Simulating photo-excitation with a laser pulse beyond the perturbative limit

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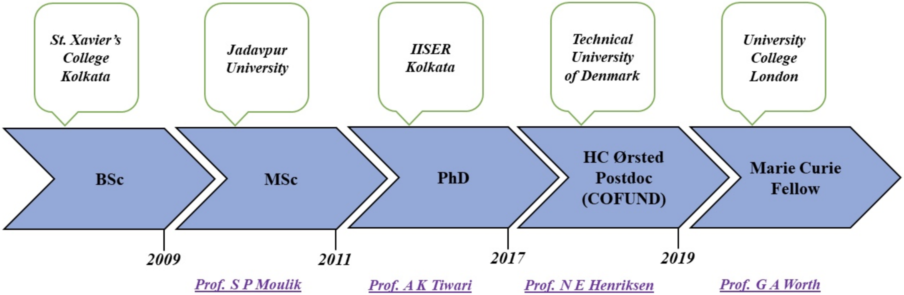
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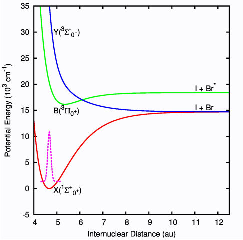
2009
2011
2017
2019
Prof. S P Moulik
Prof. A K Tiwari
Prof. N E Henriksen
Prof. G A Worth

- *Non-adiabatic effects in photochemistry*
- *Coherent control of molecular systems*
- *Environmental effects (solvent, temperature)*



- *Dynamics Methods: MCTDH, ML-MCTDH, DD-vMCG, Quantum-Ehrenfest, Surface Hopping, Density Matrix*
- *Quantum Chemistry: CASSCF//CASPT2, EOM-CCSD, ADC(2), TDDFT*

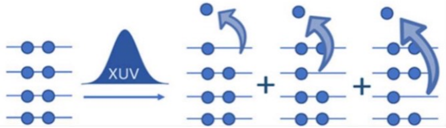
Project#1

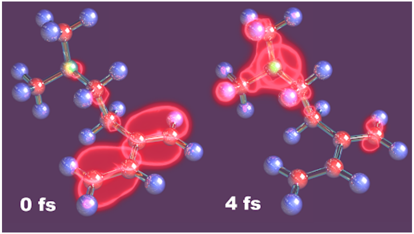
- *Simulating Intramolecular Charge Migration on Attosecond Timescales (SICMA)*
  - *Prof. Alex Kuleff (Heidelberg University)*
  - *Profs. Mike Robb & Jon Marangos (Imperial College London)*

Project#2

- *Time-Resolved Photoelectron Spectroscopy (TRPES)*
  - *Prof. Helen Fielding (University College London)*

Simulating Intramolecular Charge Migration on Attosecond timescales





Short pulse $\rightsquigarrow$ localized 'Hole'; undergoes periodic oscillations..

- ❑ *Coherent superposition of electronic states is a non-stationary WP!*

① *How to create a superposition of electronic states (WP)?*

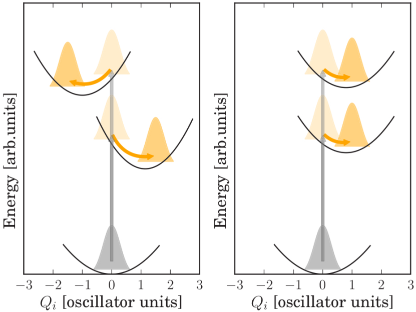
② *How the electronic dynamics will be affected by nuclear motion?*

③ *Can this correlated motion be controlled?* *Charge-directed reactivity!*

☞ *Understanding electron correlation & fast electron-nuclear coupling*

[1] F. Remacle and R. D. Levine, PNAS **103**, 6793 (2006).

