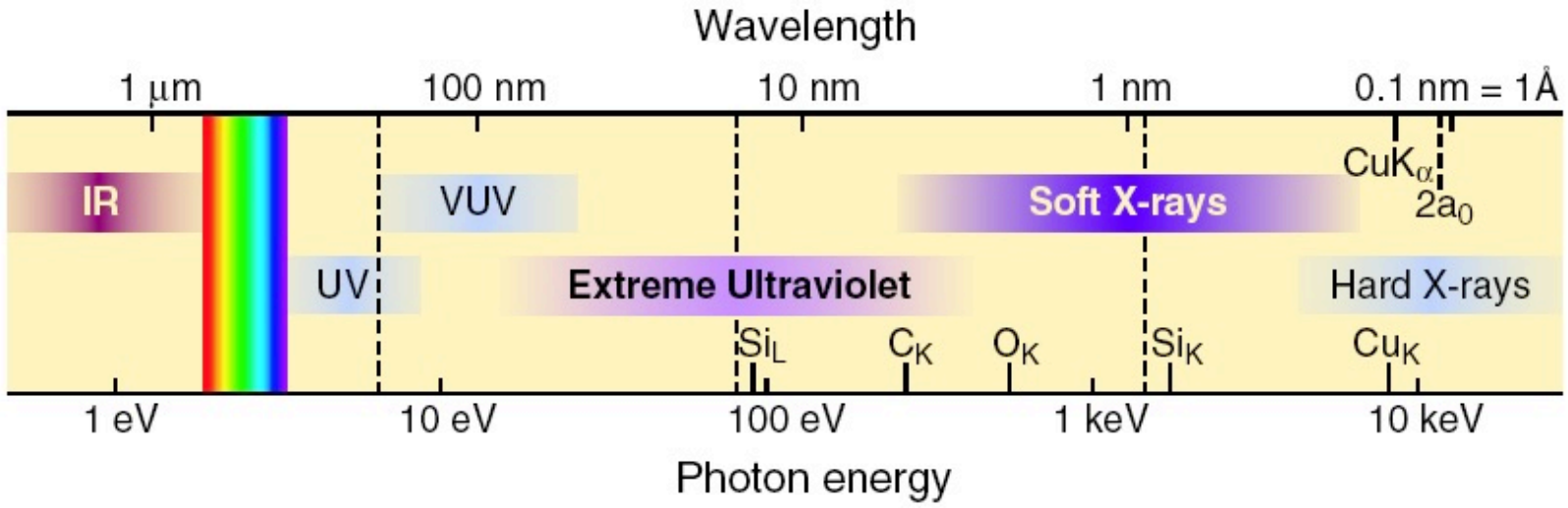
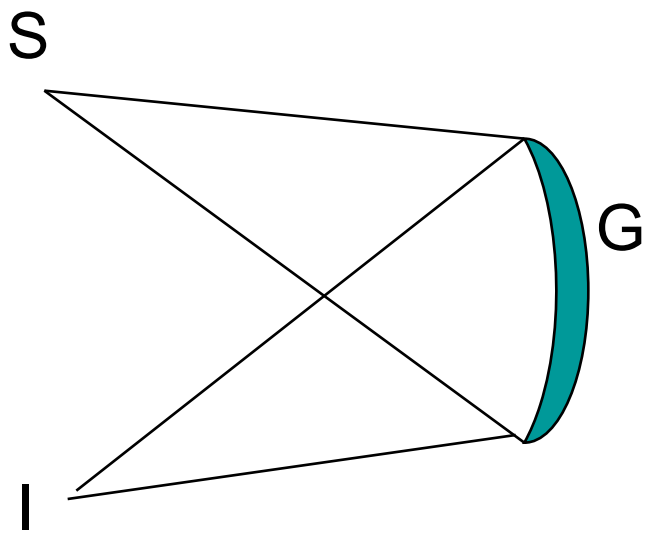
Dual Laser Plasma Photoabsorption (DLPP) - The Idea

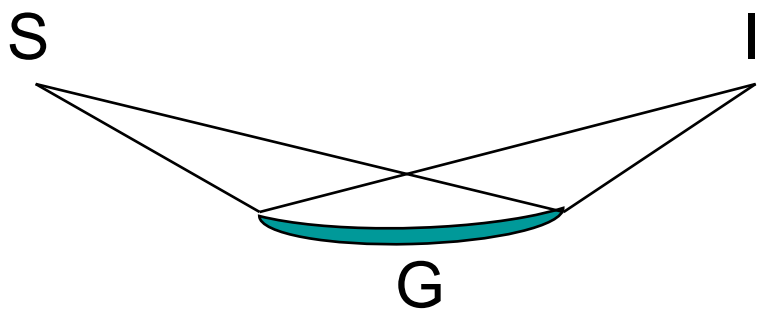
- Use two (normally) electronically synchronised LPPs
- One acts as the sample of atoms, ions or molecules
- The other acts as a source of continuum radiation
- The continuum emission is usually in the Vacuum-UV (VUV) or the Extreme UV (EUV) spectral region



Vacuum-UV and Extreme-UV Spectral Ranges



VUV - Normal Incidence Region



XUV - Grazing Incidence Region

$$E(eV) = (hc/\lambda) = (1239.8)/\lambda(nm)$$

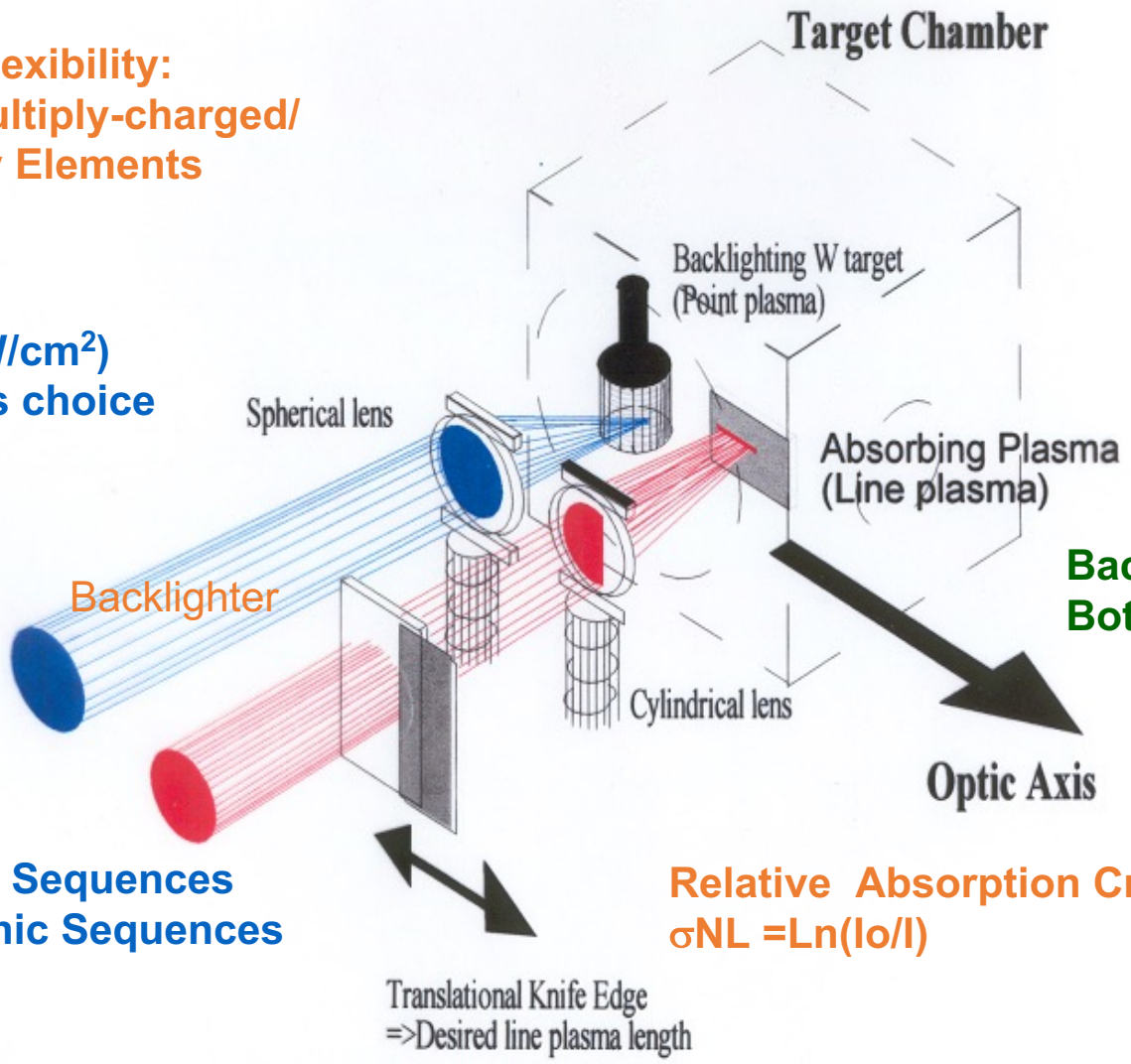
The Dual Laser Plasma Photoabsorption Set-up

J T Costello et al., Phys. Scr. **T34**, 77 (1991),
E T Kennedy et al., Opt. Eng **33**, 3984 (1994)

No tuning required
No vapour required

Species Flexibility:
Neutral/Multiply-charged/
Refractory Elements

Δx, ΔT, I(W/cm^2)
➔ Species choice



Backlighting Plasma I_o
Both Plasmas $I = I_o e^{-\sigma n L}$

Isonuclear Sequences
Isoelectronic Sequences

Relative Absorption Cross Section
$\sigma NL = Ln(Io/I)$

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Why Do Photoabsorption?

- Access to ground state (non-emitting) atomic and molecular species in the sample (vapour, plasma, etc.)

- You can then also detect (and potentially quantify) metastable state species

- Photon excitation => electric dipole excitation => less cluttered and quite tractable (from a theoretical perspective) spectra

Why Do X-VUV Photoabsorption?

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Why specifically at X-VUV photon energies?

- Access to more highly charged ions
- Photoionization continua
- Inner-shell/multi-electron excitations

Data relevant to:

- Astrophysical spectra and models
- Laboratory *plasma modelling & diagnostics*
- Fundamental many-body theory
- Plasma/atomic X-ray laser schemes
- MCF & ICF
- DLP data guides large scale synchrotron expts

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Laser Plasma Continua – History & Physical Origin

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Quick reminder - Radiative Processes in Laser Plasmas

1. Bound - Bound Transitions - Line Absorption/Emission

$$A^{n+} + h\nu \leftrightarrow A^{n+*} \text{ or } A^{n+*} \rightarrow A^{n+} + h\nu'$$

2. Bound - Free Transitions - Recombination/Photoionization*

$$A^{(n+1)+} + e \leftrightarrow A^{n+} + h\nu$$

3. Free - Free Transitions - Bremsstrahlung/Inv. Bremsstrahlung

$$A^{n+} + e(T_1) \leftrightarrow A^{n+} + e(T_2) + h\nu,\ T_1 > T_2$$

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Free-Free and *Free-Bound* processes yield continuum emission spectra suitable for application in absorption spectroscopy

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Short wavelength continua emitted from laser produced rare-earth (and neighbouring element) plasmas are predominantly free-bound in origin

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Laser Plasma Continua – History & Physical Origin

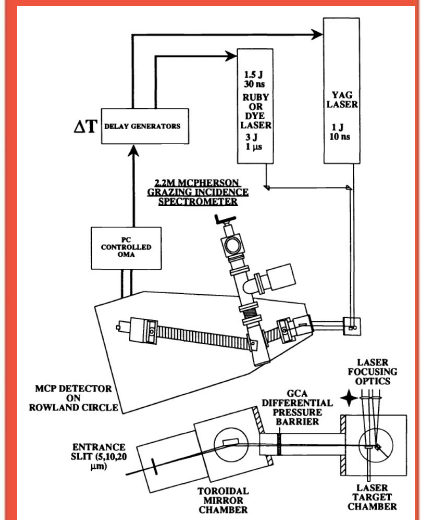

Fig. 1 Schematic diagram of the multilaser multichannel spectrometer system. The inset shows the optical configuration of the dual laser plasma experiment in enhanced detail.

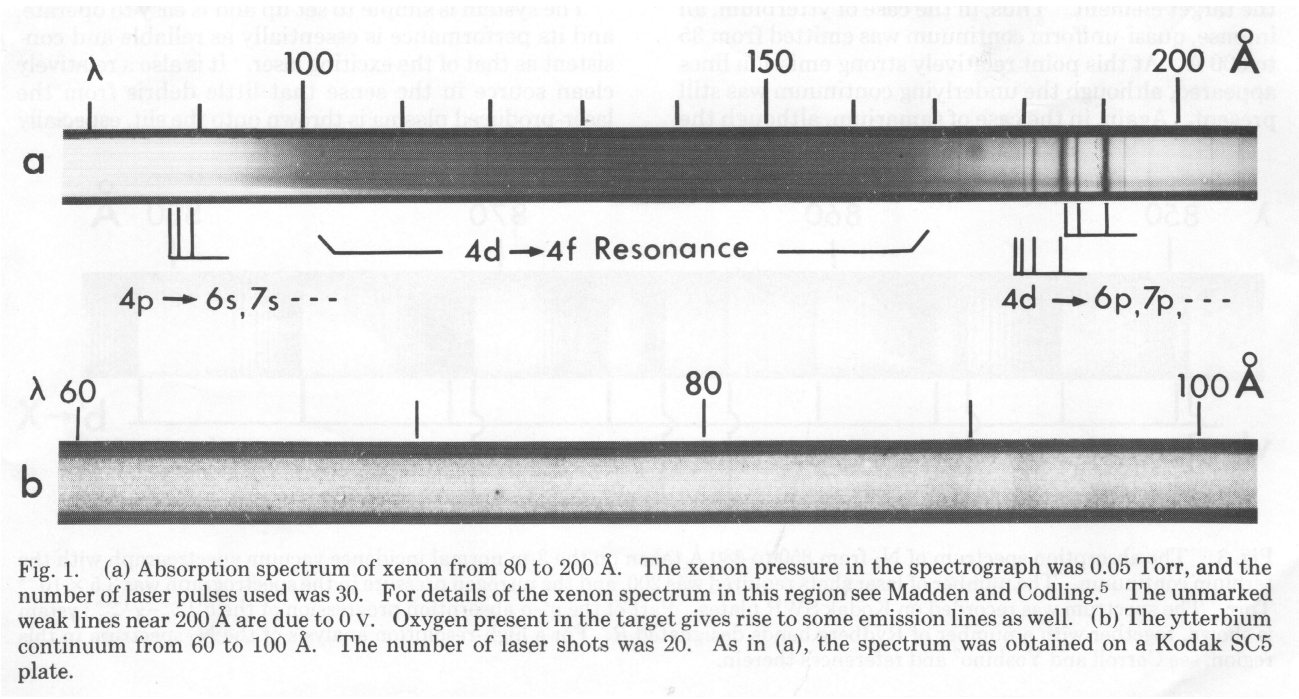

Fig. 1. (a) Absorption spectrum of xenon from 80 to 200 Å. The xenon pressure in the spectrograph was 0.05 Torr, and the number of laser pulses used was 30. For details of the xenon spectrum in this region see Madden and Codling.[5] The unmarked weak lines near 200 Å are due to O V. Oxygen present in the target gives rise to some emission lines as well. (b) The ytterbium continuum from 60 to 100 Å. The number of laser shots was 20. As in (a), the spectrum was obtained on a Kodak SC5 plate.

