Exploring Intermolecular Coulombic Decay by Free Electron Lasers

or

How energy deposited by FEL on one site in a medium can be transferred fast to the surrounding

Lorenz S. Cederbaum

Theoretische Chemie
Physikalisch-Chemisches Institut
Universität Heidelberg

How does an isolated excited ion decay?

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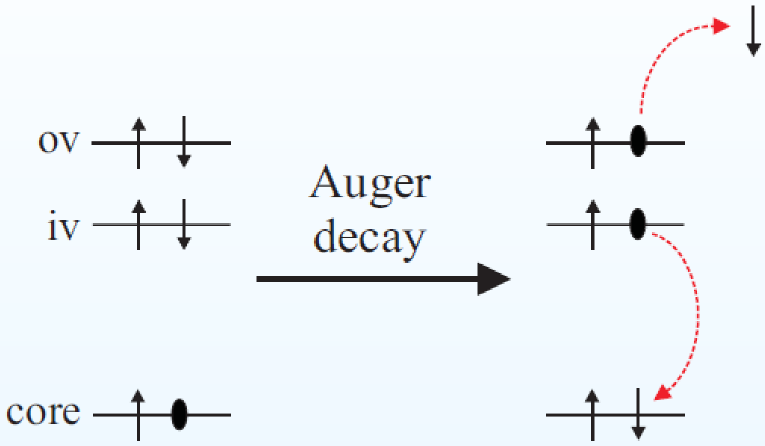

$$A^{+^*} \rightarrow A^{++} + e^-$$

- wide range of applications
- ultrafast process – fs ÷ as

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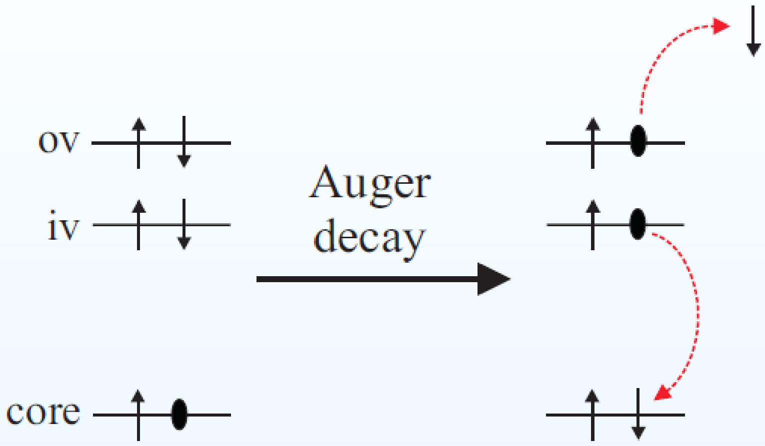

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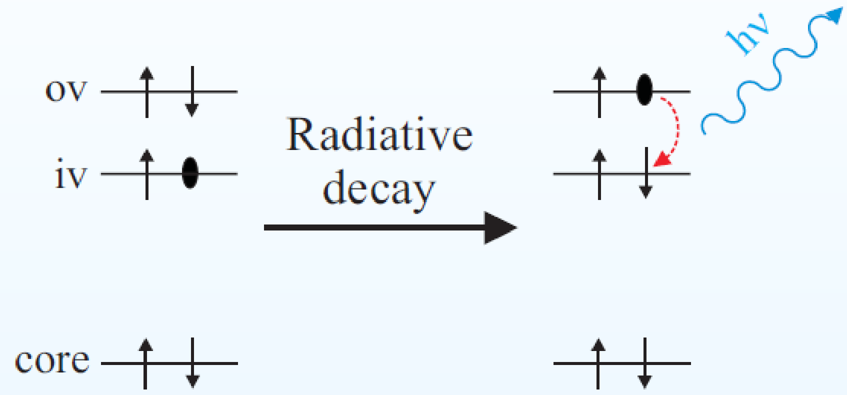
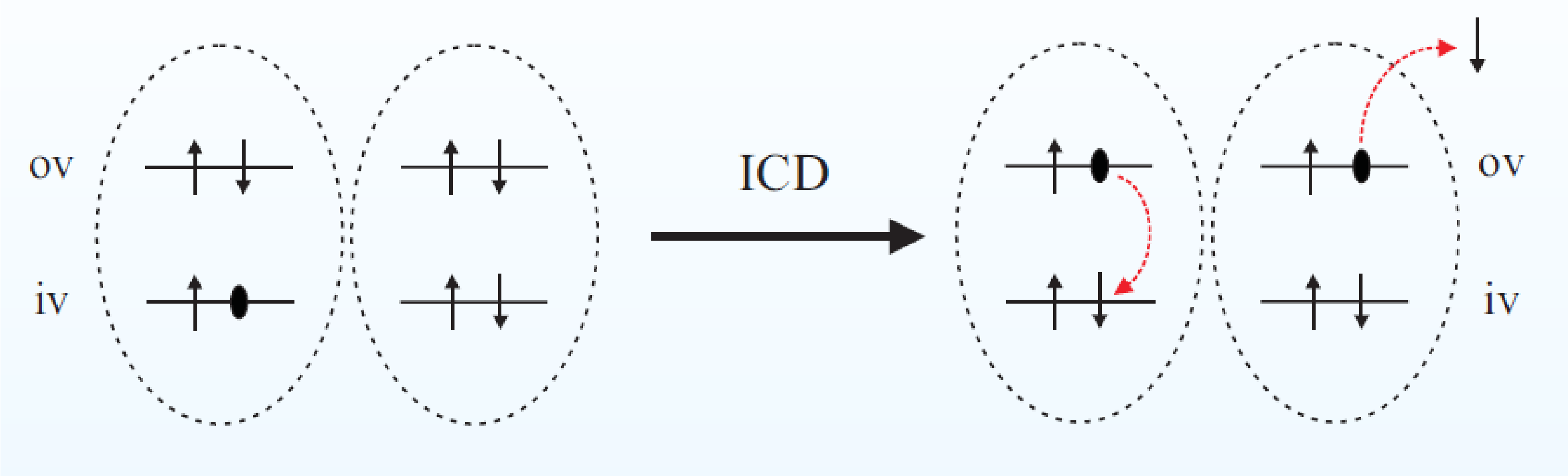


$$A^{+^*} \rightarrow A^{+} + h\nu$$

- wide range of applications
- slow process – ns

ICD L.S. Cederbaum, J. Zobeley, and F. Tarantelli, *PRL* **79**, 4778 (1997)



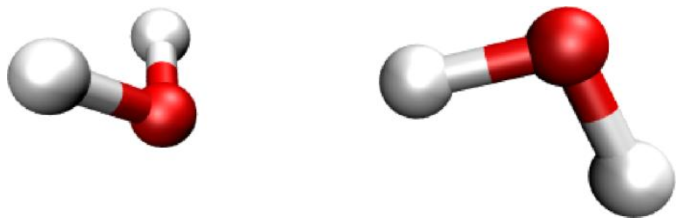
$$A^{+*} \cdots\cdots B \longrightarrow A^{+} \cdots\cdots B^{+} + e^{-}$$

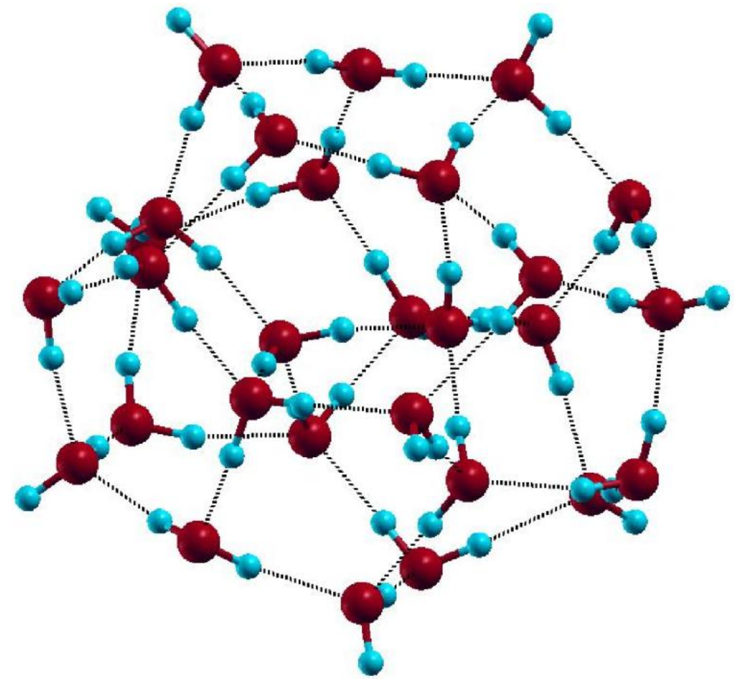
- ICD is a general phenomenon
  - hydrogen bonded clusters – $(H_2O)_n$, $(HF)_n$,...
  - van der Waals clusters – Ne_n, Ne_nAr_m, MgNe, CaNe,... even He_2
  - quantum dots
- Ultrafast process – fs regime • Faster with more neighbors
- Source of LEE → biological relevance

