Molecular Frame Photoemission: a sensitive probe of ultrafast electronic and nuclear dynamics

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Probing and control the induced ultrafast electronic and nuclear (coupled) dynamics

Time-resolved experiments with ultrashort light pulses

\[ \text{EUV (10fs HHG) - IR } 10^{12} \text{ Watt/cm}^2 \]

\[ \text{XUV pump - XUV probe } \]

\[ \text{FLASH } \]
\[ \text{(80fs, } 10^{13}\text{ Watt/cm}^2) \]

\[ \text{Nuclear WP dynamics } \]

Magrakvelodke et al
PRA 86 013415 (2012)

Controled directional ion emission
... driven by a few-cycle laser field

Betsch et al
PRA 86 063403 (2012)

Probing time-dependent Molecular dipoles on the as time scale (NIR-pump- as XUV probe)

Cao et al PRA 84 053406 (2011)

Neidel et al PRL 111 033001 (2013)
Photoionisation of molecules:

\[ AB + h\nu \rightarrow AB^+ + e \]

**Molecular states:**
Initial neutral and final ionic bound states
Electronic correlations in the initial and final excited states

**Dynamics:** \( e^{-}AB^{**} \) scattering

**Molecular frame photoemission (MFPADs)**

**Role of resonances**
Autoionization, Quantum interferences
Coupling between electron and nuclear motion
Femtosecond Time scale
Photoionisation of molecules: fundamental processes and applications

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**Molecular frame photoemission (MFPADs)**
\[ I_{l m i}^{M_i M_f} = \langle \psi_{M_i}^i | d_{m} | \phi_{M_f}^f | \psi_{l m}^(-) \rangle \]

**Role of resonances**
Autoionization, Quantum interferences
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Femtosecond Time scale

Photoionization as a probe of ultrafast phenomena: charge migration, vibronic couplings, photodissociation, isomerization, first steps of chemical reactions...
Photoionisation of molecules: fundamental processes and applications

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Molecular states:
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Molecular frame photoemission (MFPADs)
\[ I_{lmu}^{M_iM_f} = \langle \psi_M^i | d_{\mu} | \phi_{M_f}^f \psi_{lm}^{(-)} \rangle \]

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Photoionization as a probe of ultrafast phenomena: charge migration, vibronic couplings, photodissociation, isomerization, first steps of chemical reactions...
Molecular-frame photoelectron angular distributions (MFPADs)

Guest Editors R.R. Lucchesce and A. Stolow

RFPADs in core O(1s) ionization of H$_2$CO

Imaging molecular isomerization using MFPADs (C$_2$H$_2^+$)

Imaging molecular shapes with MFPADs from core hole ionization (CH$_4$)

Probing the dynamics of dissociation of methane following core ionization using 3D MFPADs

Vibrationnally resolved MFPADs from N$_2$ and CO

Probing MFPADs via HHG from aligned molecules

MFPADs in DPI of H$_2$ and D$_2$ induced by HHG fs XUV pulses

On the information content of time- and angle-resolved PES

Nuclear and electron dynamics from femto- and sub-femtosecond time-resolved PADs (NO$_2$)
Outline

Electron-ion coincident momentum spectroscopy
\[ AB + h\nu(k) \rightarrow A^+ + B^* + e \]
\[ (V_n, V_e, k) \rightarrow I(\chi, \theta_e, \phi_e) \]

One-photon dissociative PI of \( \text{H}_2 \) at resonance with \( Q_1 \) and \( Q_2 \) Rydberg states:
From VUV synchrotron radiation to HHG secondary sources
Signature of quantum interferences in PI in the femtosecond regime.
General expression of the MFPAD for single-photon ionization

MFPADs for multiphoton processes (time-resolved studies)

Two VUV photon resonant dissociative and non-dissociative PI of \( \text{H}_2 \)
Extension of the MFPAD description to multiphoton processes

Multiphoton PI of \( \text{NO}_2 \) and \( (\text{NO}^+-\text{O}^-) \) Ion Pair formation induced by fs pulses
Recoil frame PADs in PI of \( \text{NO}_2 \) : electron-nuclei dynamics of autoionizing
Rydberg resonances, conical intersections

Conclusions, perspectives
Vector Correlations: 3D electron-ion coincidence imaging
Time and position sensitive detection

\((V_n, V_e, \hat{e})\)  
4\(\pi\) collection  
Ion fragments and electrons

Single ionization: valence shell

\[ AB + h\nu(k) \rightarrow AB^+ + e \]
\[ AB + h\nu(k) \rightarrow A^+ + B^* + e \] \((V_n, V_e, k)\)

Inner-shell PI, double ionization...

\[ AB + h\nu(k) \rightarrow AB^{+++} + e_{ph} + e_{Au} \]
\[ \rightarrow A^+ + B^+ + e_{ph} + e_{Au} \]

\((V_{A^+}, V_{B^+}, V_{e1}, V_{e2}, k)\)

\(n\) events/pulse \(<\ll 1\)