P K Carroll et al., *Optics Letters* **2**, pp72-74 (1978)

E T Kennedy et al., *Optical Engineering* **33**, pp3894-3992 (1994)

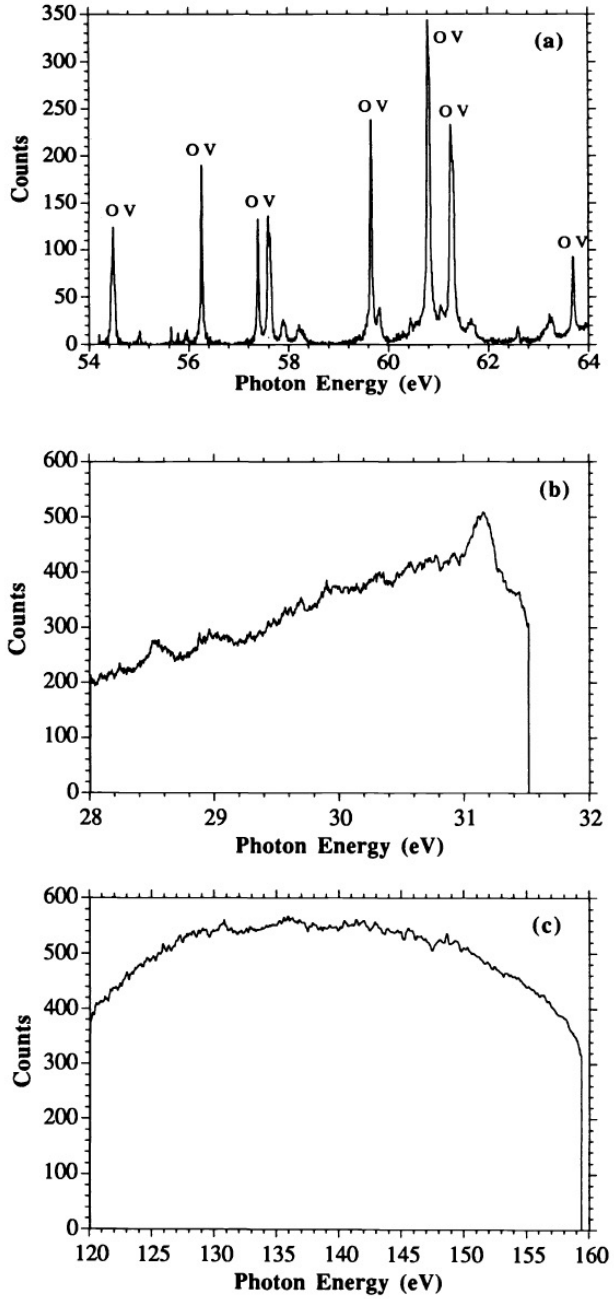

Fig. 2 (a) EUV emission spectrum of an aluminum oxide plasma showing the predominance of lines from O^{4+} in the 54→64 eV photon energy range. (b) and (c) Continuum emission from a tungsten plasma in the 30- and 140-eV spectral ranges.

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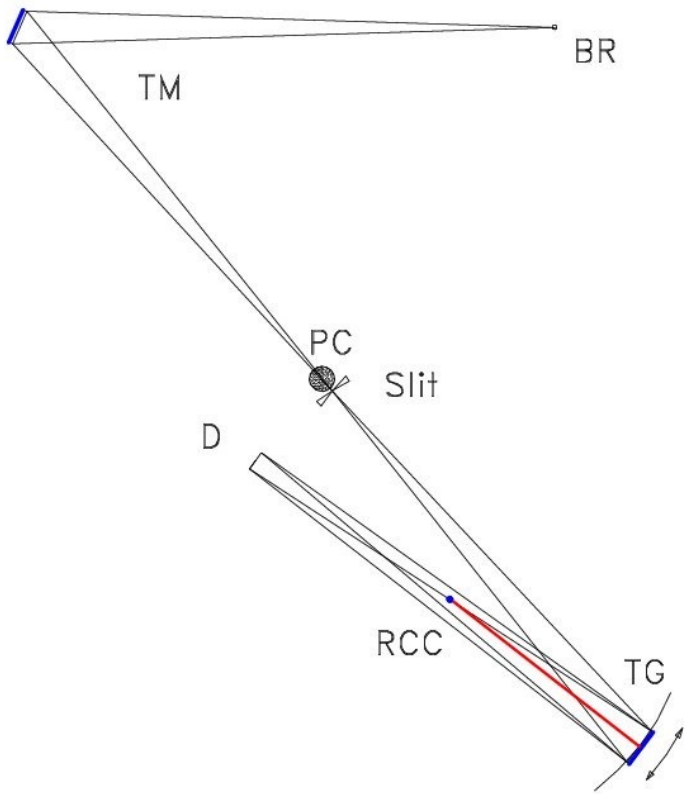
Laser Plasma Continua – History & Physical Origin

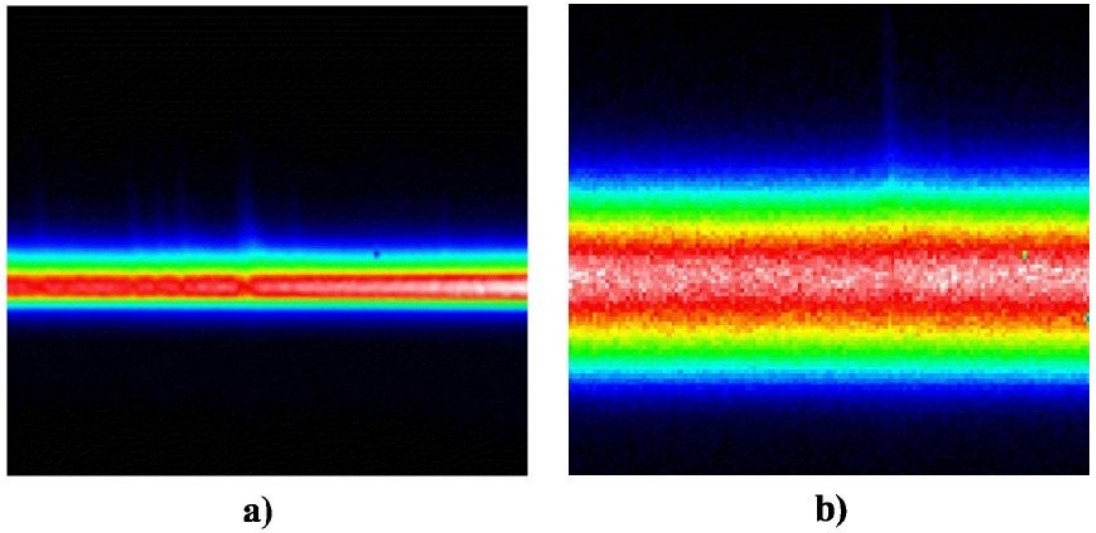
Nice space resolved VUV continuum from P Nicolosi et al. (Padua)

Motivation: Measure ions of astrophysical interest, tests of databases (e.g., Opacity, etc.)



Normal Incidence DLP Setup

P Recanatini, P Nicolosi & P Villoresi,
Phys. Rev. A **64**, Art. No. 012509 (2001)



Spaced resolved emission from a W plasma in the VUV around (a) 49 nm and (b) 69 nm

But why is no line emission observed ?

Line emission is due to complex 4d-4f transition arrays in (typically) 7 - 20 times ionized atoms:

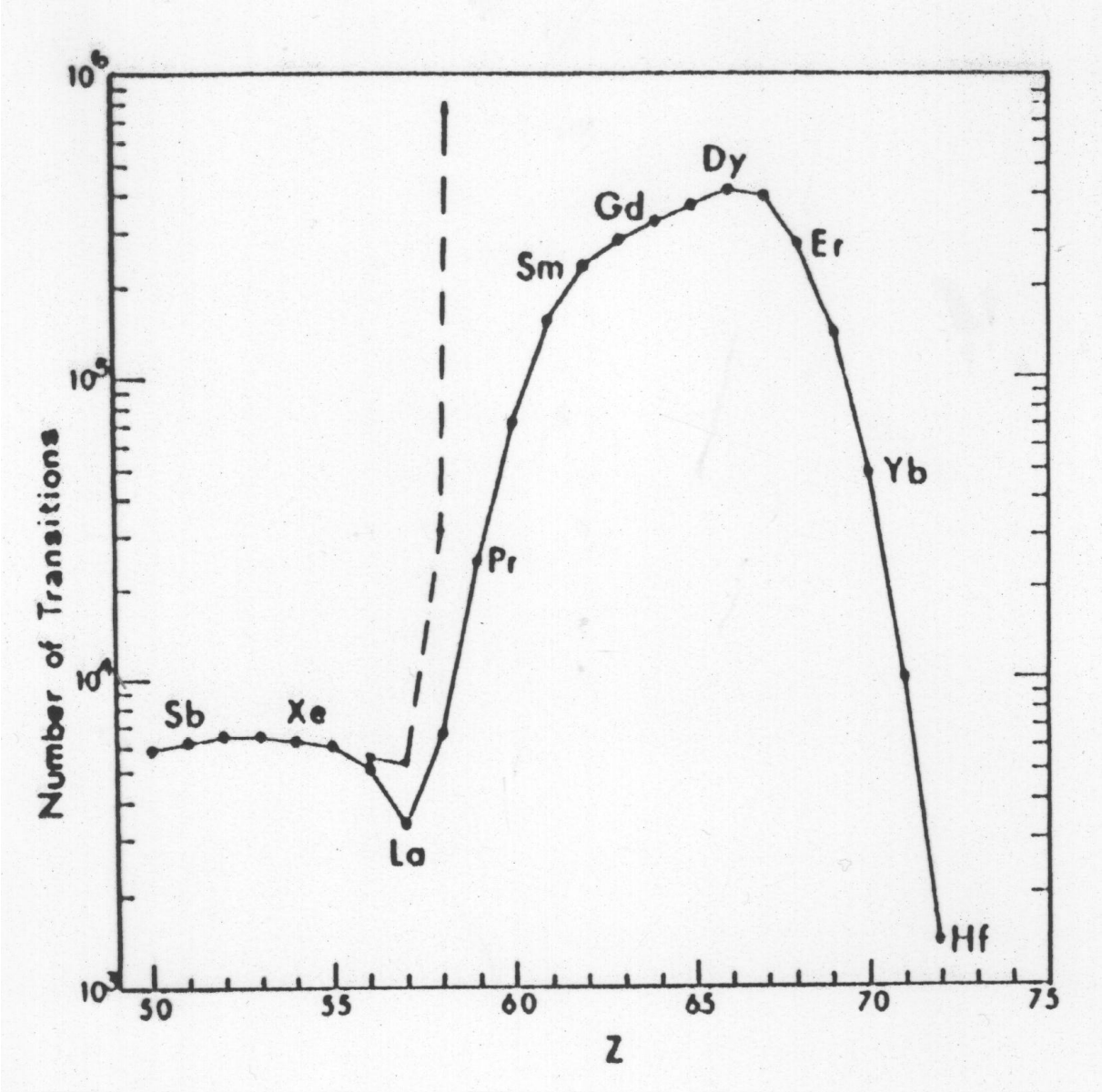
$$4d^n5s^q5p^s4f^m \rightarrow 4d^{n-1}5s^r5p^t\,4f^{m+1},\ q+s = r+t$$

Furthermore 4f/5p and 4f/5s degeneracy and level crossing gives rise to overlapping bands of low-lying configurations, most of which are populated in the ca.10 - 50 eV plasma

Result - the summed oscillator strength for each 4d - 4f (XUV) and 5p - 5d (VUV) array is spread out over a *supercomplex* of transitions producing bands of unresolved pseudo continua (so called Unresolved Transition Arrays - 'UTA') superimposed on the background continuum

In addition, strong emission lines from simple 4f - 4f transition arrays, e.g., $4d^{10}$-$4p^94f$ in Xe-like ions, are washed out by plasma opacity

Laser Plasma Continua – History & Physical Origin



There are up to 0.5 million allowed transitions (in LS coupling) over the ~10 eV bandwidth of a UTA

In fact, this is a lower bound since many additional LS forbidden transitions are 'switched on' by the breakdown in LS coupling here - G O'Sullivan et al., J.Phys.B **32**, 1893 (1999)

Brief Early History/ Highlights of Laser Plasma High-Z/Rare-Earth Continua

1. First report of line free continua - P K Carroll et al., Opt. Letts. **2**, 72 (1978)
2. First full study/ applications - P K Carroll et al., Appl. Opt. **19**, 1454 (1980)
3. VUV Radiometric Transfer Standard - G O'Sullivan et al., Opt. Letts. **7**, 31 (1982)
4. Absolute Calibration with Synchrotron - J Fischer et al, Appl. Opt. **23**, 4252 (1984)
5. Photoelectron Spectroscopy - Ch. Heckenkamp et al., J. Phys. D **14**, L203 (1981)
6. First Study for EUV lithography - D J Nagel et al., Appl. Opt. **19**, 1454 (1980)
7. EUV Reflectometer - S Nakayama et al., Physica Scripta **41**, 754 (1990)
8. First Industrial Application - DuPont - Insulator Band Structure
   VUV Reflectance Spectroscopy - R H French, Physica Scripta **41**, 404 (1990) - System subsequently made available commercially from ARC

For a review of the early years including applications in photoabsorption spectroscopy see :
1. J T Costello et al., Physica Scripta **T34**, 77 (1991)
2. P Nicolosi et al., J. Phys. IV **1**, 89 (1991)

Laser Plasma Continua – History & Physical Origin

- Ease of Production
- Ease of Location
- Purity (Spectral)
- Wide Spectral Coverage - (4 → 200 nm)
- Small Emitting Size (almost point-like, radiography & microscopy)
- Short Pulse Duration (< 100 ps - 50 ns)*
- Easy Synchronisation (Optical or Electro-Optic)
- **Insensitivity to ambient pressure**
- Shot to shot intensity reproducibility ≤ 5%
- **~10^{14} Photons/pulse/sr/nm****

*Depending on exciting laser pulse

J Fischer et al, Appl. Opt. **23, 4252 (1984) – *800 mj Nd:YAG plasma generation*

Economy, Ease of Use & Versatility

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Dual Laser Plasma Photoabsorption – Some History

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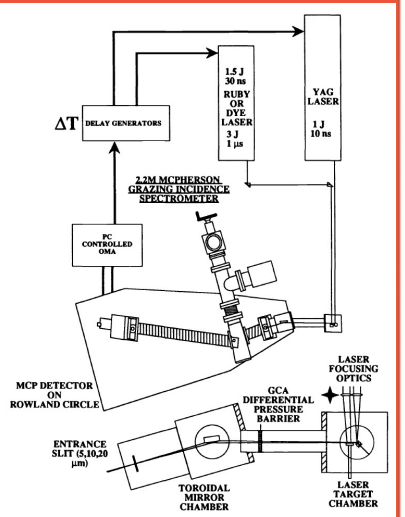

Fig. 1 Schematic diagram of the multilaser multichannel spectrometer system. The inset shows the optical configuration of the dual laser plasma experiment in enhanced detail.

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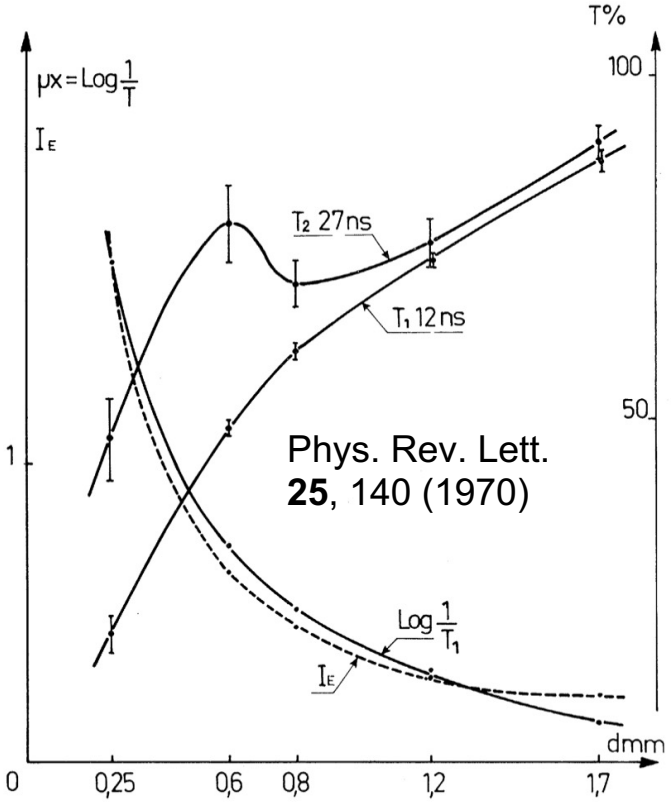
EXTREME-ULTRAVIOLET CONTINUUM ABSORPTION BY A LASER-GENERATED ALUMINUM PLASMA

A. Carillon, P. Jaegle, and P. Dhez
Laboratoire de Chimie Physique de la Faculté des Sciences de Paris, 91-Orsay, France
(Received 29 April 1970)



Phys. Rev. Lett. **25**, 140 (1970)

FIG. 2. Transmittance T and absorption μx of extreme uv (98 Å) through the plasma. d is the distance from the observed zone to the hottest part, situated at about 0.5 mm from the target. T_1, transmittance measured with a 12-nsec time lag; T_2, transmittance measured with a 27-nsec time lag; I_E, intensity of the continous spectrum emitted by the plasma at the same wavelength.