ICD
in water

L. S. Cederbaum, J. Zobeley and F. Tarantelli, *PRL* **79**, 4778 (1997)
I. B. Müller and LSC, *J. Chem. Phys.* **125**, 204305 (2006)
O. Vendrell, S. Stoychev and LSC, *Chem. Phys. Chem.* **11**, 1006 (2010)

ICD in water





Dimer:

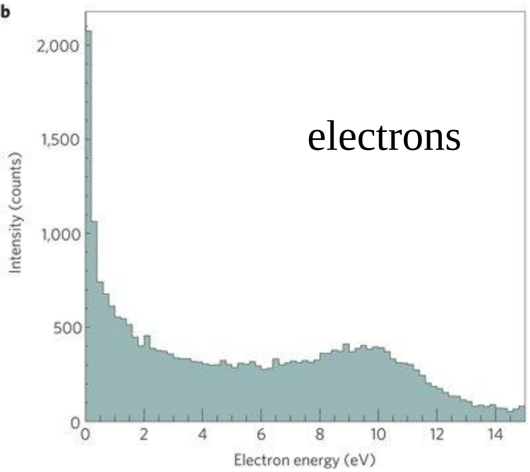
T. Jahnke, R. Dörner *et al.*,
Nature Phys. **6**, 139 (10)

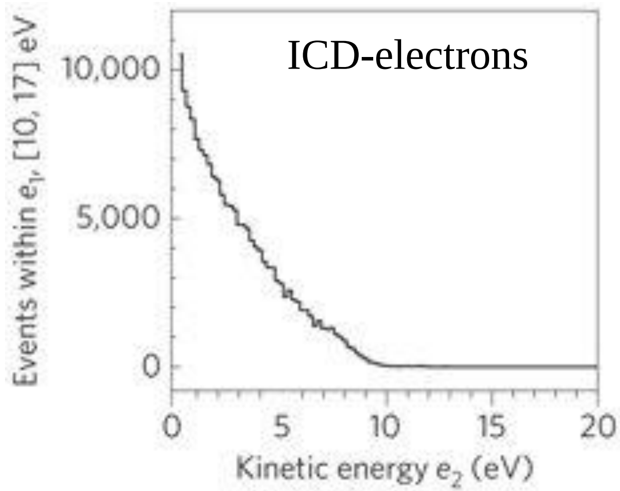
Electron-ion coincidence experiments

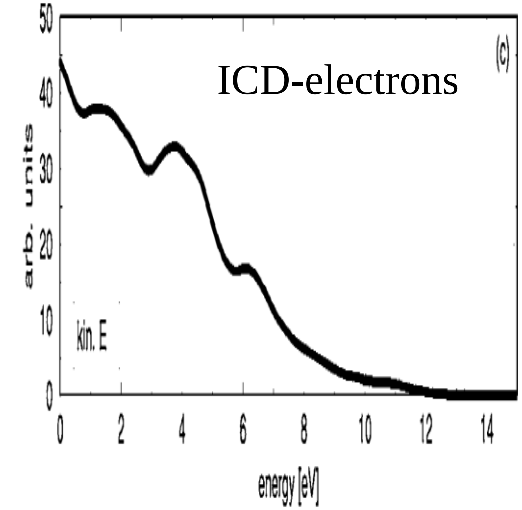
Large clusters:

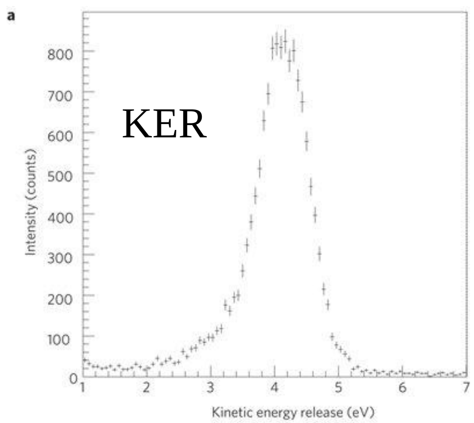
M. Mucke, U. Hergenhahn *et al.*,
Nature Phys. **6**, 143 (10)