[2] Image Source: Internet; http://ngolubev.com/



- *The topology of PESs modulate loss-of-overlap or de-coherence*
- *Electronic coherence typically lasts for 10 fs or less! (Problem)*

Challenge:

☞ *to understand to what extend the electronic coherence will retain in presence of interactions with nuclear DOF*

Central aspect in diverse fields like Quantum Computing, Light Harvesting

[3] C. Arnold, O. Vendrell and R. Santra, Phys. Rev. A **95**, 033425 (2017).

attosecond XUV pump // NIR probe

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REPORT

Ultrafast electron dynamics in phenylalanine initiated by attosecond pulses

F. CALEGARI, D. AYUSO, A. TRABATTONI, L. BELSHAW, S. DE CAMILLIS, S. ANUMULA, F. FRASSETTO, L. POLETTO, A. PALACIOS, [...] M. NISOLI +4 authors Authors Info & Affiliations

SCIENCE • 17 Oct 2014 • Vol 346, Issue 6207 • pp. 336-339 • DOI: 10.1126/science.1254061

HHG spectroscopy

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REPORT

Measurement and laser control of attosecond charge migration in ionized iodoacetylene

P. M. KRAUS, B. MIGNOLET, D. BAYKUSHEVA, A. RUPENYAN, L. HORNÝ, E. F. PENKA, G. GRASSI, O. I. TOLSTIKHIN, J. SCHNEIDER, [...] H. J. WÖRNER +5 authors
Authors Info & Affiliations

SCIENCE • 22 Oct 2015 • Vol 350, Issue 6262 • pp. 790-795 • DOI: 10.1126/science.aab2160

X-ray pump // X-ray probe (XAS, XPS)

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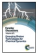
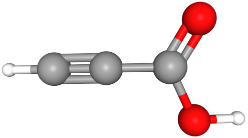
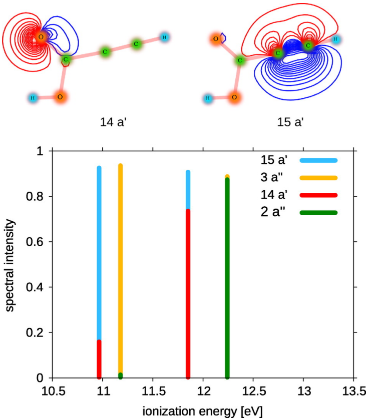


From the journal:
Faraday Discussions

Analysis of a measurement scheme for ultrafast hole dynamics by few femtosecond resolution X-ray pump–probe Auger spectroscopy

Bridgette Cooper,[a] Přemysl Kolorenč,[b] Leszek J. Frasinski,[a] Vitali Averbukh[a] and Jon P. Marangos*[a]





$$(core)^{10}(6a')^2(7a')^2(8a')^2(9a')^2(10a')^2$$
$$(11a')^2(12a')^2(1a'')^2(13a')^2(2a'')^2$$
$$(14a')^2(15a')^2(3a'')^2$$

4 Lowest Cationic States

$+$

15 Vibrational Normal Modes

[4] N. V. Golubev, V. Despré and A. I. Kuleff, J. Mod. Opt. **64**, 1031 (2017).
[5] V. Despré, N. V. Golubev and A. I. Kuleff, Phys. Rev. Lett. **121**, 203002 (2018).

❑ *Multi-Configuration Time-Dependent Hartree (MCTDH)*

$$MC\ Ansatz: \quad \Psi(Q_1, ..., Q_f, t) = \sum_{j_1=1}^{n_1} ... \sum_{j_f=1}^{n_f} A_{j_1...j_f}(t) \prod_{\kappa=1}^{f} \varphi_{j_\kappa}^{(\kappa)}(Q_\kappa, t)$$

MCTDH expansion coefficients, $A_{j_1...j_f}$

Single particle functions (SPFs), $\varphi_{j_\kappa}^{(\kappa)}(Q_\kappa, t) = \sum_{i_\kappa=1}^{N_\kappa} c_{i_\kappa j_\kappa}^{(\kappa)}(t)\chi_{i_\kappa}^{(\kappa)}(Q_\kappa)$

❑ *Vibronic Coupling (VC) Hamiltonian (diabatic basis)*

$$\hat{\mathbf{H}} = H^{(0)} + W^{(0)} + W^{(1)} + W^{(2)} + ...$$

$$H^{(0)} = T_N + V_0 = \sum_\alpha \frac{\omega_\alpha}{2}\left(-\frac{\partial^2}{\partial Q_\alpha^2} + Q_\alpha^2\right)$$

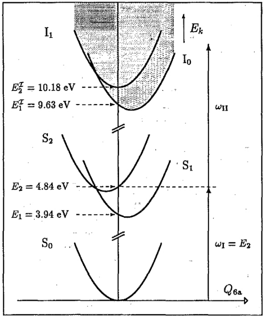
$$W^{(0)} = E_i \qquad W_{ii}^{(1)} = \sum_\alpha \kappa_\alpha^{(i)} Q_\alpha \qquad W_{ij}^{(1)} = \sum_\alpha \lambda_\alpha^{(i,j)} Q_\alpha$$

QUANTICS

A suite of programs for molecular QUANTum dynamICS simulations.