Doubly Excited Autoionization Resonances in the Absorption Spectrum of Li^+ Formed in a Laser-Produced Plasma*

P. K. Carroll and E. T. Kennedy
Physics Department, University College Dublin, Dublin, Ireland
(Received 3 February 1977)

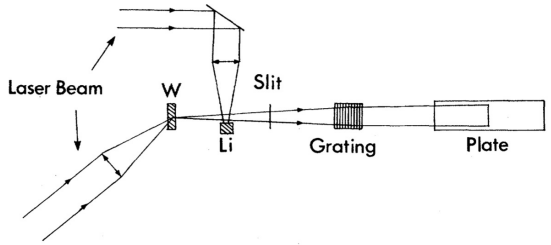


FIG. 1. Schematic diagram of experimental arrangement.

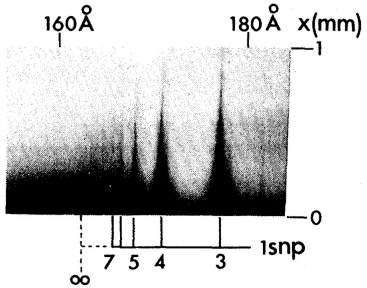
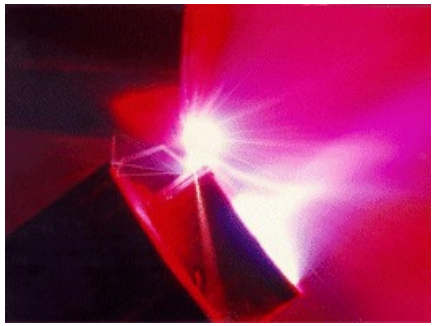


FIG. 2. One-electron of Li^+. The scale in the vertical (x) direction measures the distance from the target surface.



Phys. Rev. Lett. 38, 1068 (1970)

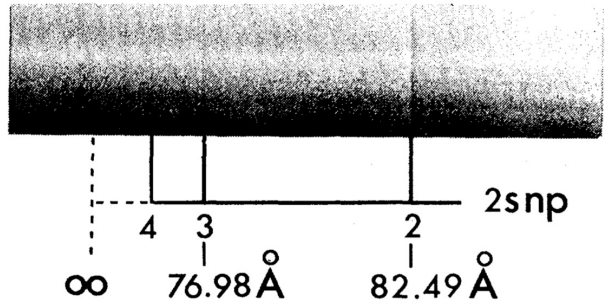


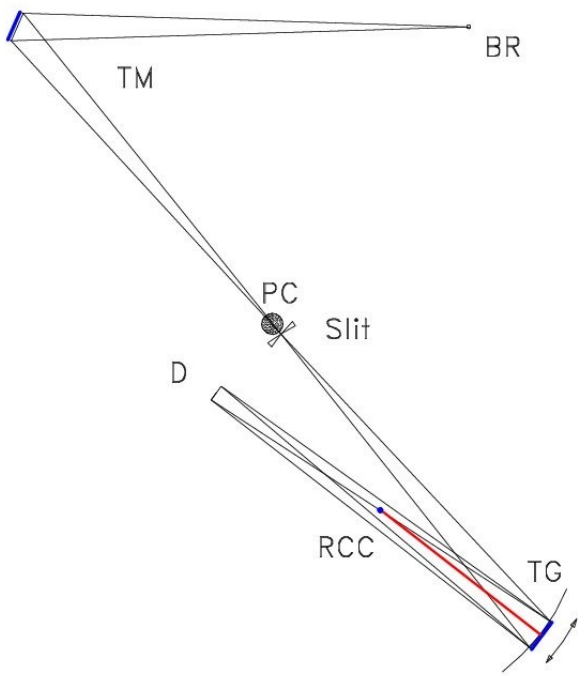
FIG. 3. Two-electron absorption of Li^+.

1. J T Costello et al., Physica Scripta **T34**, 77 (1991)
2. P Nicolosi et al., J. Phys. IV **1**, 89 (1991)

Laser Plasma Continua – History & Physical Origin

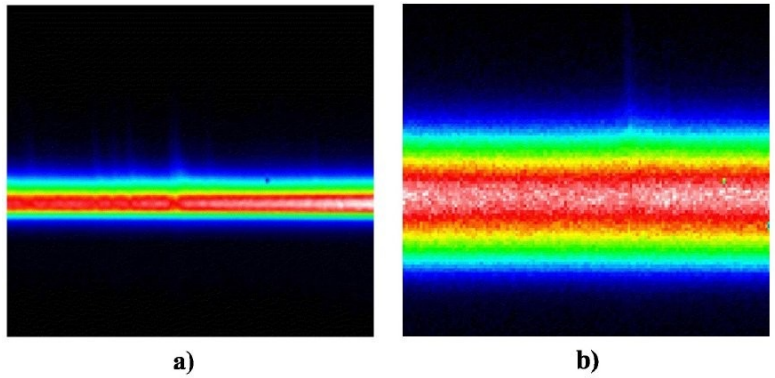
VUV Photoabsorption of carbon ions - from P Nicolosi et al. (Padua)

Motivation: Measure ions of astrophysical interest, tests of databases (e.g., Opacity, etc.)

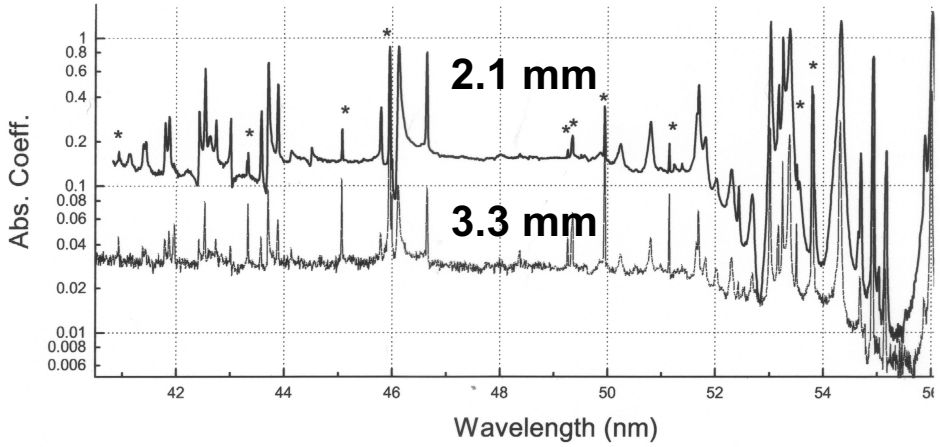


Normal Incidence DLP Setup

P Recanatini, P Nicolosi & P Villoresi, Phys. Rev. A **64**, Art. No. 012509 (2001)



Spaced resolved emission from a W plasma in the VUV around (a) 49 nm and (b) 69 nm

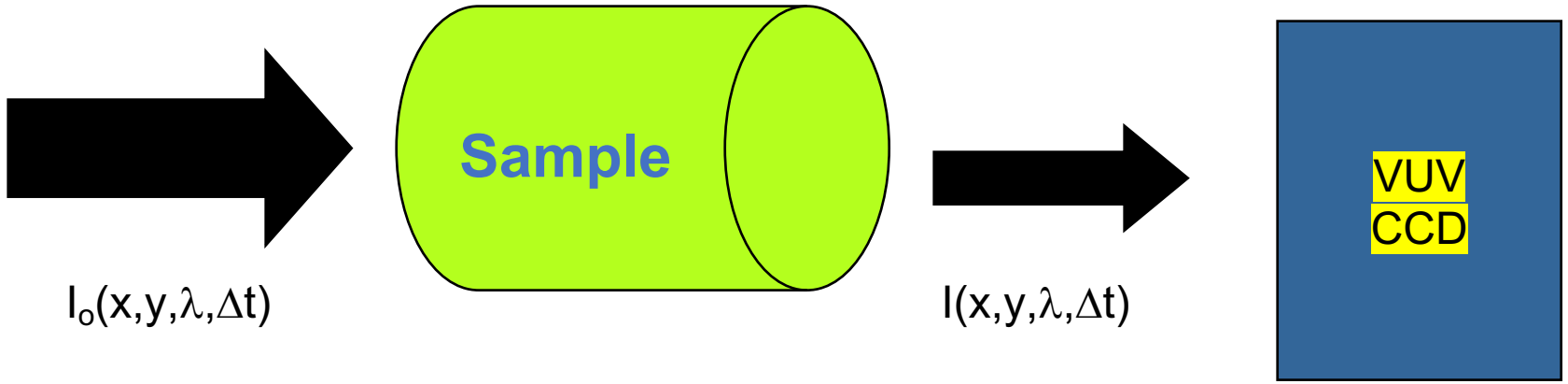


C^+. 1.2 J on target in line focus: 9 mm X 0.01 mm / Delay = 58 ns

Dual Laser Plasma Photoabsorption – Some History

VUV Photoabsorption Imaging

J Hirsch, E T Kennedy, J T Costello, L Poletto & P Nicolosi Rev. Sci. Inst. **74**, 2992 (2003)



Motivation

1.Direct imaging of light emitted by a plasma using gated array detectors (e.g., I-CCD) provides information on excited species only

2.Probing plasma plumes using tuneable lasers provides information on non-emitting species but is limited to wavelengths > 200 nm or so

Idea: Pass a *collimated VUV beam* through the plasma sample and measure the spatial distribution of the absorption.

Dual Laser Plasma Photoabsorption – Some History

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Why a pulsed, tuneable and collimated beam ?

- **Pulsed**

Automatic time resolution: the VUV pulse duration ~ laser pulse duration (~1 - 100 ns)

- **Tuneable**

Can access resonance lines of all atoms & moderately charged ions with resonances between 30 nm and >120 nm

Can tune into photoionization continua (cross sections known)

- **Collimated**

Can place the sample and CCD anywhere along the beam

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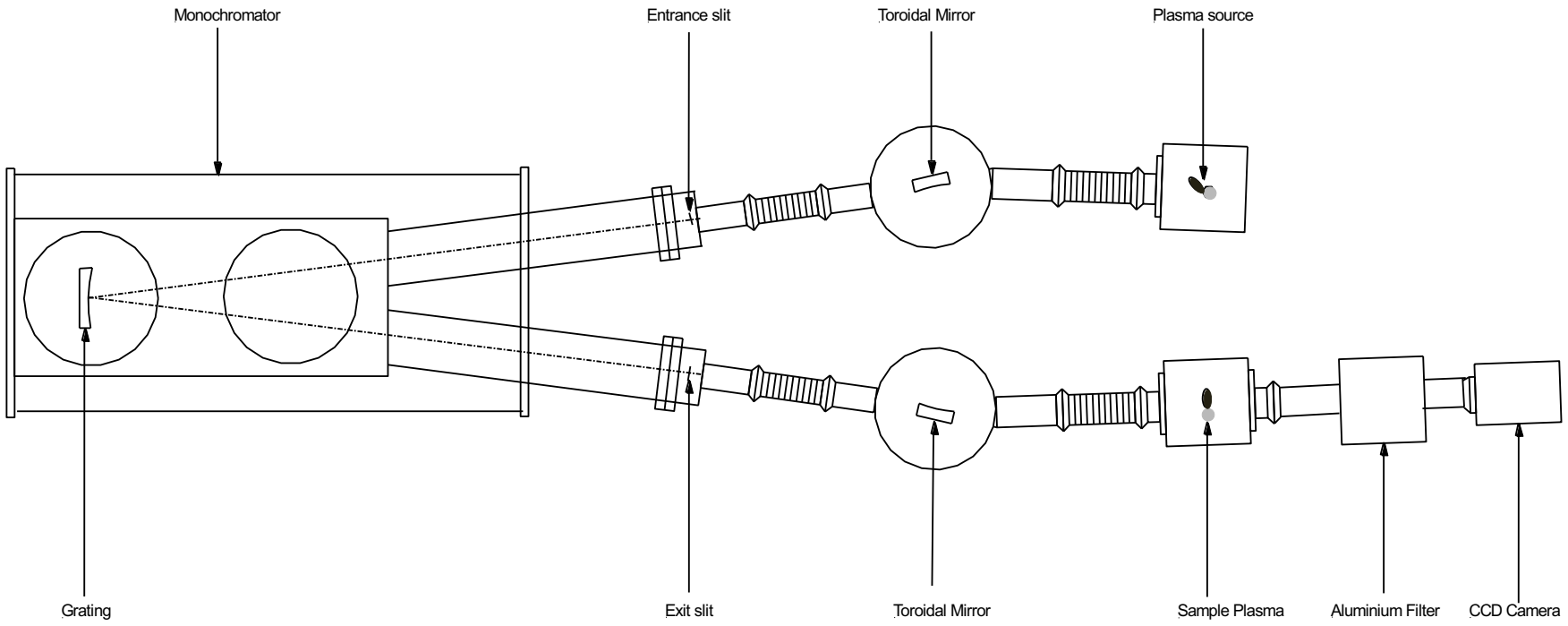
VUV Photoabsorption Imaging