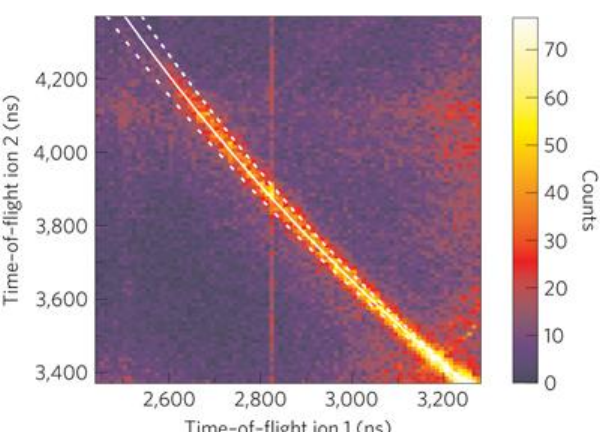
Sum of electron energy experiments

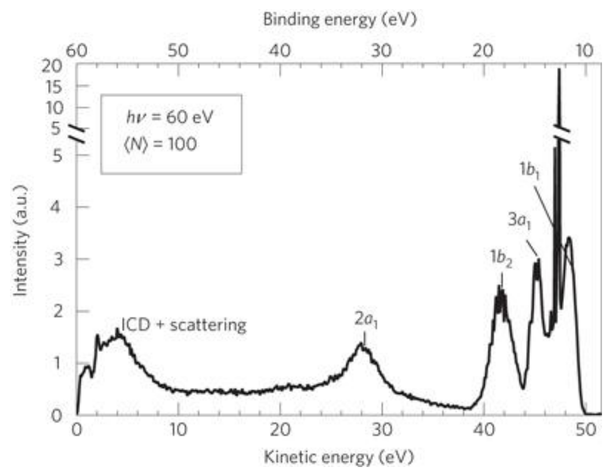








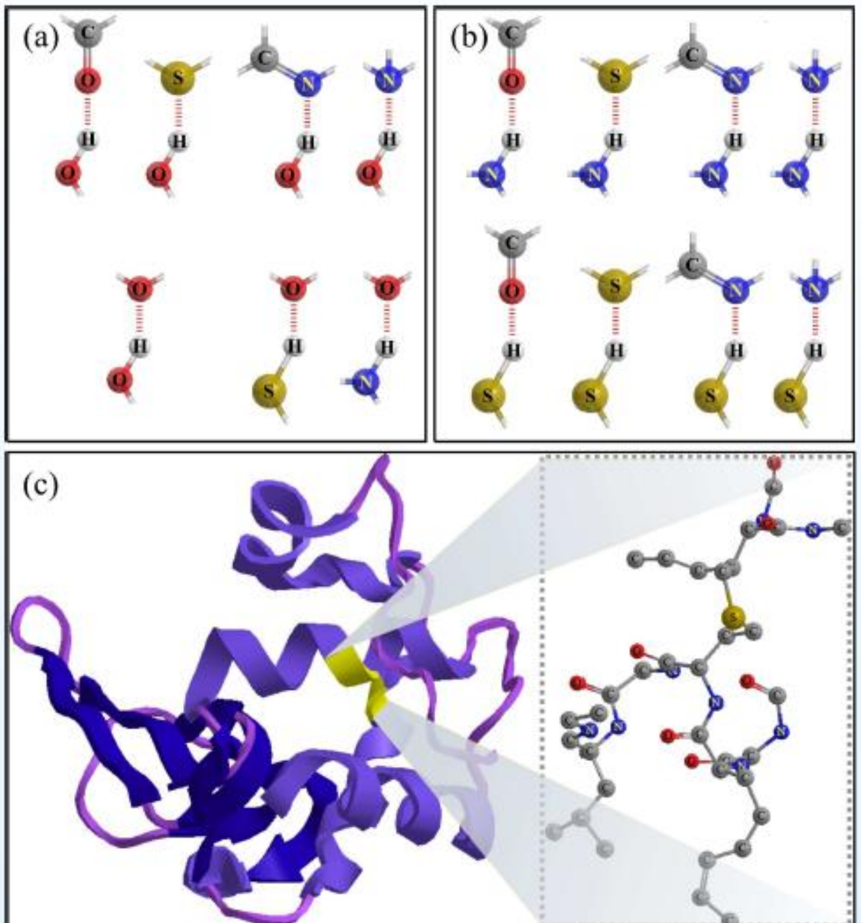


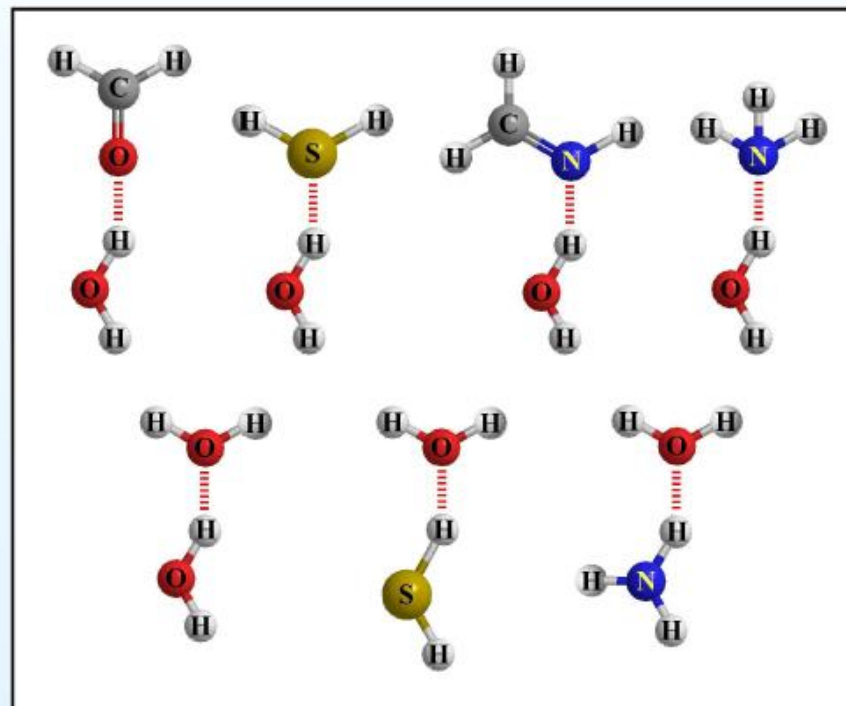


Photoelectron spectrum

ICD generates low-energy electrons in water exactly in the energy range where electrons are known to cause DNA strand breaks by dissociative attachment.