[6] G. A. Worth and L. S. Cederbaum, Annu. Rev. Phys. Chem. **55**, 127 (2004).

☞ *Electronic (model) space: ionization continua*
$+$
lowest cationic states

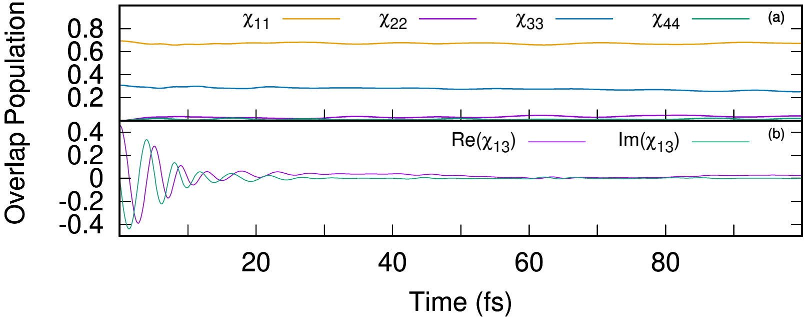


- *Ionization continua added explicitly to represent ejected electrons*
- *No interaction of ejected electron & molecular ion – Approximation!*
- *Photoelectron spectrum: population of continuum states (long time)*

[7] M. Seel and W. Domcke, J. Chem. Phys. **95**, 7806 (1991).
[8] G. A. Worth, R. E. Carley and H. H. Fielding, Chem. Phys. **338**, 220 (2007).

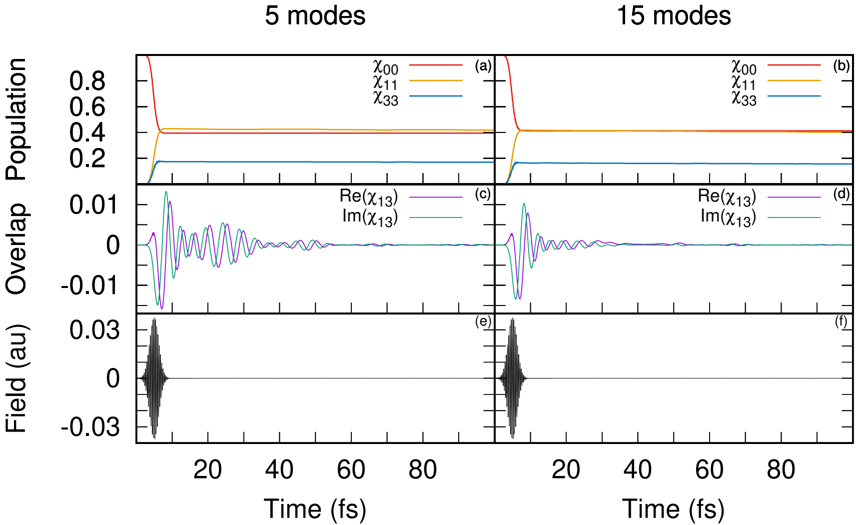
☞ *Modeling the onset of charge migration via Sudden Ionization*

- ❑ *1st & 3rd cationic states are linear combinations of two 1h configurations (66.7% + 33.3% population)*
- ❑ *in-phase superposition!*