Experimental Schematic

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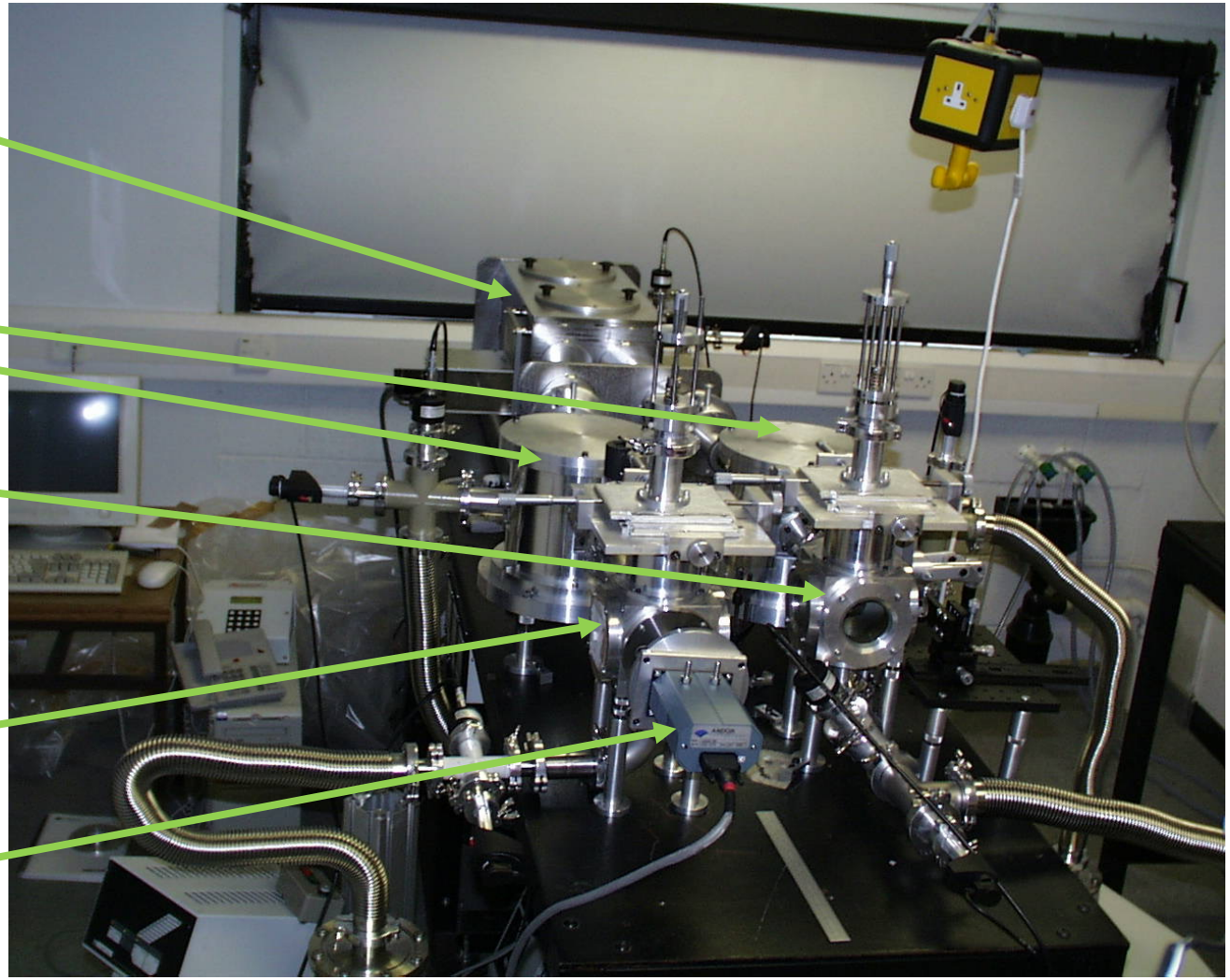
VUV Photoabsorption Imaging



Dual Laser Plasma Photoabsorption – Some History

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VUV Photoabsortion Imaging - Specifications

Time resolution:	~10 - 30 ns
Inter-plasma delay range:	0 - 10 μsec
Delay time jitter:	± 1ns
Monochromator:	Acton™ VM510 (f/12, f=1.0 m)
VUV range:	10 - 35 eV (35 – 120 nm)
VUV bandwidth:	0.025 eV @25 eV (50mm/50mm slits)
	~0.05 nm @ 50 nm
Detector:	Andor™ BN-CCD,
	2048 x 512/13 μm x 13 μm pixels
Spatial resolution:	~120 μm (H) x 150 μm (V)

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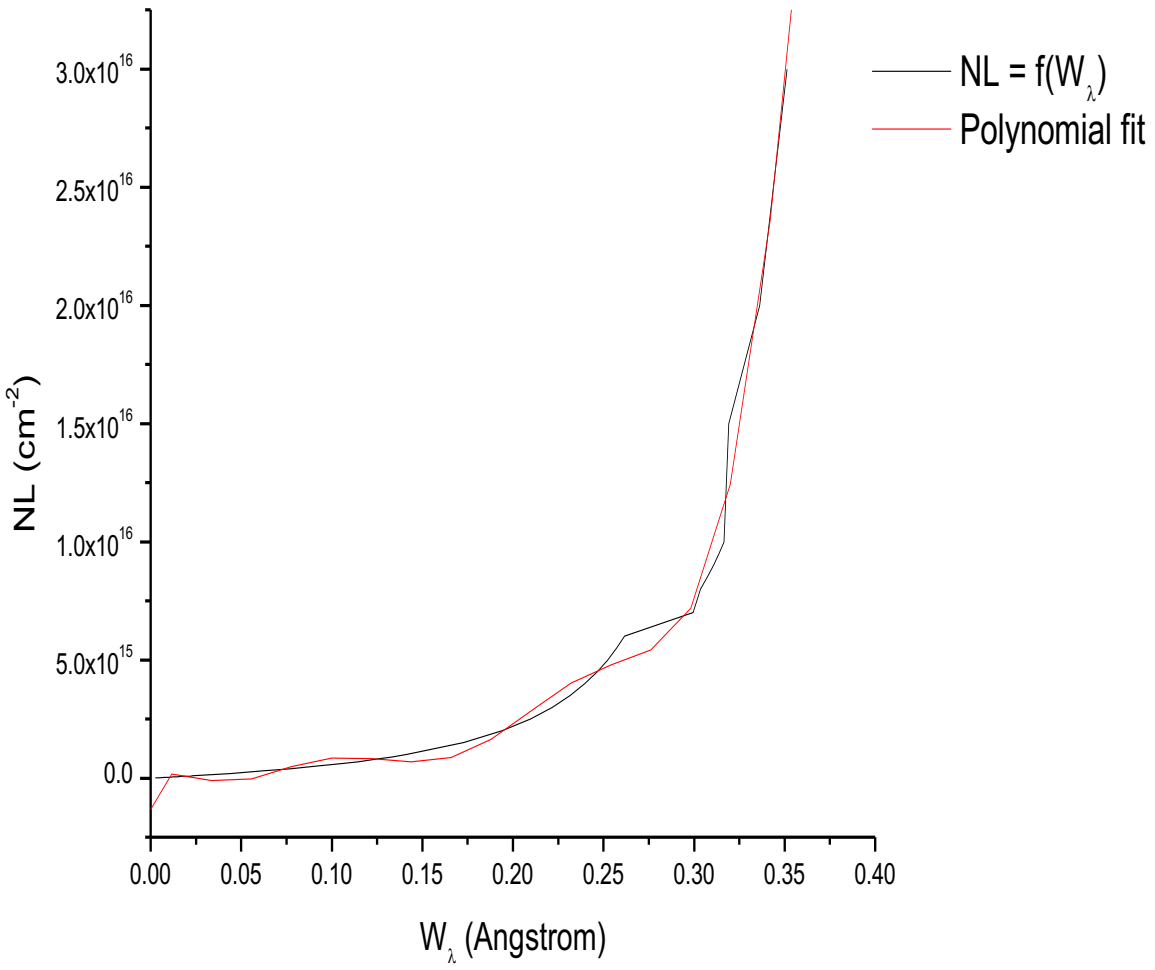
Dual Laser Plasma Photoabsorption – Some History

Extract 'equivalent width' W_λ maps from I & I_0 images.

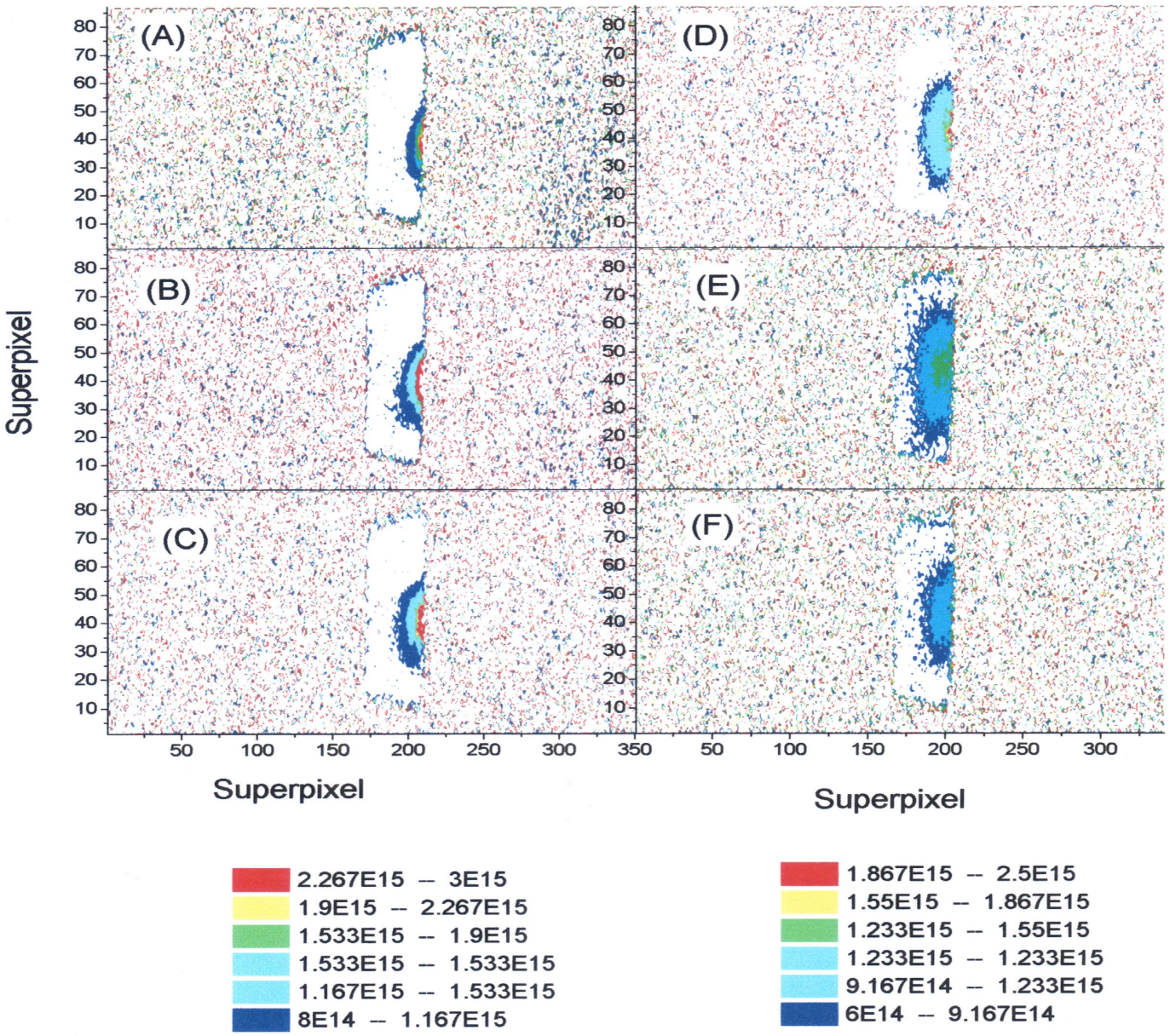
$$W_\lambda = \Delta\lambda \times \frac{\int_{\Delta\lambda} I_0(\lambda)\,d\lambda - \int_{\Delta\lambda} I(\lambda)\,d\lambda}{\int_{\Delta\lambda} I_0(\lambda)\,d\lambda}$$

$$W_\lambda = \int_{\Delta\lambda} \left(1 - \exp\left(-n_i L \int_{\Delta\lambda} \sigma_\lambda\,d\lambda\right)\right) d\lambda$$

Here σ(l) is the total absolute photoionization cross section, and the integral is taken over the 46.7 nm (26.5 eV) 5p – 5d resonance profile of Ba+. If 'σ' is known, one can extract the column density NL



Dual Laser Plasma Photoabsorption – Some History



(A) 100 ns
(B) 150 ns
(C) 200 ns
(D) 300 ns
(E) 400 ns
(F) 500 ns

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Some Recent VUV/EUV DLPP Results on Atoms and Molecules

Let's jump forward 20 years to take two recent examples:

- VUV Photoabsorption by Pb & Bi ions [1,2]
- Oxygen K-shell Photoabsorption in CH4 & CO_2 [3]

1. ***The 5d → 6p EUV photoabsorption spectra of Pb II and Bi III: evidence of excited states,*** H Lu, L Varvarezos, M Bilal Alli, P Nicolosi, J T Costello and P Hayden, *J. Phys. B: At. Mol. Opt. Phys.* **53** 115001 (2020) - https://doi.org/10.1088/1361-6455/ab7e1c

Cf. Reply to Comment on *"The 5d → 6p photoabsorption spectra of Pb II and Bi III: evidence of excited states" by A. N. Ryabtsev,* H Lu, L Varvarezos, M B Alli, P Nicolosi, J T Costello and P Hayden, J. Phys. B: At. Mol. Opt. Phys. **54** Art. No. 068001 (2021) - https://iopscience.iop.org/article/10.1088/1361-6455/abe394

2. ***The 5d-6p VUV Photoabsorption Spectrum of Bi^+,*** H Lu, L Varvarezos, P Hayden, E T Kennedy, J-P Mosnier and J T Costello, Atoms **8**, Art. No. 55 (2020) - https://doi.org/10.3390/atoms8030055

3. ***Soft x-ray photoabsorption spectra of photoionized CH_4 and CO_2 plasmas***
L Varvarezos, H Lu, **J T Costello**, A Bartnik, P Wachulak, T Fok, L Wegrzynski and H Fiedorowicz, J. Phys. B: At. Mol. Opt. Phys. **53** 045701 (2020) - https://iopscience.iop.org/article/10.1088/1361-6455/ab5e31

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Some Recent VUV/EUV DLPP Results on Atoms and Molecules

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Motivation - VUV Photoabsorption by Pb & Bi ions

- Spectroscopic observations by the EUVE, Chandra and XMM-Newton satellites emphasise the need for highly accurate atomic data in the extreme VUV (X-VUV) and soft x-ray(SXR).
- Pb II [1] and Bi III [2,3] spectra have attracted attention in the study of stellar evolution and the investigation of the chemical composition of peculiar stars
- Soft x-ray emission measurements in heavy atoms, including Bi and Pb, have been performed in the e.g., the TEXT tokamak [4].
- Generally interested in the short wavelength behaviour of potential metal ions for next generation EUVL resists

[1] Cardelli J A, Federman S R, Lambert D L and Theodosiou C E, 1993 Astrophys. J. **416** L41
[2] Leckrone D S, Johansson S G, Wahlgren G M, Brage T and Profitt C R 1998 Highlights Astron. **11** pp650–652
[3] Wahlgren G M, Brage T, Brandt J C, Fleming J, Johansson S, Leckrone D S, Proffitt C R, Reader J and Sansonetti C J 2001 Astrophys. J. **551** pp520–35
[4] Finkenthal M, Lippmann S, Huang L K, Zwicker A, Moos H W, Goldstein W H and Osterheld A L 1992 Phys. Rev. A 45 pp5846–53

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On short wavelength behaviour of potential metal ions for next generation EUVL (nanoparticle) resists

Related poster: P_FUN8 - L. Varvarezos - Photoabsorption Spectra of CsI Plasmas in the 50-75 nm Wavelength Range