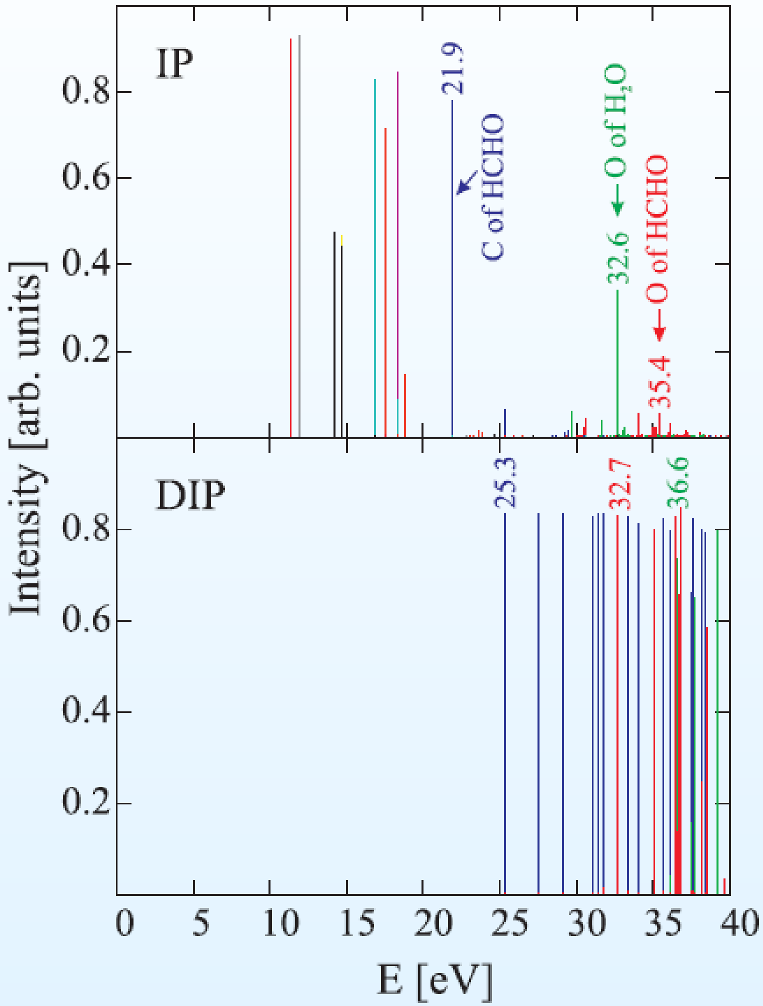
ICD in H-bonded systems



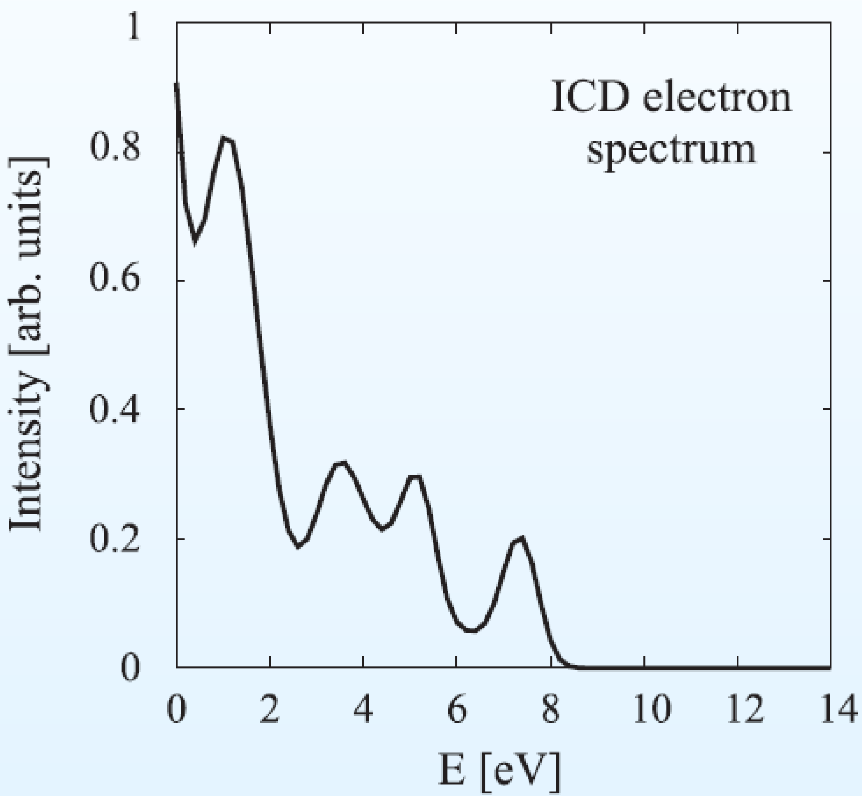


S. D. Stoychev, A. I. Kuleff, and L. S. Cederbaum, JACS **133**, 6817 (2011)

ICD in H-bonded systems



$H_2O\cdots HCHO$



S. D. Stoychev, A. I. Kuleff, and L. S. Cederbaum, JACS **133**, 6817 (2011)

I C D

in

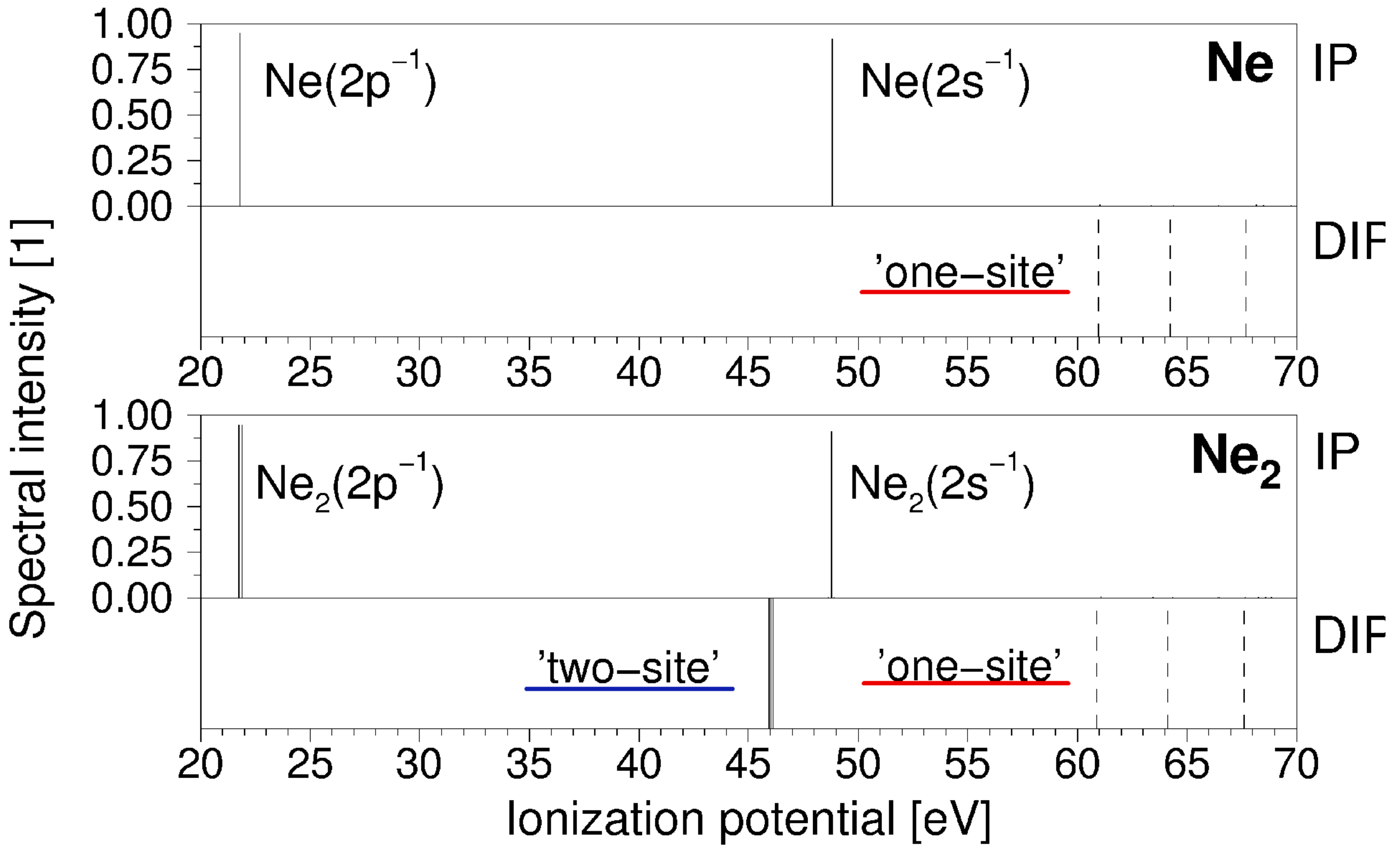
van der Waals clusters

R. Santra, J. Zobeley, L. S. Cederbaum, and N. Moiseyev, *Phys. Rev. Lett.* **85**, 4490 (2000).

R. Santra, J. Zobeley, and L. S. Cederbaum, *Phys. Rev.B* **64**, 245104 (2001).

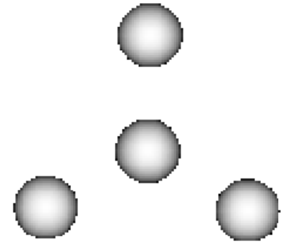
N. Sisourat, N. V. Kryzhevoi, P. Kolorenc, S. Scheit and L. S. Cederbaum, *Nature Phys.* (2010)