- ❑ *Oscillation period ∼6.2 fs corresponds to the energy gap!*

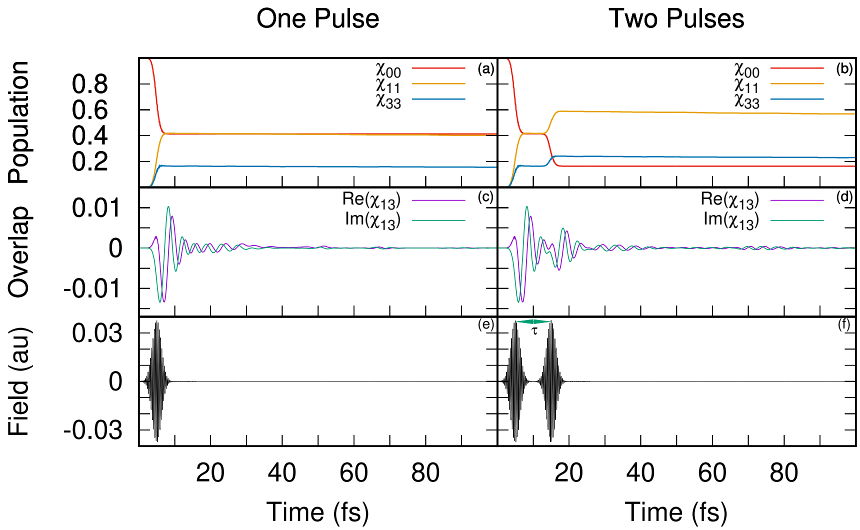
XUV-Pulse Ionization $11.8\ \mathrm{eV} \sim 105\ \mathrm{nm}$ $3\ \mathrm{fs}$ $10^{15}\ \mathrm{Wcm}^{-2}$



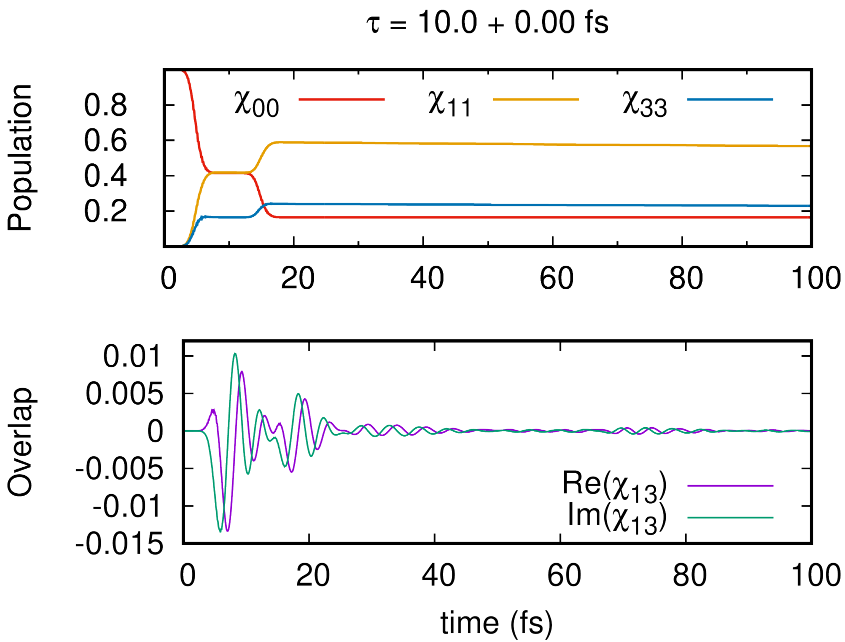
☞ *fs nuclear dynamics governs as electron dynamics*