Wednesday – December 1st

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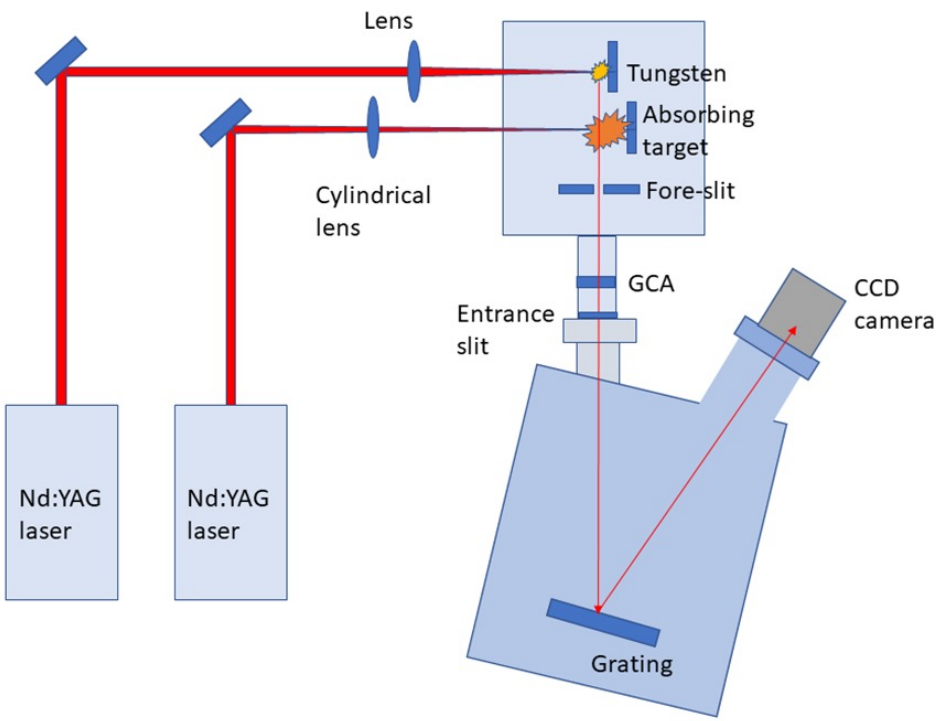
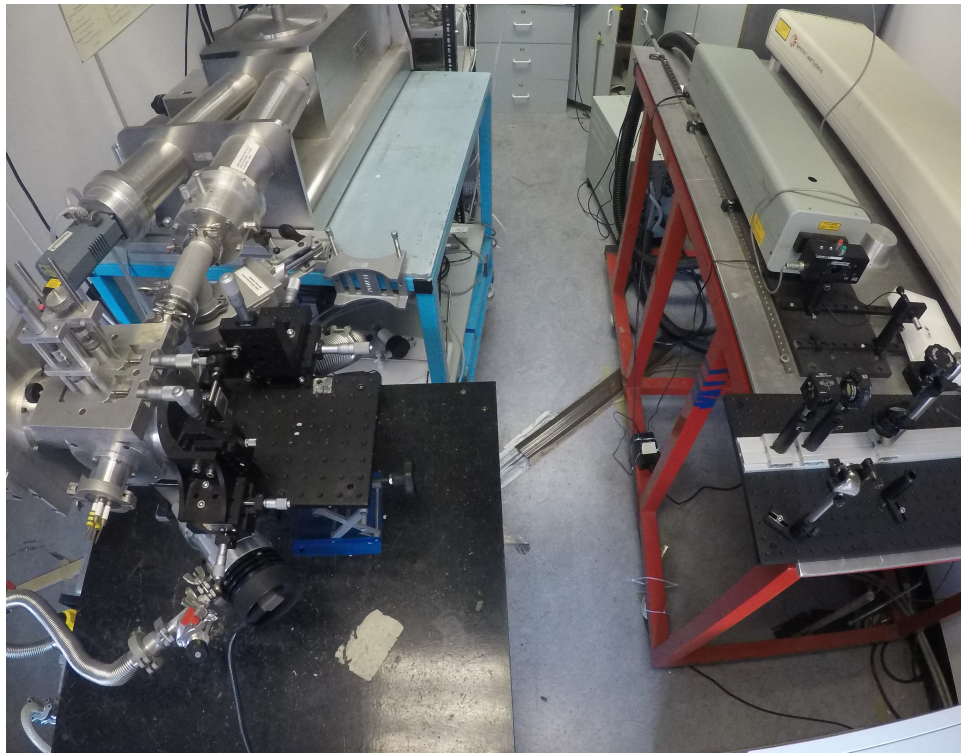
VUV Photoabsorption by Pb & Bi ions





VUV DLPP Experimental set up. GCA (glass capillary array used for grating protection from plasma debris and as differential pressure barrier).

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Comparison of experiment with calculation.

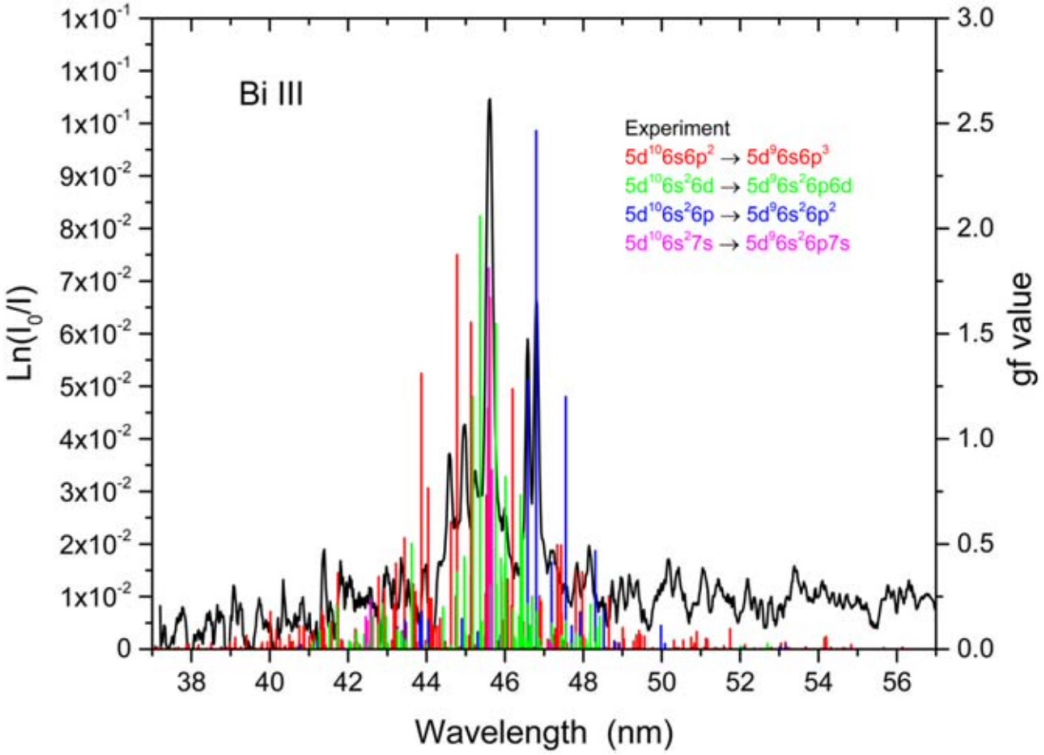

Figure 1. The experimentally recorded spectrum of Bi III together with the *gf* values for all the transitions (including $5d^{10}6s6p^2 \rightarrow 5d^96s6p^3$, $5d^{10}6s^26d \rightarrow 5d^96s^26p6d$, $5d^{10}6s^26p \rightarrow 5d^96s^26p^2$ and $5d^{10}6s^27s \rightarrow 5d^96s^26p7s$) involved.

Table 1. Lower configurations of Bi III/Pb II included in the Cowan code photoabsorption calculations.

Ground configuration	Excited configurations
$5d^{10}6s^26p$	$5d^{10}6s6p^2$
	$5d^{10}6s^26d$
	$5d^{10}6s^27s$

The 5d → 6p EUV photoabsorption spectra of Pb II and Bi III: evidence of excited states, H Lu, L Varvarezos, M Bilal Alli, P Nicolosi, J T Costello and P Hayden, *J. Phys. B: At. Mol. Opt. Phys.* **53** 115001 (2020) - https://doi.org/10.1088/1361-6455/ab7e1c

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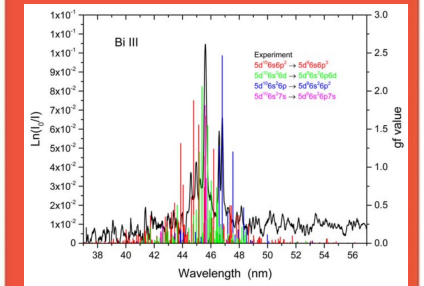

Figure 1. The experimentally recorded spectrum of Bi III together with the *gf* values for all the transitions (including $5d^{10}6s6p^2 \rightarrow 5d^96s6p^3$, $5d^{10}6s^26d \rightarrow 5d^96s^26p6d$, $5d^{10}6s^26p \rightarrow 5d^96s^26p^2$ and $5d^{10}6s^27s \rightarrow 5d^96s^26p7s$) involved.

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Comparison of experiment with calculation.

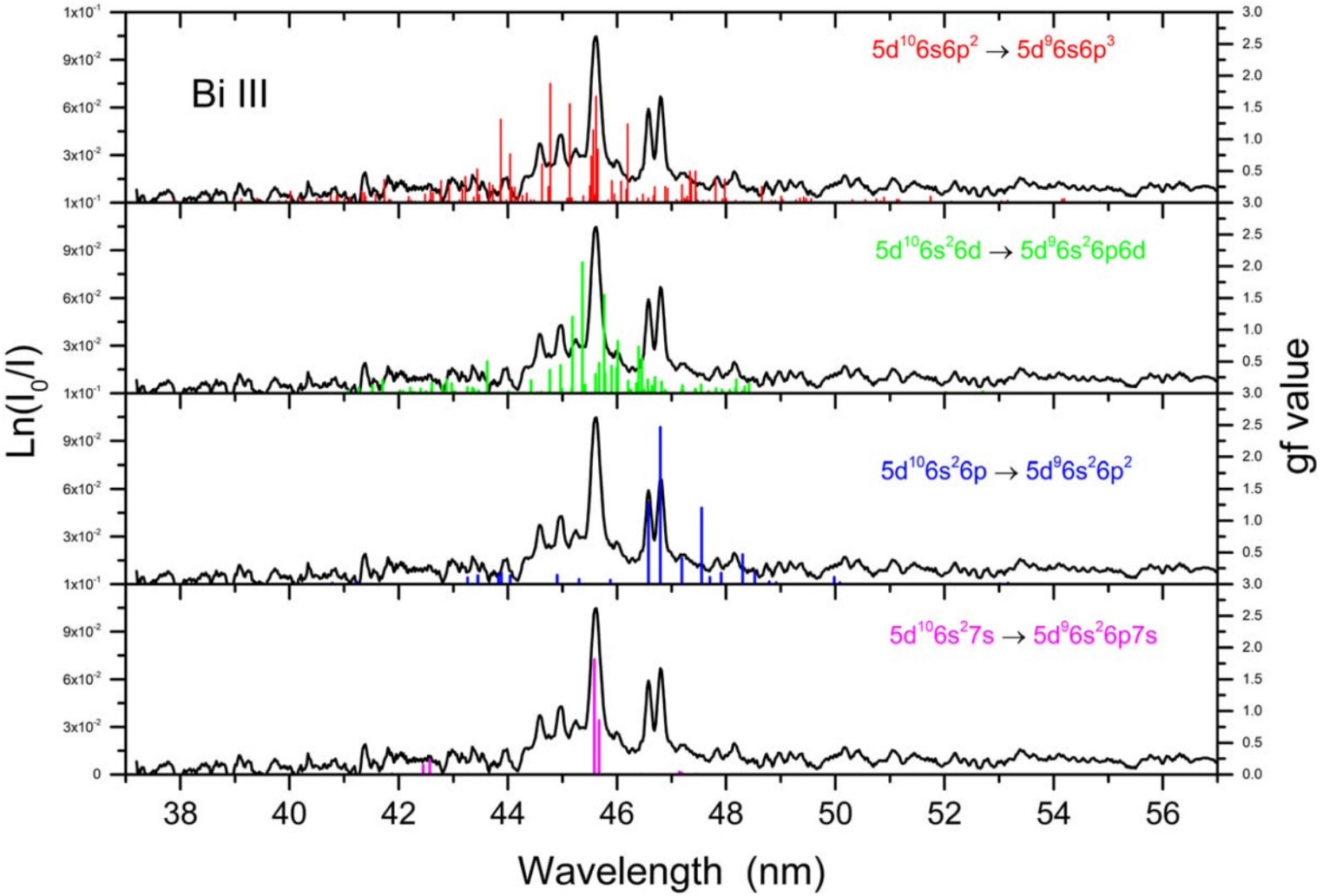

Figure 3. Calculated gf values for each Bi III configuration involved in our experiment. From top to bottom: $5d^{10}6s6p^2 \rightarrow 5d^96s6p^3$, $5d^{10}6s^26d \rightarrow 5d^96s^26p6d$, $5d^{10}6s^26p \rightarrow 5d^96s^26p^2$ and $5d^{10}6s^27s \rightarrow 5d^96s^26p7s$. A comparison with the experimental spectrum (black line) reveals the contribution of each configuration.

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Comparison of experiment with calculation.

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H Lu et al., *J. Phys. B: At. Mol. Opt. Phys.* **53** 115001 (2020)

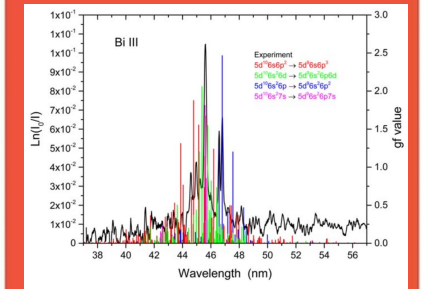

Figure 1. The experimentally recorded spectrum of Bi III together with the *gf* values for all the transitions (including $5d^{10}6s6p^2 \rightarrow 5d^9 6s6p^3$, $5d^{10}6s^2 6d \rightarrow 5d^9 6s^2 6p6d$, $5d^{10}6s^2 6p \rightarrow 5d^9 6s^2 6p^2$ and $5d^{10}6s^2 7s \rightarrow 5d^9 6s^2 6p7s$) involved.

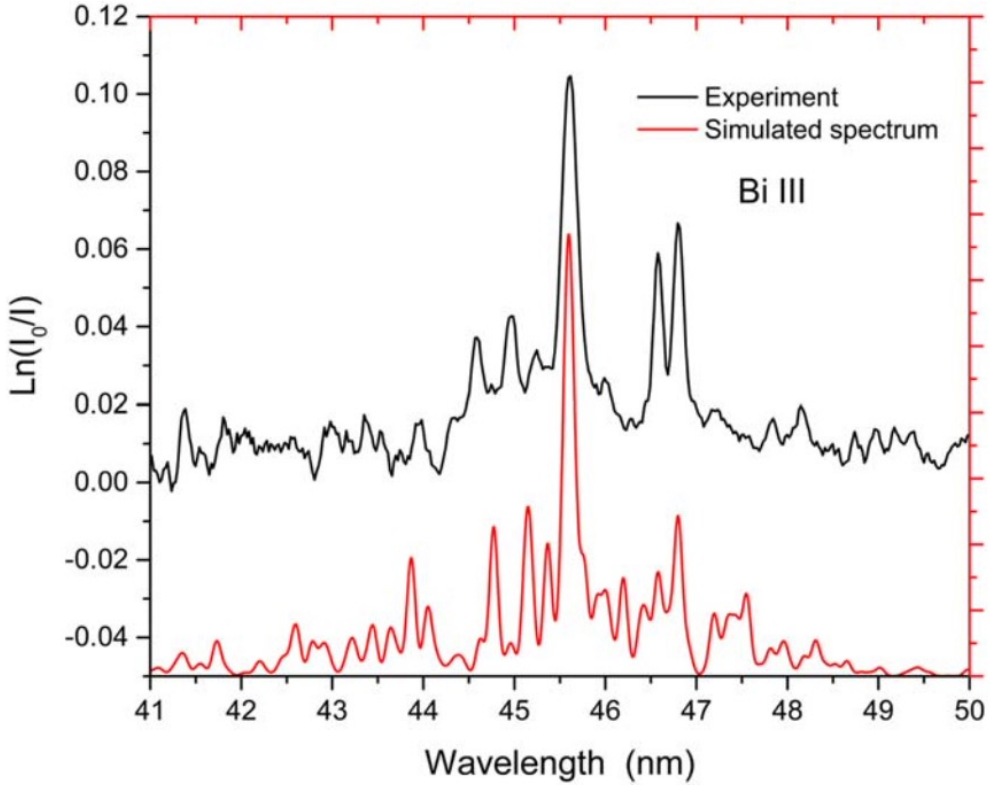

Figure 2. A comparison between the synthetic spectrum (including $5d^{10}6s6p^2 \rightarrow 5d^9 6s6p^3$, $5d^{10}6s^2 6d \rightarrow 5d^9 6s^2 6p6d$, $5d^{10}6s^2 6p \rightarrow 5d^9 6s^2 6p^2$ and $5d^{10}6s^2 7s \rightarrow 5d^9 6s^2 6p7s$) and the experimental spectrum of Bi III.

Table 3. Transitions corresponding to the most prominent features observed in the Bi III spectrum.