Ionization and double-ionization spectra of atomic *Ne* and Ne_2 dimer

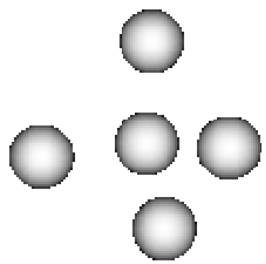


In Ne_2 dimer: 'one-site' ≡ $Ne^{2+}Ne$ 'two-site' ≡ $Ne^{+}Ne^{+}$

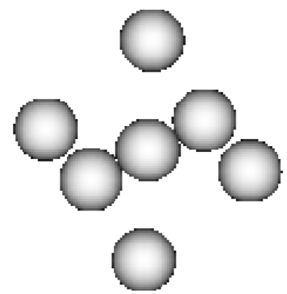
Ne_3



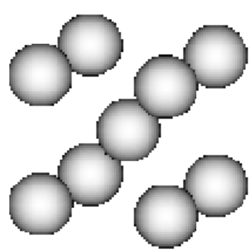
Ne_4



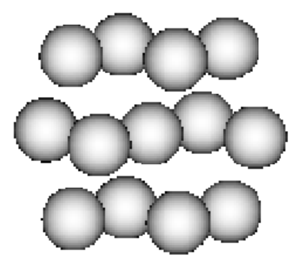
Ne_5



Ne_7

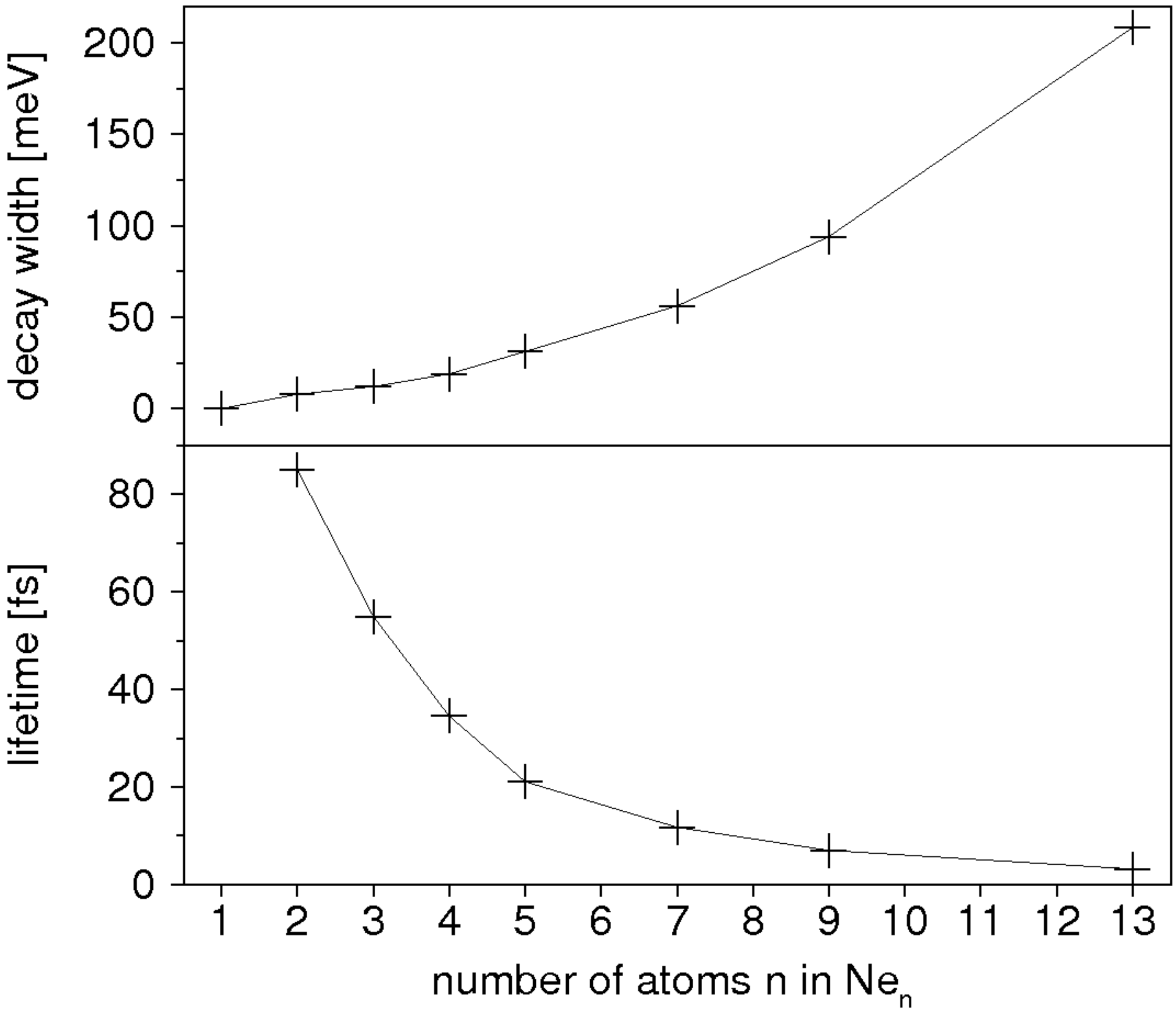


Ne_9



Ne_{13}

Interatomic Coulombic decay in Ne_n clusters

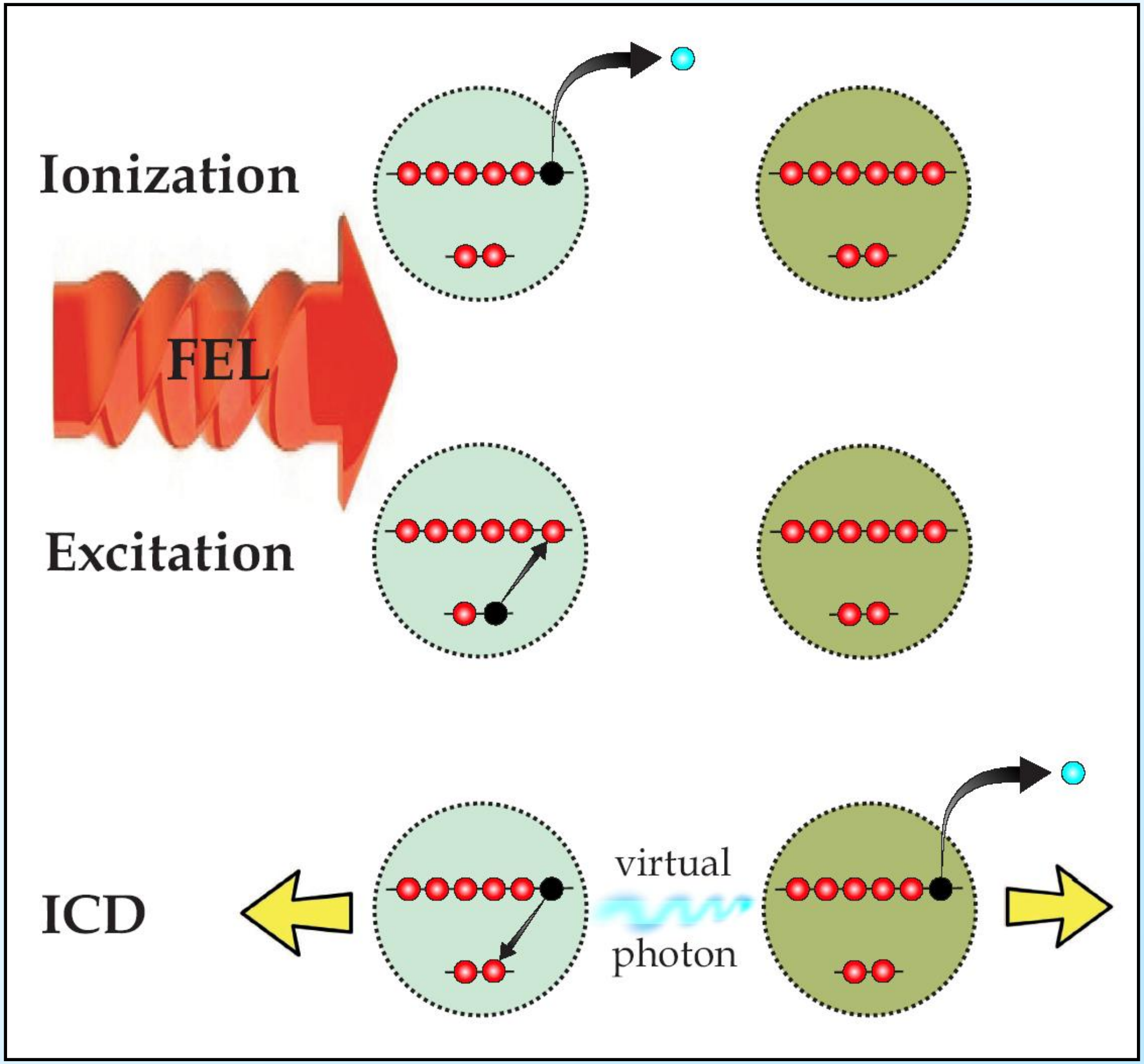


R. Santra, J. Zobeley, and L. S. Cederbaum, *Phys.Rev.B* **64**, 245104 (2001).

Exploring ICD by free electron lasers

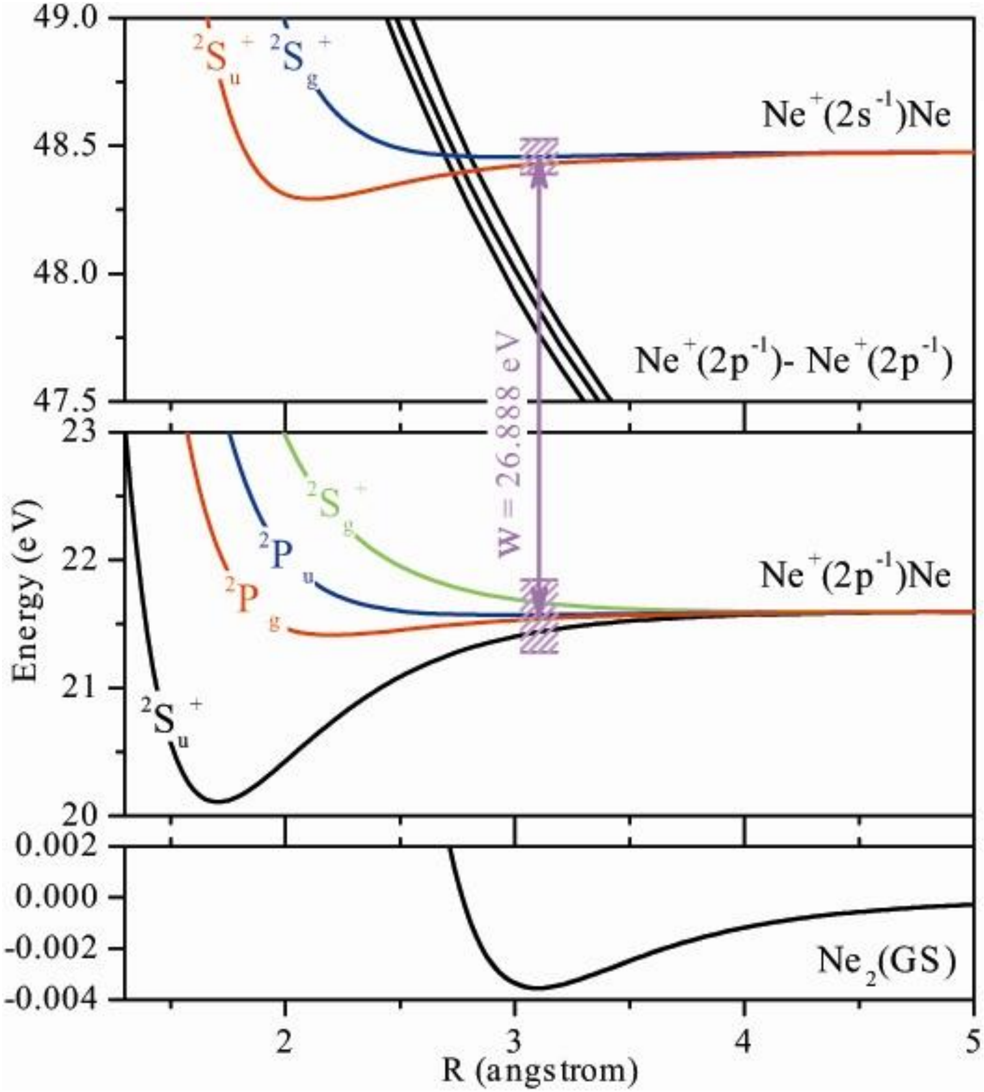
Ph. Demekhin, S. Stoychev, A. Kuleff, and L.S. Cederbaum, *PRL* **107**, 273002 (2011).