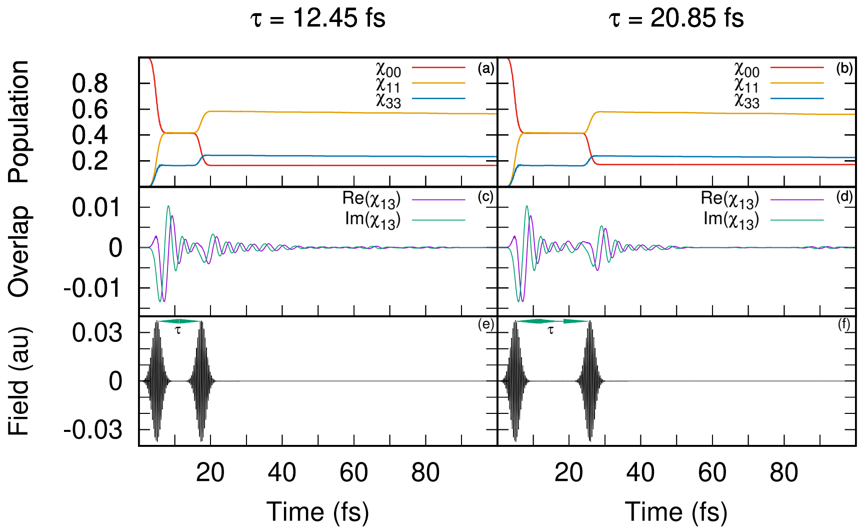
CEP=0 *No significant CEP effect!*

☞ *Can we manipulate/control electronic coherence (in a simple way)?*



$t' = t_0 + \tau$ *Time Delay* $(\tau) = 10$ fs $\Delta t = 350$ as


τ = 10.0 + 0.00 fs
Population
χ00
χ11
χ33
0.8
0.6
0.4
0.2
0
20
40
60
80
100
Overlap
0.01
0.005
0
-0.005
-0.01
-0.015
Re(χ13)
Im(χ13)
time (fs)



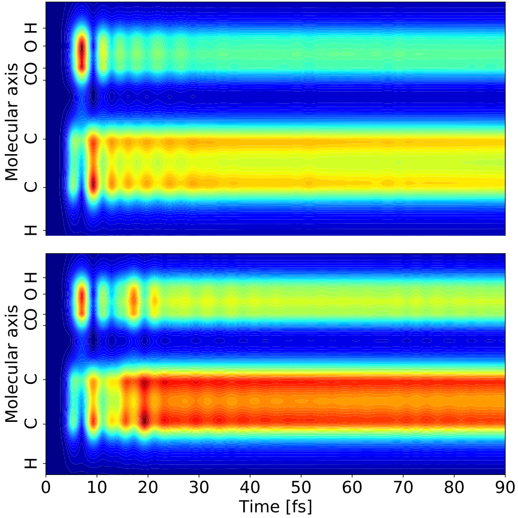
Quantum Interference (Time-Delay) Control!

[9] S. A. Rice, Nature **409**, 422 (2001).

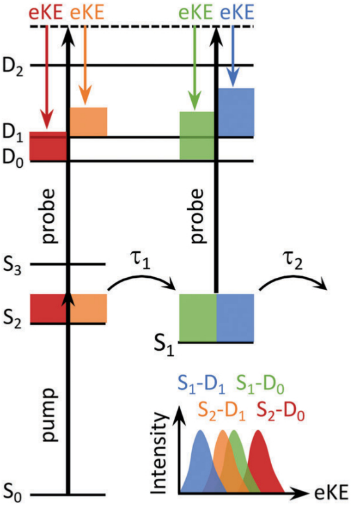
$$Q(\vec{r},t) = \chi_{00} \langle \Phi_0^N | \hat{\rho} | \Phi_0^N \rangle - \sum_{i,j} \chi_{ij}(t) \langle \Phi_i^{N-1} | \hat{\rho} | \Phi_j^{N-1} \rangle$$

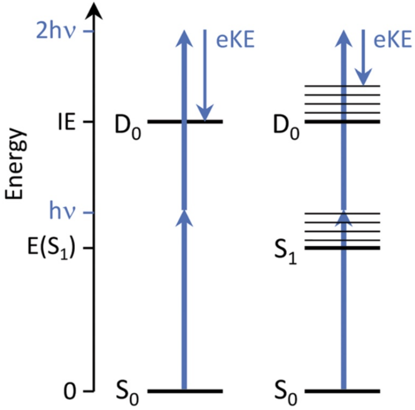
One Pulse

Two Pulses



[10] A.I. Kuleff, J. Breidbach, and L. S. Cederbaum, JCP **123**, 044111 (2005).



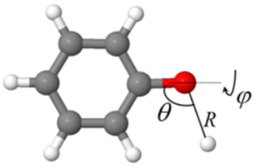


"Direct 2-Photon Ionization"