Transition $5d^{10}6s^2 6p \rightarrow 5d^9 6s^2 6p^2$	λ_{obs} (nm)	λ_{calc} (nm)	*gf* values
$^2P^o_{3/2} \rightarrow {}^2D_{5/2}$	46.80	46.79	2.47
$^2P^o_{3/2} \rightarrow {}^2P_{3/2}$	46.60	46.57	1.28
Transition $5d^{10}6s^2 7s \rightarrow 5d^9 6s^2 6p7s$	λ_{obs} (nm)	λ_{calc} (nm)	*gf* values
$^2S_{1/2} \rightarrow {}^2P^o_{3/2}$	45.62	45.58	1.82
$^2S_{1/2} \rightarrow {}^2P^o_{1/2}$	45.62	45.67	0.85
Transition $5d^{10}6s^2 6d \rightarrow 5d^9 6s^2 6p6d$	λ_{obs} (nm)	λ_{calc} (nm)	*gf* values
$^2D_{5/2} \rightarrow {}^2F^o_{7/2}$	45.25	45.36	2.06
$^2D_{5/2} \rightarrow {}^2D^o_{5/2}$	45.25	45.18	1.20
$^2D_{3/2} \rightarrow {}^2F^o_{5/2}$	45.62	45.76	1.55
Transition $5d^{10}6s6p^2 \rightarrow 5d^9 6s6p^3$	λ_{obs} (nm)	λ_{calc} (nm)	*gf* values
$^2D_{5/2} \rightarrow {}^2F^o_{7/2}$	45.62	45.57	1.15
$^4P_{3/2} \rightarrow {}^4P^o_{5/2}$	44.96	45.13	1.55
$^2P_{3/2} \rightarrow {}^2D^o_{5/2}$	44.60	44.78	1.87
$^4P_{3/2} \rightarrow {}^2D^o_{3/2}$	45.62	45.61	0.62
$^4P_{1/2} \rightarrow {}^6D^o_{3/2}$	44.60	44.63	0.61

Clear evidence of excited states contributing to the overall spectra distribution – difficult to avoid unless they lie significantly higher than plasma temperature – so for more highly charged ions.

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Comparison of experiment with calculation (the case of Pb II).

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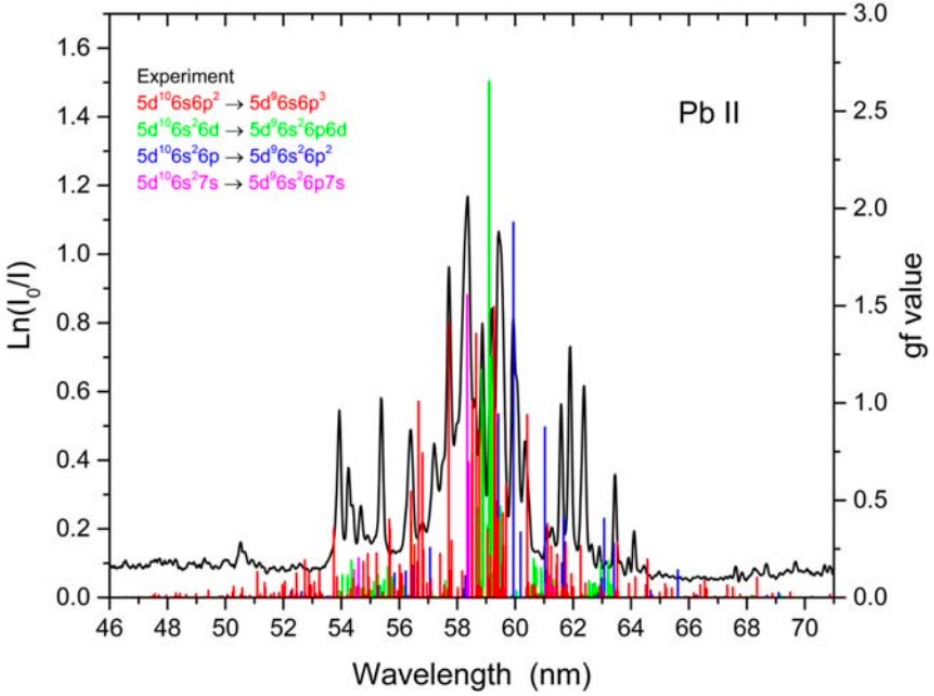

Figure 4. The experimentally recorded spectrum of Pb II together with the *gf* values for all the transitions (including $5d^{10}6s6p^2 \rightarrow 5d^96s6p^3$, $5d^{10}6s^26d \rightarrow 5d^96s^26p6d$, $5d^{10}6s^26p \rightarrow 5d^96s^26p^2$ and $5d^{10}6s^27s \rightarrow 5d^96s^26p7s$) involved.

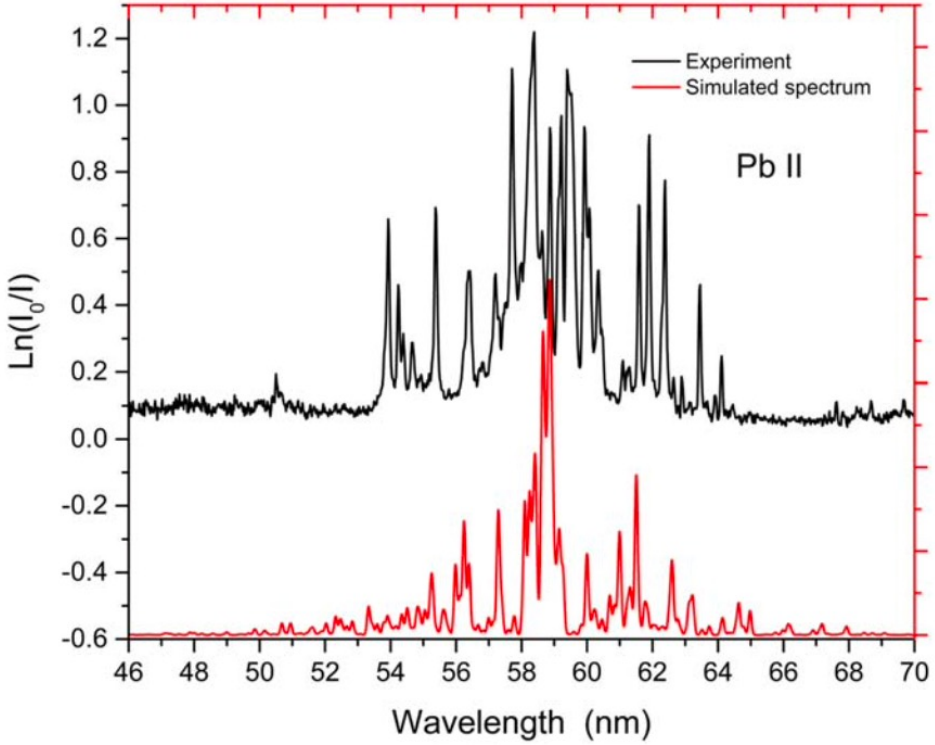

Figure 5. A comparison between the synthetic spectrum (including $5d^{10}6s6p^2 \rightarrow 5d^96s6p^3$, $5d^{10}6s^26d \rightarrow 5d^96s^26p6d$, $5d^{10}6s^26p \rightarrow 5d^96s^26p^2$ and $5d^{10}6s^27s \rightarrow 5d^96s^26p7s$) and the experimental spectrum of Pb II.

Again, clear evidence of excited states contributing to the overall spectra distribution – however simulation is not as successful in this case. Perhaps evidence of missing excited states in the HF basis set expansion or a need to scale the HF-Slater parameters differently to Bi^{2+} ?

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Comparison of experiment with calculation (Bi^+).

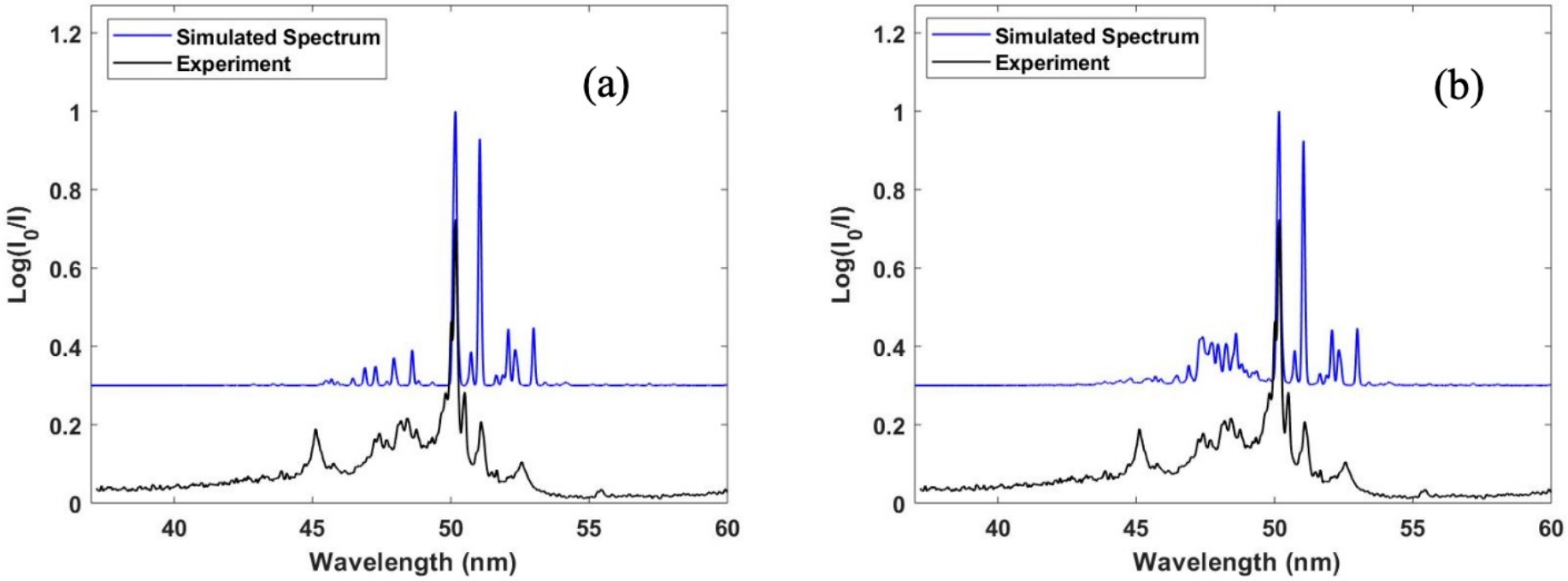

Figure 3. A comparison between the synthetic spectra and experimental data. (**a**) Simulated spectrum including photoabsorption from the ground electron configuration of Bi^+ only. (**b**) Simulated spectrum including photoabsorption both from the ground and from low-lying excited states of Bi^+.

The 5d-6p VUV Photoabsorption Spectrum of Bi^+, H Lu, L Varvarezos, P Hayden, E T Kennedy, J-P Mosnier and J T Costello, Atoms 8, Art. No. 55 (2020) - https://doi.org/10.3390/atoms8030055

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L Varvarezos et a;, J. Phys. B: At. Mol. Opt. Phys. 53 045701 (2020)

Motivation - Photoabsorption of **Photoionized Small Molecules**

- Low temperature photoionized plasmas constitute a quite unique state of matter
- Neutral atoms and molecules, radicals, ions and electrons can all be present when radiation in the SXR region is focused onto a dense gas medium
- Unlike the case of plasma formation directly by the optical laser, the SXR photon energy is high enough to ensure the release of core and valence electrons
- Photoionized plasmas are commonly encountered in astrophysics (see for example – B A Remington et al., Rev. Mod. Phys. 78 755–807 (2006)). E.g., plasmas generated in irradiated accretion disks around compact astrophysical objects such as neutron stars, black holes, or white dwarfs
- Quite and interdisciplinary area (J. Phys. D: Appl. Phys. 50 323001 (2017))

Soft x-ray photoabsorption spectra of photoionized CH_4 and CO_2 plasmas, L Varvarezos, H Lu, J T Costello, A Bartnik, P Wachulak, T Fok, L Wegrzynski and H Fiedorowicz, J. Phys. B: At. Mol. Opt. Phys. **53** 045701 (2020) - https://iopscience.iop.org/article/10.1088/1361-6455/ab5e31

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Photoabsorption of Photoionized Small Molecules

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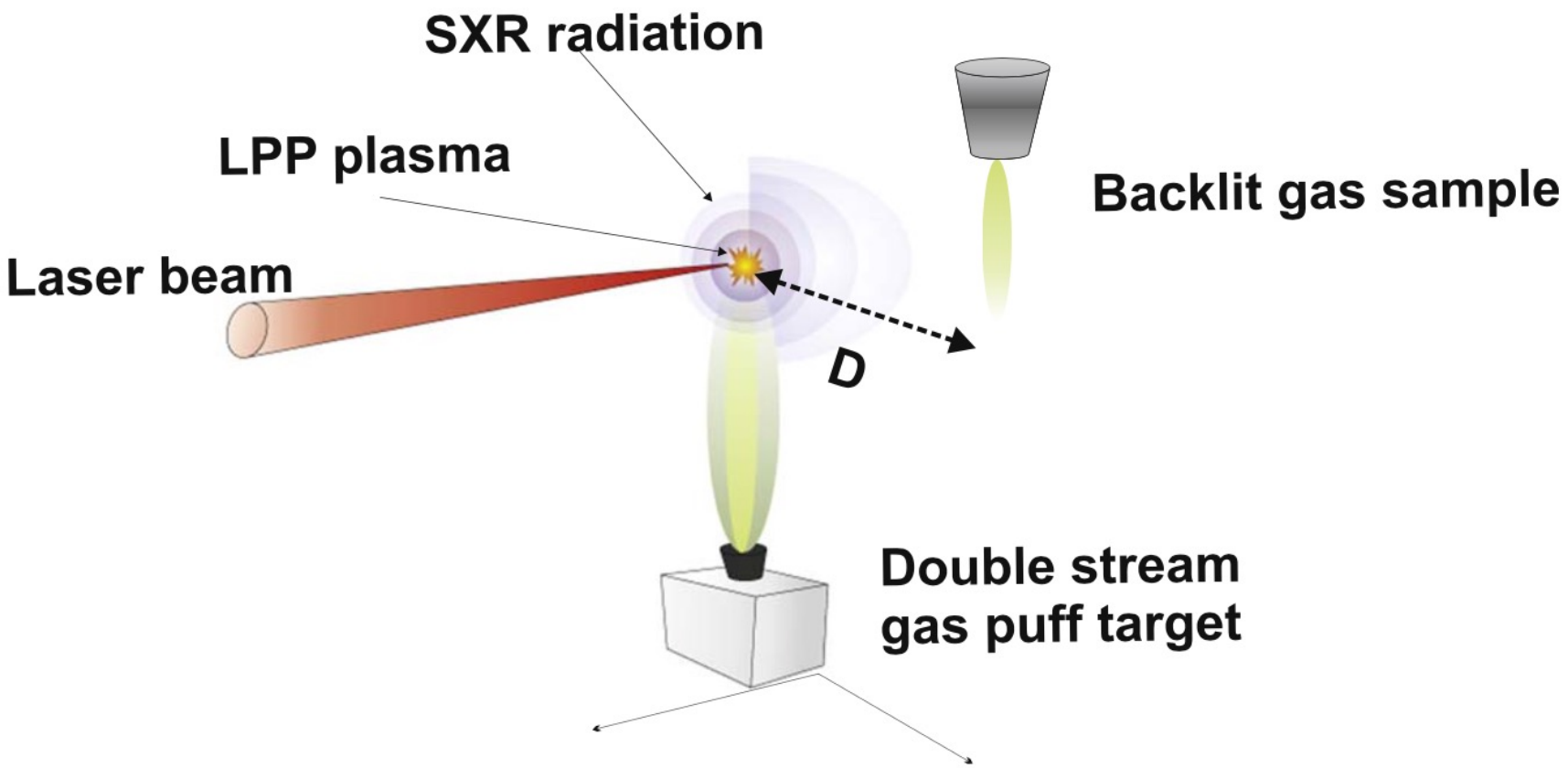
L Varvarezos et a;, J. Phys. B: At. Mol. Opt. Phys. 53 045701 (2020)