ICD by FEL



For ICD: Ph. Demekhin *et al.*, PRL **107**, 273002 (2011).
For Auger in isolated atom: E. P. Kanter *et al.*, PRL **107**, 233001 (2011).

Exploring ICD by free electron lasers



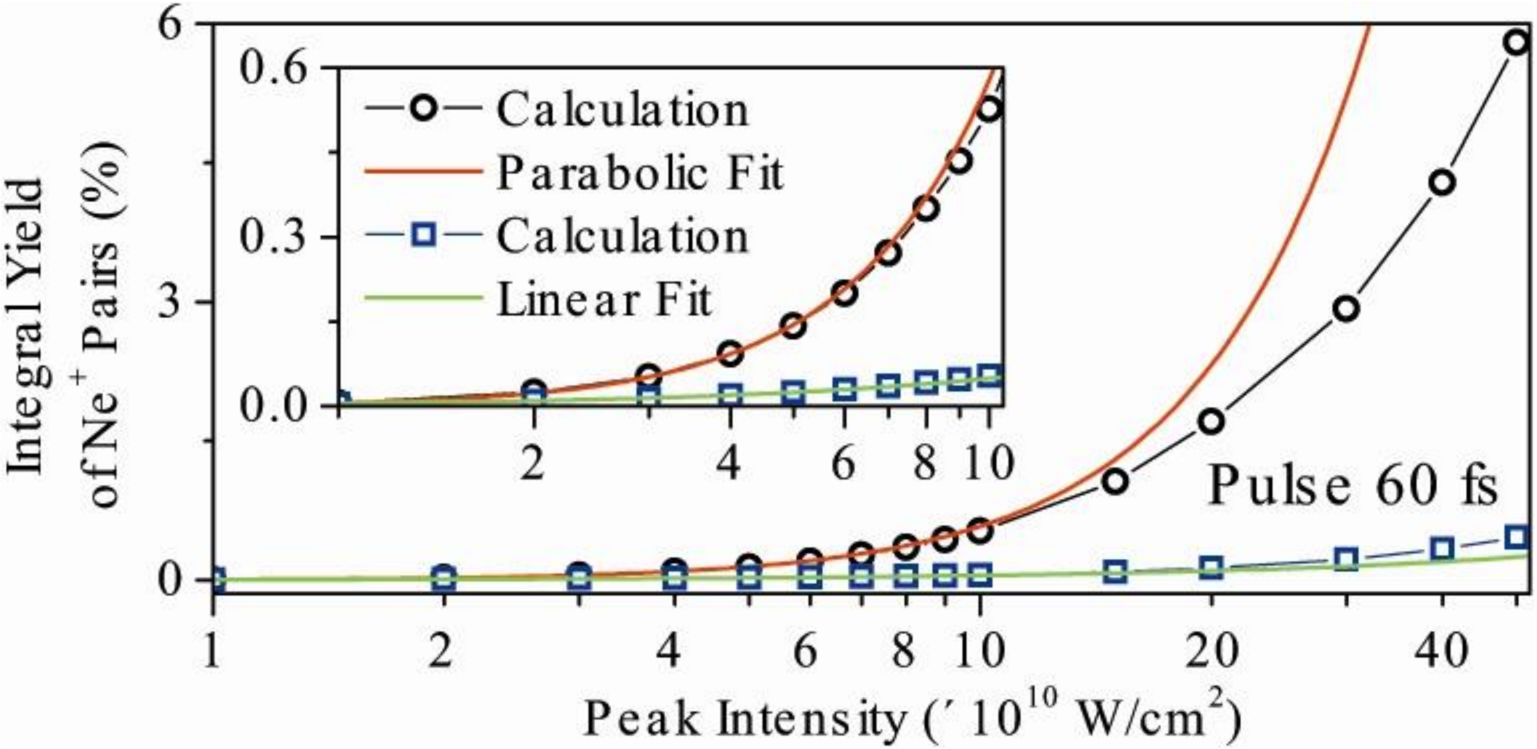
$$Ne_2 \xrightarrow{\omega} Ne^+(2p^{-1})Ne + e_{ph}$$
$$\Updownarrow \omega$$
$$Ne^+(2s^{-1})Ne$$
$$\downarrow ICD$$
$$Ne^+(2p^{-1}) + Ne^+(2p^{-1}) + e_{ICD}$$

At least two photons are needed for the ICD process.