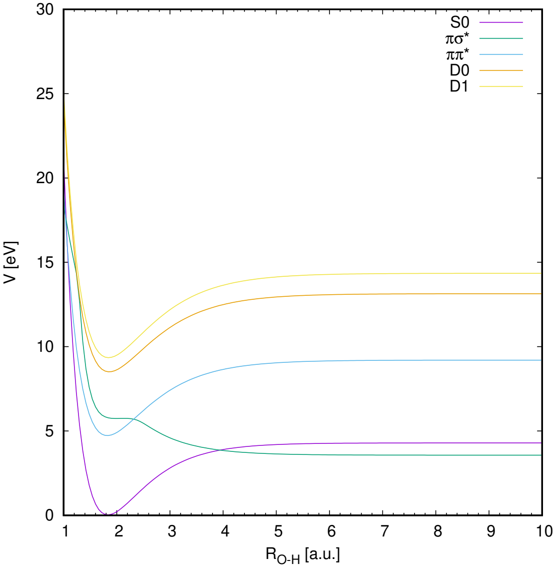
$$eBE = 2h\nu - eKE$$

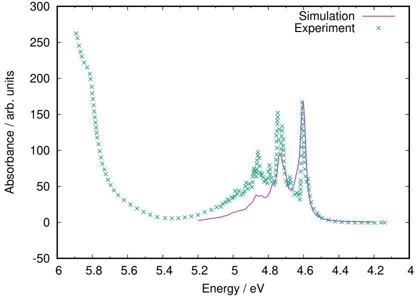
..if vibrational energy is conserved upon ionization

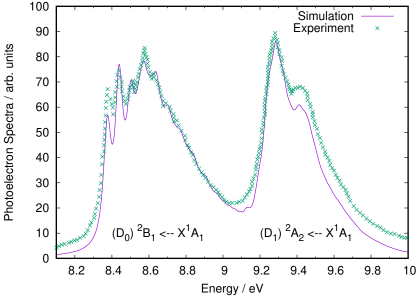
[11] H. Fielding and G. A. Worth, Chem. Soc. Rev. **47**, 309 (2018).



$^1\pi\pi^*$ *Bright*
$^1\pi\sigma^*$ *Dark*







UV Absorption Spectrum
$^1B_2 \leftarrow \tilde{X}^1A_1$

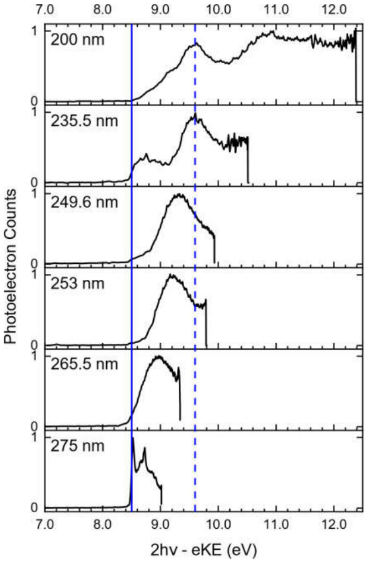
Photoelectron Spectrum
$^2B_1 \leftarrow \tilde{X}^1A_1$ & $^2A_2 \leftarrow \tilde{X}^1A_1$

Vertical Excitation..

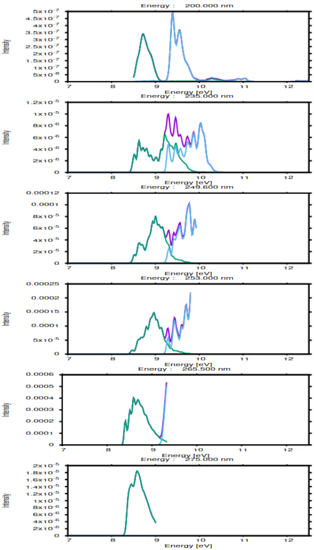
$C(t) = \langle \Psi(0) | \Psi(t) \rangle \qquad I(\omega) \propto \omega \int_{-\infty}^{\infty} dt C(t) e^{i\omega t}$

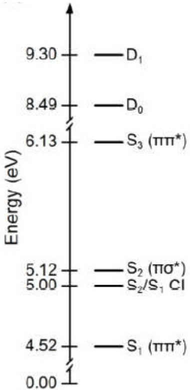
[12] M. P. Taylor and G. A. Worth, Chem. Phys. **515**, 719 (2018).

Experiment (H. Fielding)



Our Simulations





- *Prof. Graham Worth and his group*

- *Profs. Jon Marangos, Mike Robb (Imperial College London)*
- *Prof. Alex Kuleff (Heidelberg University)*
- *Prof. Helen Fielding (University College London)*

European Commission


Thank You