Soft x-ray photoabsorption spectra of photoionized CH_4 and CO_2 plasmas, L Varvarezos, H Lu, J T Costello, A Bartnik, P Wachulak, T Fok, L Wegrzynski and H Fiedorowicz, J. Phys. B: At. Mol. Opt. Phys. **53** 045701 (2020) - https://iopscience.iop.org/article/10.1088/1361-6455/ab5e31

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Photoabsorption of Photoionized Small Molecules

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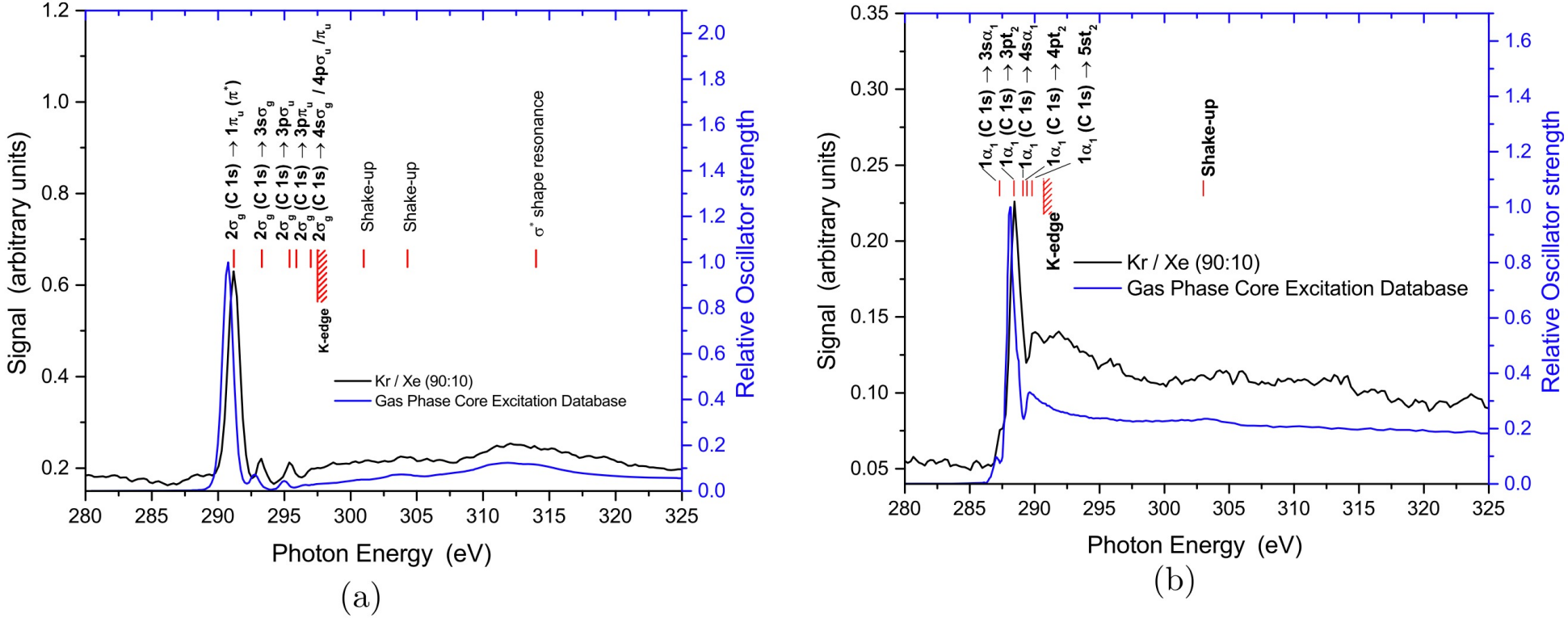

Figure 3. Experimental SXR absorption of the 'not ionized' (a) carbon dioxide and (b) methane plotted together with the normalized oscillator strength adapted from [33]. A gas mixture of xenon/krypton (90/10) was used as the medium to generate the soft x-ray backlighting radiation.

Soft x-ray photoabsorption spectra of photoionized CH_4 and CO_2 plasmas, L Varvarezos, H Lu, J T Costello, A Bartnik, P Wachulak, T Fok, L Wegrzynski and H Fiedorowicz, J. Phys. B: At. Mol. Opt. Phys. **53** 045701 (2020) - https://iopscience.iop.org/article/10.1088/1361-6455/ab5e31

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Photoabsorption of Photoionized Small Molecules

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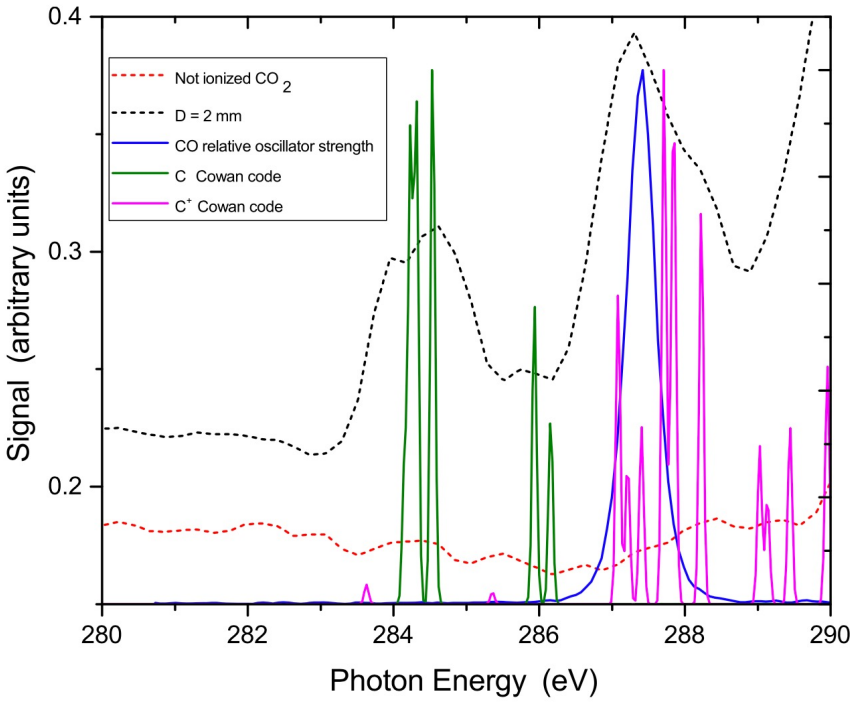
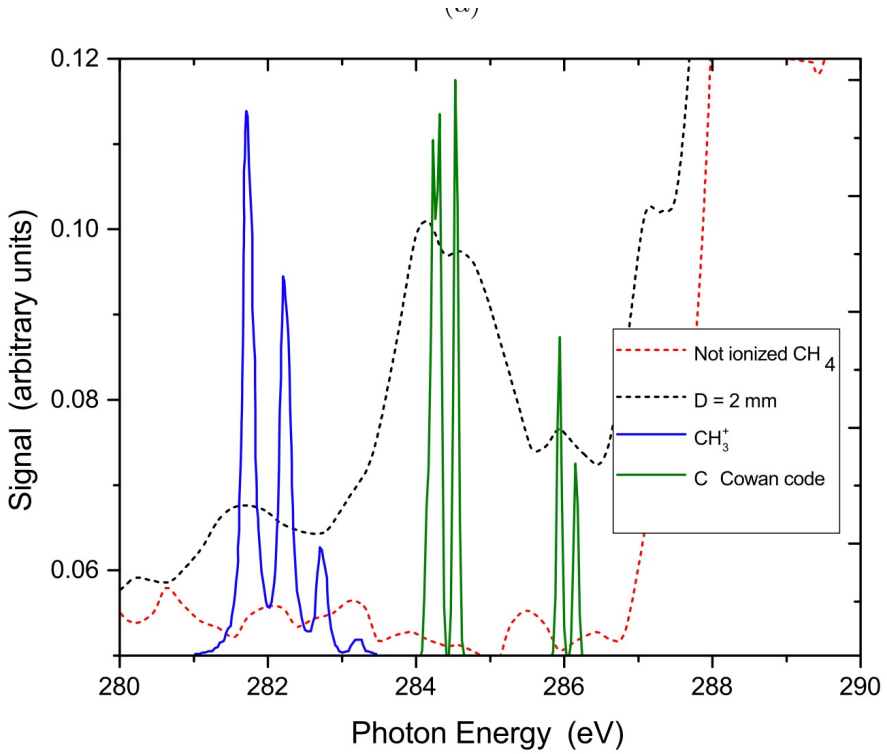


(a)



(b)

Figure 5. (a) The low-energy part of the Soft x-ray absorption spectrum of CO_2 plotted together with the normalized oscillator strength of CO [33], and calculations performed by means of the Cowan code for C and C^+. (b) Similar spectrum for CH_4 plotted together with the calculated absorption spectrum of CH_3 [41], and calculations performed by means of the Cowan code [46, 47] for C and C^+.

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Table 2. Tabulated transitions for the CO_2 and CH_4 plasmas, including transitions in CH_3^+, CO, C, C^+ species.

Photon energy (eV)	Molecular/ atomic species	Assignment
281.8	CH_3^+	$(1\alpha_1')(C1s) \longrightarrow (1\alpha_2'')\ (0-0)$
282.2	CH_3^+	$(1\alpha_1')(C1s) \longrightarrow (1\alpha_2'')\ (1-0)$
284.2	CI	$1s^22s^22p^2(^1S)^3P \longrightarrow 1s^12s^22p^3(^4S)^3S$
284.3	CI	$1s^22s^22p^2(^1S)^3P \longrightarrow 1s^12s^22p^3(^2D)^3D$
284.5	CI	$1s^22s^22p^2(^1S)^1D \longrightarrow 1s^12s^22p^3(^2D)^1D$
285.9	CI	$1s^22s^22p^2(^1S)^3P \longrightarrow 1s^12s^22p^3(^2P)^3P$
286.2	CI	$1s^22s^22p^2(^1S)^1D \longrightarrow 1s^12s^22p^3(^2P)^1P$
287.1	CII	$1s^22s^12p^2(^4S)^4S \longrightarrow 1s^12s^12p^3(^3P)^4P$
287.2	CII	$1s^22s^12p^2(^2P)^2P \longrightarrow 1s^12s^12p^3(^1S)^2S$
287.4	CII	$1s^22s^12p^2(^2D)^2D \longrightarrow 1s^12s^12p^3(^3P)^2P$
287.7	CII	$1s^22s^12p^2(^2D)^2D \longrightarrow 1s^12s^12p^3(^1D)^2D$
287.8	CII	$1s^22s^22p^1(^1S)^2P \longrightarrow 1s^12s^22p^2(^1D)^2D$
287.9	CII	$1s^22s^22p^1(^1S)^2P \longrightarrow 1s^12s^22p^2(^3P)^2P$
288.2	CII	$1s^22s^12p^2(^2D)^4D \longrightarrow 1s^12s^12p^3(^3P)^4P$
287.4	CO	$2\sigma(C1s) \longrightarrow 1\pi_u$, π *resonance*

For photoionized CO2, oxygen absorption cf.

Oxygen K-shell photoabsorption spectra of photoionized CO2 plasmas
L Varvarezos, Hu Lu, J T Costello, A Bartnik, P Wachulak, T Fok, Ł Węgrzyński and H Fiedorowicz J. Phys. B: At. Mol. Opt. Phys. **53** 105701 (2020) - https://doi.org/10.1088/1361-6455/ab78ab

Soft x-ray photoabsorption spectra of photoionized CH_4 and CO_2 plasmas, L Varvarezos, H Lu, J T Costello, A Bartnik, P Wachulak, T Fok, L Wegrzynski and H Fiedorowicz, J. Phys. B: At. Mol. Opt. Phys. **53** 045701 (2020) - https://iopscience.iop.org/article/10.1088/1361-6455/ab5e31

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L Varvarezos et a;, J. Phys. B: At. Mol. Opt. Phys. 53 045701 (2020)

DLPP - Some final points

- Opens up both valence and inner shell excitation of atoms and molecules inn neutral to moderately ionized states
- Offers a degree of control over the ion stage under study (dx, dt/ laser-I, λ, etc)
- Opens up the study of photoabsorption along isonuclear and isoelectronic sequences
- Has the possibility to track and extract 'column densities' in space and time
- Can complement optical diagnostics – sense cool environments
- Can complement/augment work on merged ion beams with synchrotron experiments (e.g., [1]) or multiple photoionization with FELs [e.g., 2])

1. *The photon-ion merged-beams experiment PIPE at PETRA III - The first five years*, S Schippers et al., *X-Ray Spectrometry* **49** pp11–20 (2020)

2. *Near-Threshold Two-Photon Double Ionization of Kr in the Vacuum Ultraviolet*, L Varvarezos et al, *Phys. Rev A* **103** Art. No. 022832 (2021)

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Perspectives for X-VUV laser/laser plasma based research

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L Varvarezos et a;, J. Phys. B: At. Mol. Opt. Phys. 53 045701 (2020)

- Will mainly remain a ‘niche’ research area but works where offline is possible
- Benefits of access to resonance lines and continua of all atomic species remain
- New frontiers e.g., attosecond transient absorption spectroscopy (ATAS) [1]
- Non linear photoionization processes involving inner shells. E.g., two X-VUV photon absorption leading to femtosecond photo and Auger electron emission [2,3].
- Pump-probe with fs jitter (using injection seeded X-VUV FELs) [4,5]

1. *UF dissociation of vinyl bromide: An attosecond transient absorption spectroscopy and non-adiabatic molecular dynamics study*, R Flott et al., Struct. Dyn. **8**, 034104 (2021) / J. Phys. B: At. Mol. Opt. Phys. 49 (2016) 062001
2. *Two-photon inner-shell ionization in the extreme-ultraviolet*, V Richardson et al., Phys. Rev. Lett 105, Art. No. 013001 (2010)
3. *Clocking Auger electrons*, D C Haynes et al., Nature Physics 17 pp.512–518 (2021)
4. *Coherent control with a short-wavelength free-electron laser*, K. C. Prince et al., Nat. Phot. **10**, 176 - 180 (2016)
5. Tracking attosecond electronic coherences using phase-manipulated extreme ultraviolet pulses, A. Wituschek et al., Nature Communications volume 11, Article No. 883 (2020)

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Perspectives for X-VUV laser/laser plasma based research

Impulsive alignment of C2H2 with ionization dissociation of molecules: BEAMTIME NO. 20194063

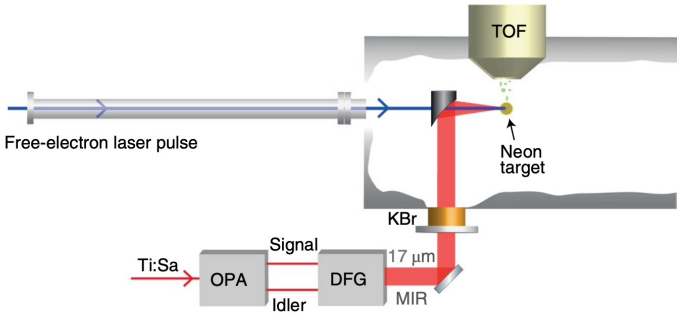
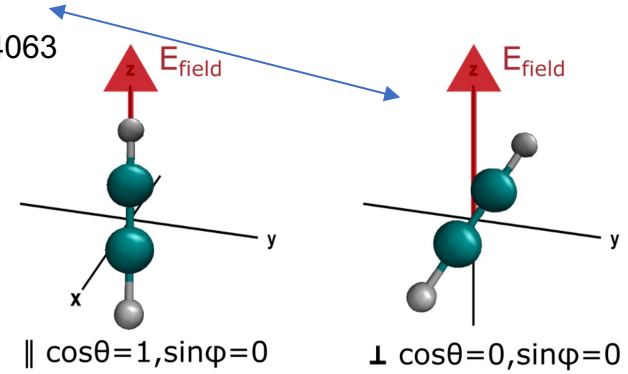


Fig. 1 | Mid-infrared streaking. 17 μm mid-infrared (MIR) streaking laser pulses are generated by downconversion of a near-infrared titanium:sapphire (Ti:Sa) laser pulse, using an optical parametric amplifier (OPA) and difference frequency generation (DFG), and coupled into a chamber through a potassium bromide (KBr) window. The mid-infrared pulses are focused with a parabola of focal length 100 mm and overlapped with 7 fs, 1,130 eV free-electron laser pulses in a neon gas target. The resultant streaked photo and Auger electron emission is measured using a large-acceptance time-of-flight (TOF) spectrometer.