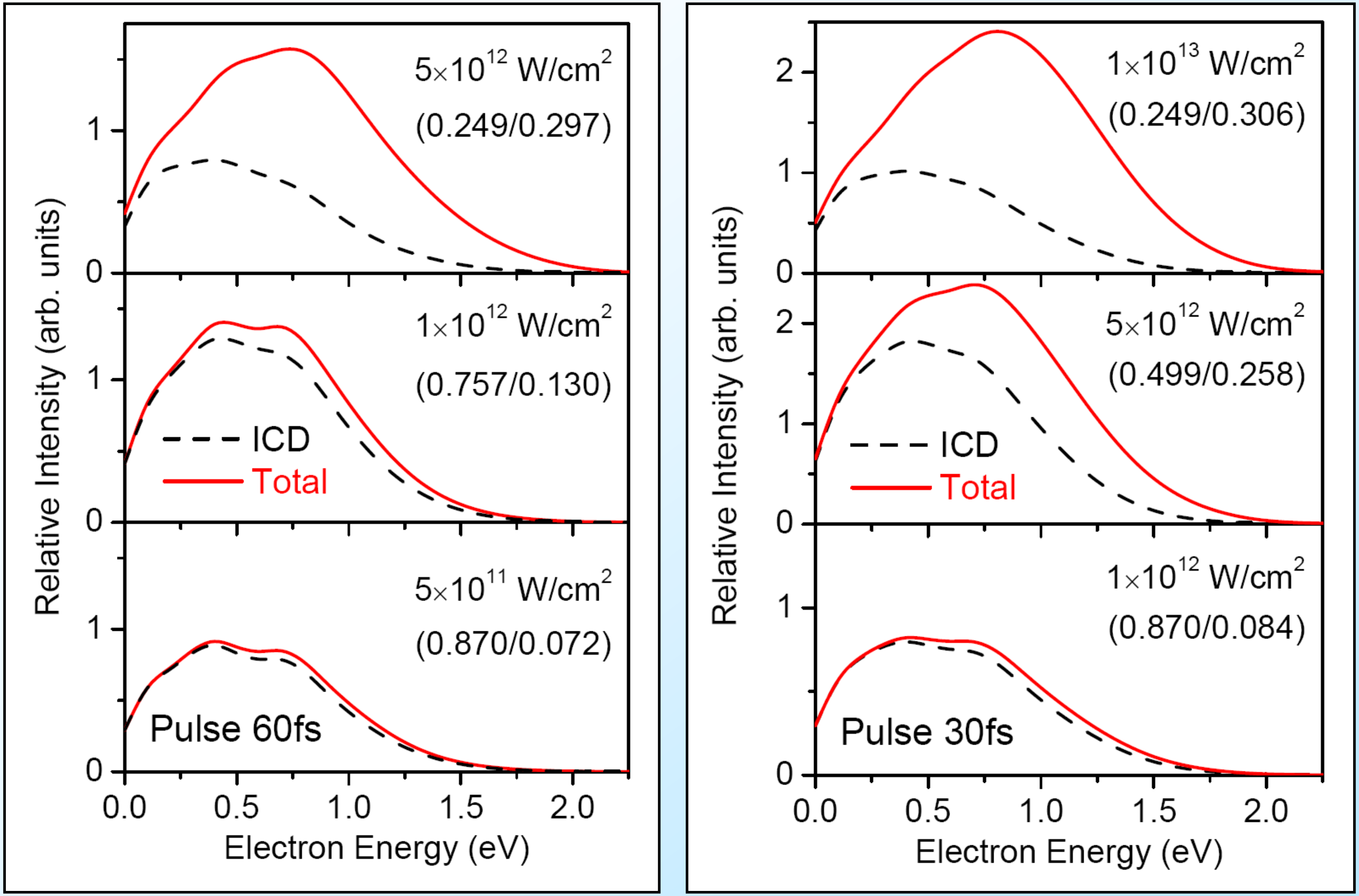
$\omega = 26.888$ eV

Exploring ICD by free electron lasers

Integral yield of Ne^+ ion pairs

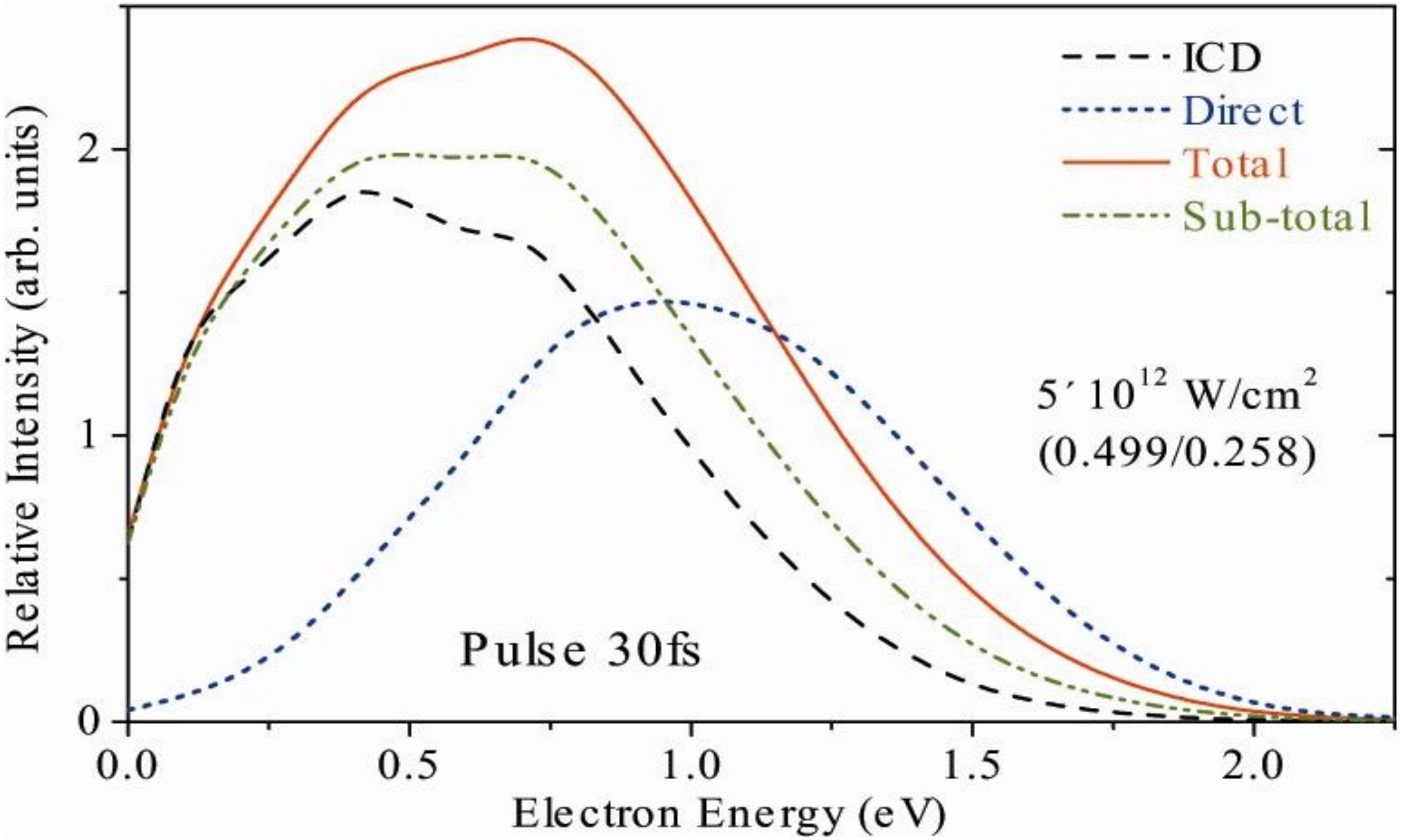


Comparison of yields for a pulse of central frequency ω = 26.888 eV (**two-photon process**) and a pulse doubling the central frequency, ω = 53.776 eV (**one-photon process**). Same peak intensity.



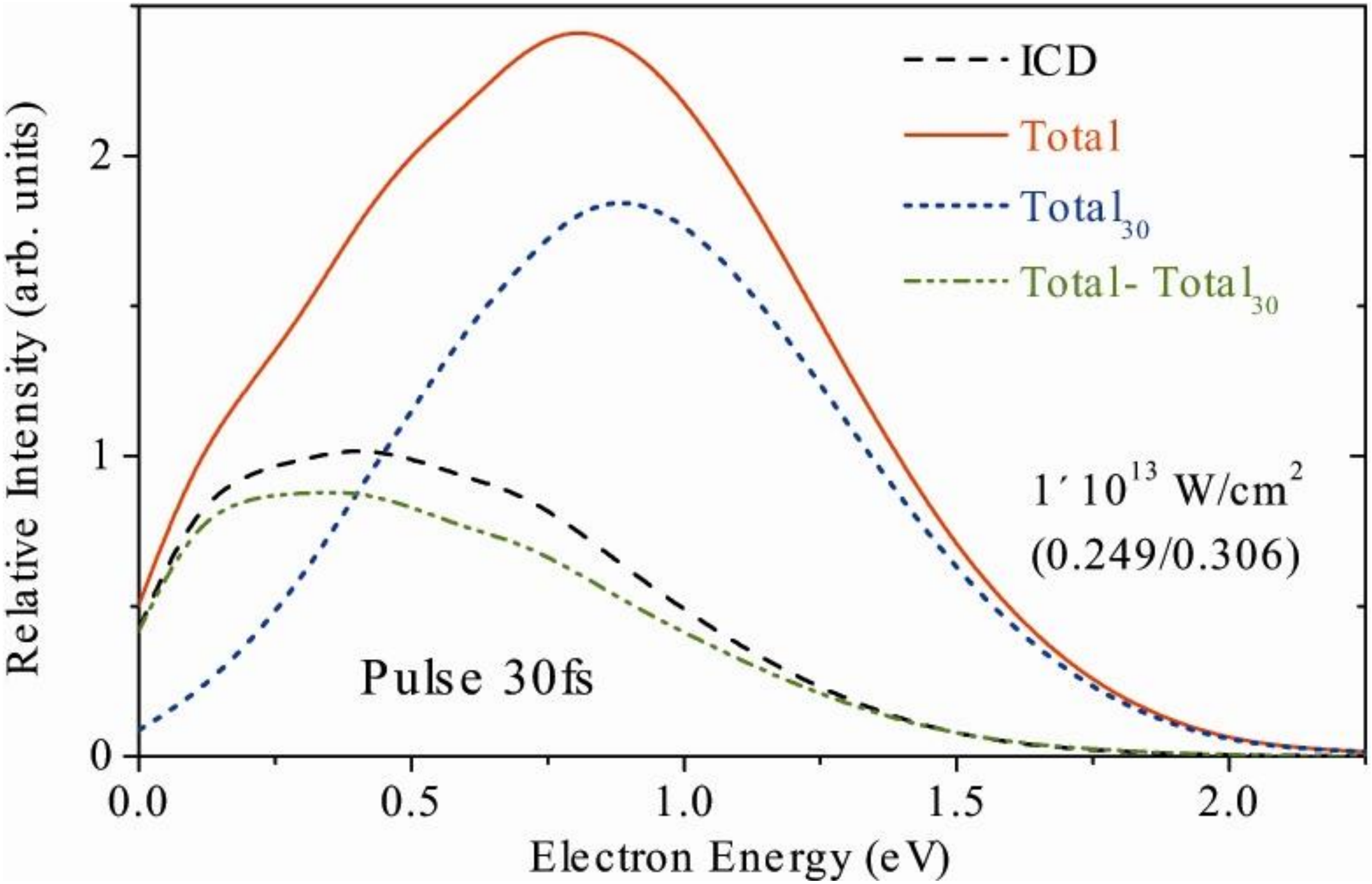
Electron spectra for different pulse durations and intensities

Exploring ICD by free electron lasers



Contributions to the electron spectrum.
There are strong interference effects between the ICD electrons and those produced by direct ionization of the two Ne atoms.

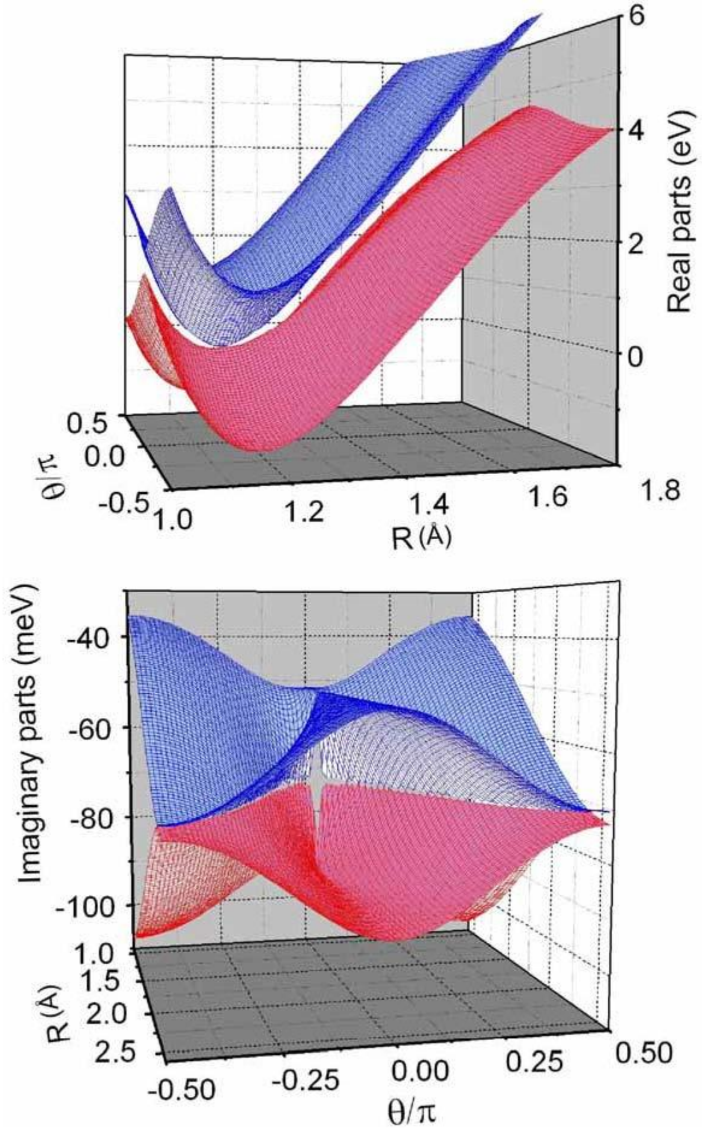
Exploring ICD by free electron lasers



Measuring the individual contribution of ICD.

Total electron spectrum – that measured 30 fs after pulse maximum.

Exploring ICD by free electron lasers



In a laser field at resonant frequency the potential energy surfaces of the initial state and of the excited state possess a **light-induced conical intersection** even for a **diatomic** [1].

If decay processes (like ICD) are involved, the surfaces become complex and their intersections are **light-induced DICES** (Doubly Intersecting Complex Energy Surfaces) [2].

[1] M. Sindelka, N. Moiseyev, and L.S. Cederbaum, *J. Phys. B* **44**, 045603 (2011).
[2] L.S. Cederbaum, Y.-C. Chiang, P.V. Demekhin, and N. Moiseyev, *PRL* **106**, 123001 (2011).

Theory

Ansatz for the total WF:

$$\Psi(t) = \Psi_I(t)\Phi_I + \sum_j \int \widetilde{\Psi}_{OV_j}(\varepsilon_{ph},t)\Phi^{\varepsilon_{ph}}_{OV_j} d\varepsilon_{ph} + \sum_j \int \widetilde{\Psi}_{IV_j}(\varepsilon_{ph},t)\Phi^{\varepsilon_{ph}}_{IV_j} d\varepsilon_{ph} + \sum_j \iint \widetilde{\Psi}_{OVOV_j}(\varepsilon_{ph},\varepsilon_{ICD},t)\Phi^{\varepsilon_{ph}\varepsilon_{ICD}}_{OVOV_j} d\varepsilon_{ph} d\varepsilon_{ICD},$$

Nuclear WP propagation

$$i|\dot{\overline{\Psi}}(\varepsilon_{ph},\varepsilon_{ICD},t)\rangle = \hat{\mathbf{H}}(t)\,|\overline{\Psi}(\varepsilon_{ph},\varepsilon_{ICD},t)\rangle.$$

$$|\overline{\Psi}(\varepsilon_{ph},\varepsilon_{ICD},t)\rangle = \begin{pmatrix} |\Psi_I(t)\rangle \\ |\Psi_{OV}(\varepsilon_{ph},t)\rangle \\ |\Psi_{IV}(\varepsilon_{ph},t)\rangle \\ |\Psi_{OVOV}(\varepsilon_{ph},\varepsilon_{ICD},t)\rangle \end{pmatrix}$$

Molecular Hamiltonian matrix

$$\hat{\mathbf{H}}(R,\theta,t) = \hat{\mathbf{T}}(R,\theta) +$$

$$\begin{pmatrix} V_I(R) - \frac{i}{2}\Gamma_I^{ph}(t) & 0 & 0 & 0 \\ d_x(t)\sin\theta + d_z(t)\cos\theta & V_{OV}(R) - \frac{i}{2}\Gamma_{OV}^{ph}(t) + \varepsilon_{ph} - \omega & \left(D_x^\dagger(t) - \frac{i}{2}W^\dagger(t)\right)\sin\theta & 0 \\ 0 & \left(D_x(t) - \frac{i}{2}W(t)\right)\sin\theta & V_{IV}(R) + \varepsilon_{ph} - 2\omega - \frac{i}{2}[\Gamma_{IV}^{ICD}(R) + \Gamma_{IV}^{ph}(t)] & 0 \\ 0 & \widetilde{d}_x(t)\sin\theta + \widetilde{d}_z(t)\cos\theta & V_{ICD}(R) & V_{OVOV}(R) + \varepsilon_{ph} + \varepsilon_{ICD} - 2\omega \end{pmatrix}$$

Summary

- **Enhancement of ICD by strong fields: Two-photon absorption is more efficient than one-photon absorption of double frequency (traditional scheme)**

- **Sequential two-photon absorption by one subunit competes with the absorption of two photons by two different subunits**

- **Coherent superposition of these two-photon ionization mechanisms: two physical mechanisms – two different timescales**

- **Measurement of the spectrum after a time delay will allow to identify the individual contributions and determine ICD**

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Spas Stoychev	ICD following Auger	Ying-Chih Chiang	cascades
Nicolas Sisourat	He dimer	Philipp Demekhin	cascades

External collaboration - Theory

Francesco Tarantelli	computational techniques	Perugia/Italia
Nimrod Moiseyev	Ne_2 dynamics	Haifa/Israel

External collaboration - Experiment

U. Hergenhahn	München/BESSY
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P. Lablanquie	Paris
E. Rühl	Berlin
K. Ueda	Sendai