Nature Physics **17** pp.512–518 (2021)



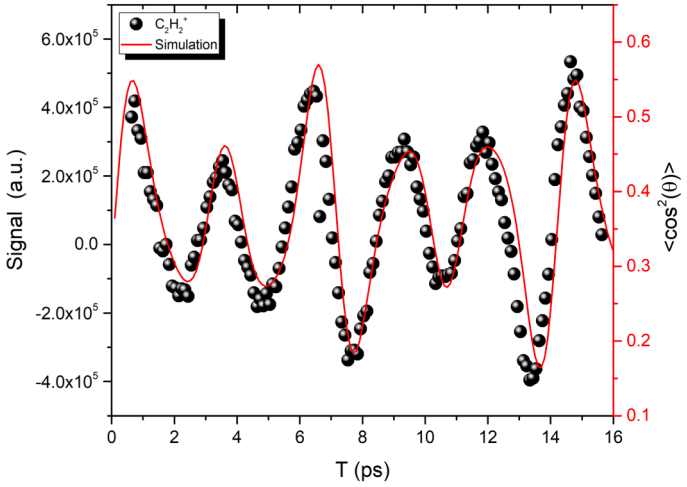
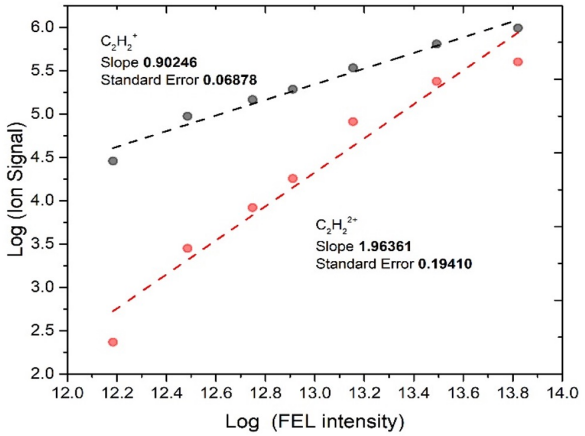


Figure 1. Measured signal (black circles) and simulation (<cos²θ>, red line) for the singly charged acetylene ion. The experimental data were obtained by subtracting the (optical) 'laser-off' signal from the 'laser-on' signal.



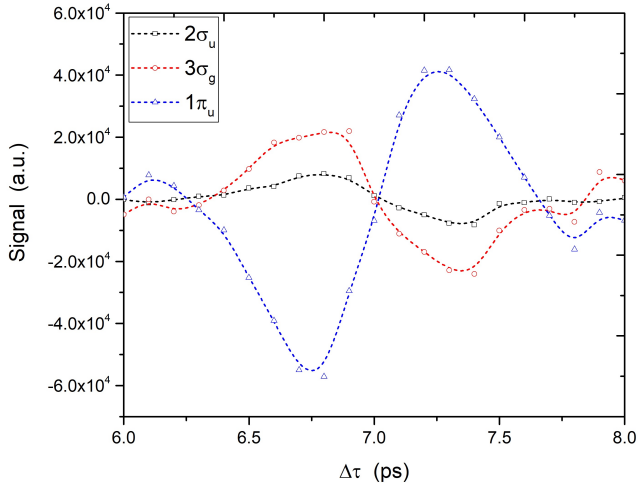


FIG. 2. Photoelectron yields for a range of time delays in the vicinity of the half revival period.

L Varvarezos et a;, J. Phys. B: At. Mol. Opt. Phys. 53 045701 (2020)

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EMSLIBS 2021

Perspectives for X-VUV laser/laser plasma based research

DCU
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Dublin City University

TA – LIBS in the UV—Visible-NIR?

Current (TA)-LIBS Focus and Future Developments

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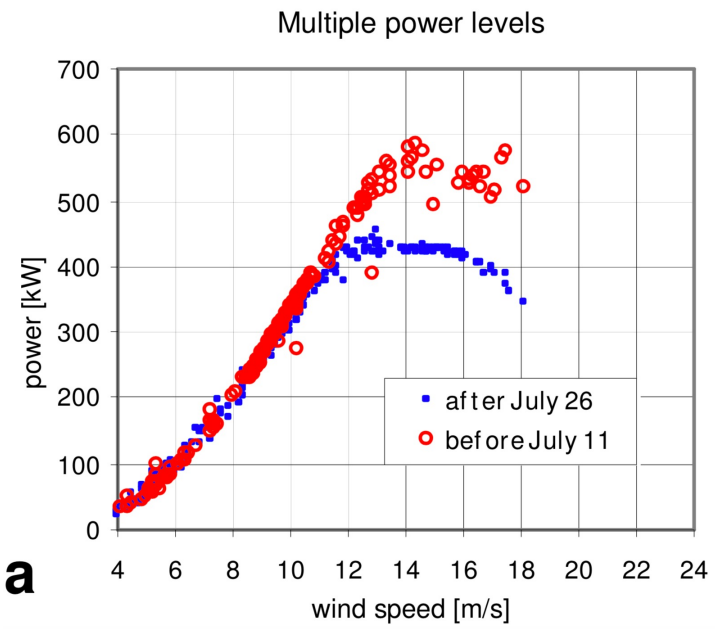
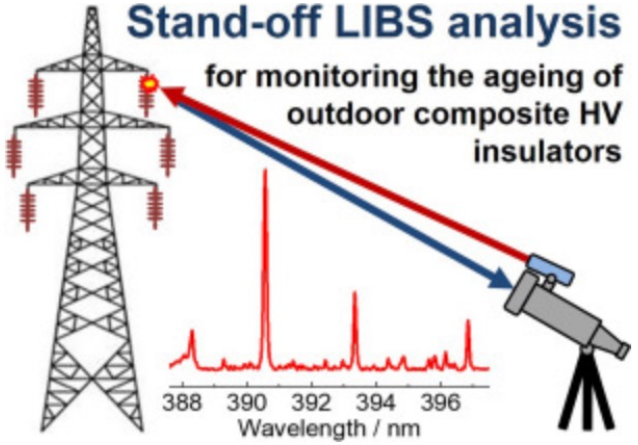
Dublin City University

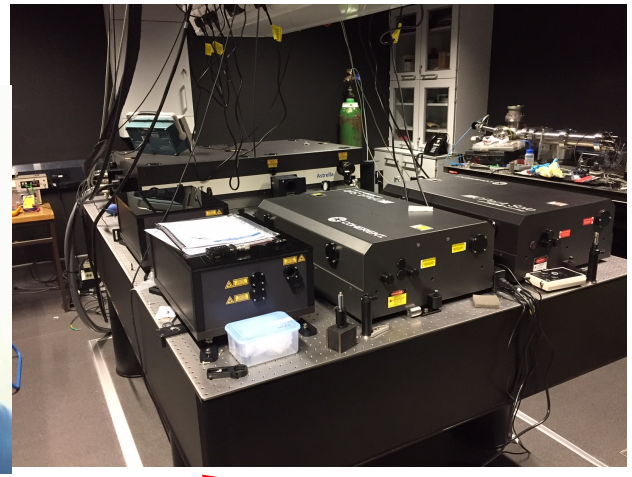
Focus: Wind Energy – Wind Turbine Blades

NATURE | VOL 412, 2001, pp42-43



Spectrochimica Acta Part B 165 (2020) 105768





EUVL Resist Materials (Synthesis & Dynamics)

Current (TA)-LIBS Focus and Future Developments

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Dublin City University

On Wind Turbine LIBS and LA

Related Poster - P_IND6 - S. Cummins - UV-Visible and Vacuum-UV LIBS on Wind Turbine Blade Samples

Wednesday – December 1st

Current LIBS Focus and Future Developments

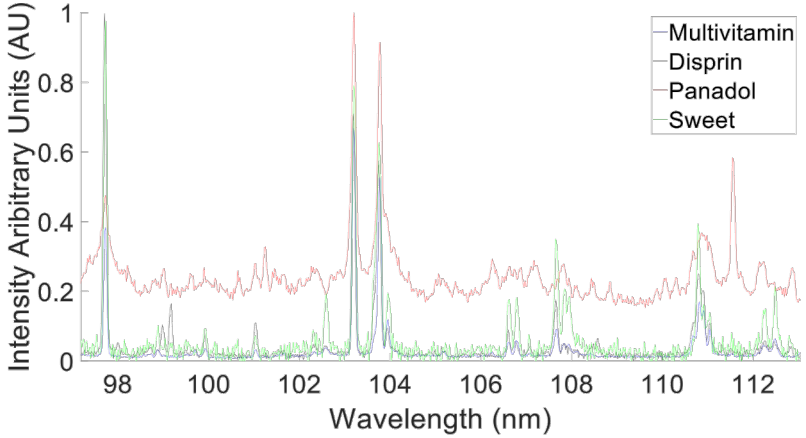
Ollscoil Chathair Bhaile Átha Cliath
Dublin City University

Theme: ***LIBS for Future Pharmaceutical PATs***

Focus: ML- Assisted Chemometrics (P Hayden (now UCD) + IBM)

M B Alli, PhD Thesis, DCU (2021)

A)



B)

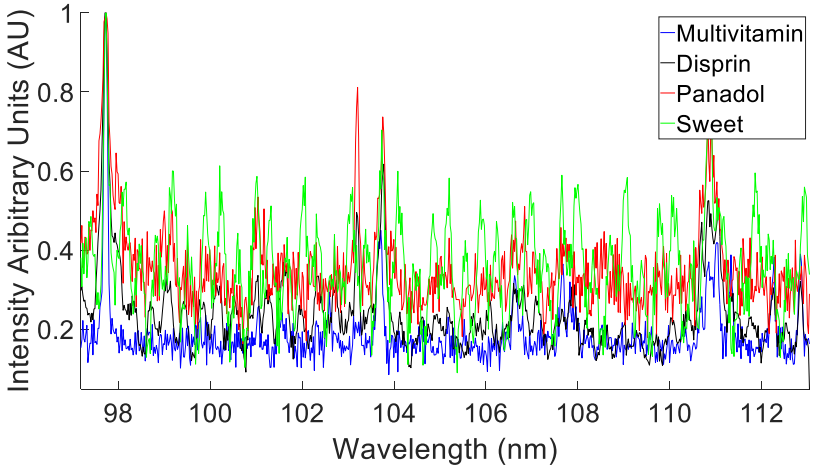


Table 5.4: % Accuracy ,comprehensive study, 160 spectra tested.

	Wavelength Range		
Technique	**65 nm**	**105 nm**	**Average**
SOM 2x2	52.50	0.00	**26.25**
SOM 3x3	81.25	10.63	**45.94**
SOM 4x4	73.13	32.50	**52.81**
SOM 5x5	81.25	13.75	**62.50**
PCA	66.25	41.88	**54.06**
COMP	69.38	0.63	**35.01**
CNN	95.00	91.88	**93.44**

Current LIBS Focus and Future Developments

Ollscoil Chathair Bhaile Átha Cliath
Dublin City University

Theme: ***Light Elements in Steel***
Focus: Line focus VUV LIBS (and Time Resolved LIBS)

Related Poster - P_CQ8 – S S Zehra, L Varvarezos et al. - Limit of Detection for Carbon in Steel using Time Integrated Space Resolved (TISR) VUV LIBS: Line versus Point Plasma Plumes.

Wednesday – December 1st

Current Students/PDs

DCU
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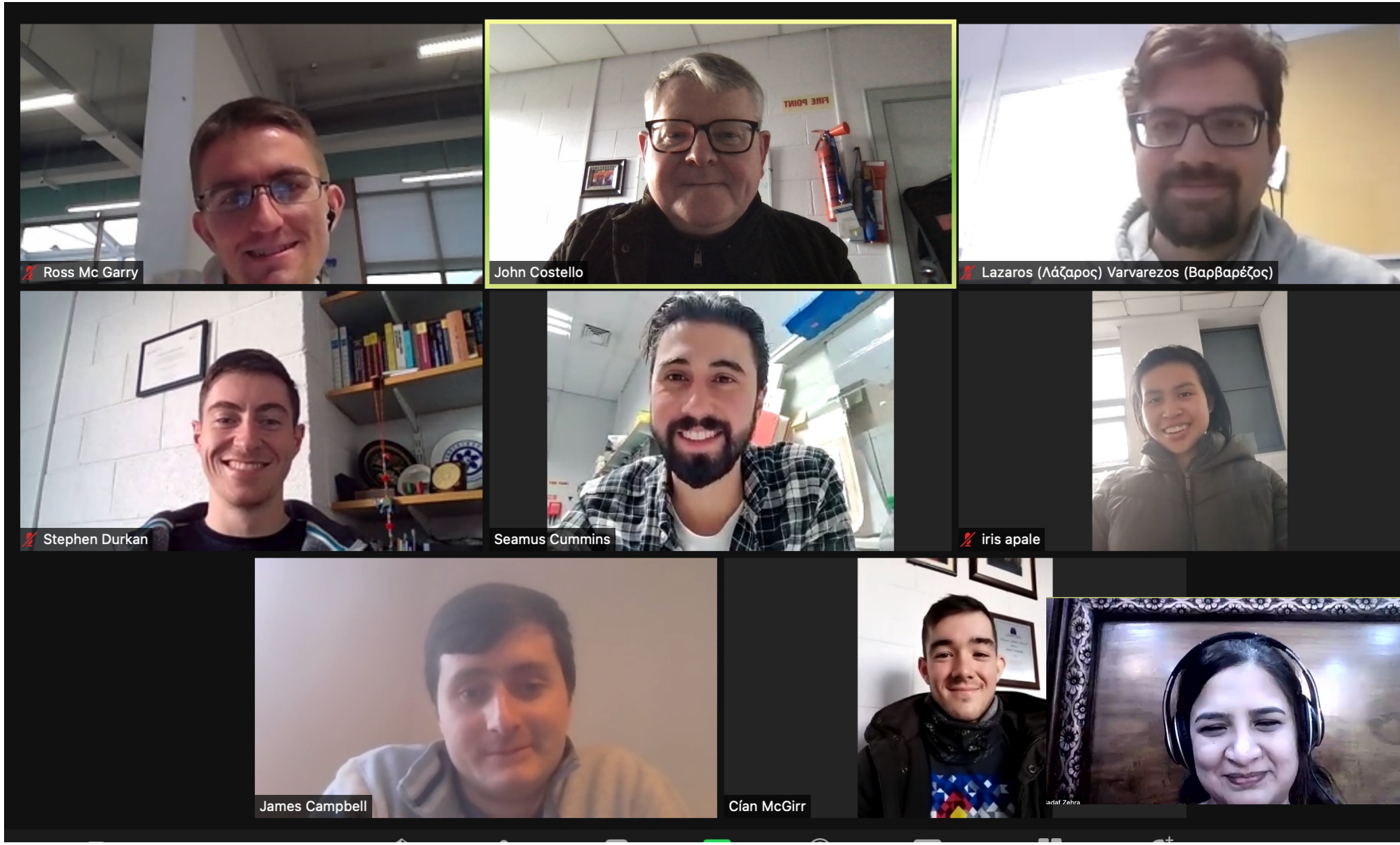
Bhaile Átha Cliath
Dublin City University



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SEAI - Sustainable Energy Authority Of Ireland - Research, Development & Demonstration (RD&D) programme