SOLEIL SR few MHz (time structure)  
Femtosecond Lasers and HHG kHz range

Repetition rate 100 kHz, 1 nJ: an issue for coincidences at ELI-ALPS  
Photon energy: inner-shell, water window, dications…
Single ionization: valence shell

$$AB + h\nu(k) \rightarrow A^+ + B^* + e \quad (V_n, V_e, k)$$

$\Lambda_i$ events/pulse $\ll 1$

SOLEIL SR few MHz (time structure)
Femtosecond Lasers and HHG kHz range

Electron-ion kinetic energy correlation

$$MFPAD \rightarrow I(\chi, \theta_e, \phi_e)$$

Lafosse et al PRL 84 5987 (2000)
Lebech et al RSI 73 1866 (2002)
Dissociative Photoionization of $H_2$ at resonance with $Q_1$ and $Q_2$ series

$Q_1(2p\sigma_u, nl\lambda), Q_2(2p\pi_u, nl\lambda)$

Direct ionization: $H_2(X^1\Sigma^+_g) + h\nu \rightarrow H_2^+(2\Sigma^+_g(1s\sigma_g) \text{ or } 2\Sigma^+_u(2p\sigma_u)) + e$

Autoionization: $H_2(X^1\Sigma^+_g) + h\nu \rightarrow H_2(Q_1^1\Sigma^+_u) \rightarrow H_2^+(2\Sigma^+_g) + e$

$H_2(X^1\Sigma^+_g) + h\nu \rightarrow H_2(Q_2^1\Pi_u) \rightarrow H_2^+(2\Sigma^+_g) \text{ or } (2\Sigma^+_u) + e$

Martin et al Science, 315 629 (2007)
Glass-Maujean et al PRA 86 (2012) 052207

3D TDSE calculations: pulse 10 fs
JF Pérez-Torres, JL Sanz-Vicario, F. Martin
General expression of the MFPAD for single-photon ionization

\( (V_n, V_e, \hat{e}) \)

Photoionization of a linear molecule induced by linearly polarized light

\[
I(\chi, \theta_e, \phi_e) = F_{00}(\theta_e) + F_{20}(\theta_e) P_{20}(\cos \chi) + F_{21}(\theta_e) P_{21}(\cos \chi) \cos(\phi_e)
\]

\[
+ F_{22}(\theta_e) P_{22}(\cos \chi) \cos(2\phi_e)
\]

\[
P_{20}(\cos \chi) = \frac{1}{2} [3\cos^2 \chi - 1] \quad P_{21}(\cos \chi) = 3\cos \chi \sqrt{1 - \cos^2 \chi} \quad P_{22}(\cos \chi) = 3\sin^2 \chi
\]

\[
F_{LN}(\theta_e) = \sum L' C_{L'LN} P_{L'N}(\cos \theta_e)
\]

\[
I^{MiMf}_{lm\mu}
\]

Generate the MFPADs for any specific molecular orientation using the statistics of the whole measurement

Beyond the axial recoil approximation: Recoil Frame PADs for Polyatomic molecules

A mean to determine a predissociation life-time or estimate a bending angle

General expression of the MFPAD for single-photon ionization

\((V_n, V_e, \hat{e})\)

Photoionization of a linear molecule induced by circularly polarized light \((\mu_0=\pm 1)\)

\[
I_{\mu_0=\pm 1}(\chi, \theta_e, \phi_e) = F_{00}(\theta_e) - 0.5 F_{20}(\theta_e) P_{20}(\cos \chi) - 0.5 F_{21}(\theta_e) P_{21}(\cos \chi) \cos(\phi_e)
- 0.5 F_{22}(\theta_e) P_{22}(\cos \chi) \cos(2\phi_e)
\pm F_{11}(\theta_e) P_{11}(\cos \chi) \sin(\phi_e)
\]

\[
P_{20}(\cos \chi) = \frac{1}{2} \left[ 3\cos^2 \chi - 1 \right]
\]

\[
P_{21}(\cos \chi) = 3\cos \chi \sqrt{1 - \cos^2 \chi}
\]

\[
P_{22}(\cos \chi) = 3\sin^2 \chi
\]

\[
P_{11}(\cos \chi) = \sqrt{1 - \cos^2 \chi}
\]

\[
F_{LN}(\theta_e) = \sum L' C_{L'LN} P_{LN}(\cos \theta_e)
\]

\[
I_{lim\mu}^{MiMf}
\]

Generate the MFPADs for any specific molecular orientation using the statistics of the whole measurement

Circular dichroism in the MF frame: a sensitive probe of quantum interferences

Applications for polarimetry of elliptically polarized light: Stokes parameter \(s_1, s_2, s_3\)

Lebech et al JCP 118 9653 (2003); Johnke et al PRL 88 073002 (2002); Veyrinas et al PRA in press (2014)
Dissociative Photoionization of $H_2$ at resonance with $Q_1$ and $Q_2$ series


$H_2 + 2\Sigma_g^+ (1s\sigma_g)$

$H_2^+ + H(1s) \rightarrow 2p\sigma_u$

$\perp 1s\sigma_g \rightarrow 2p\pi_u$

$\parallel 1s\sigma_g \rightarrow 2p\sigma_u$

$E_{H^+} = 4 \text{eV}$

Dissociative Photoionization of $H_2$ at resonance with $Q_1$ and $Q_2$ series

Autoionization

KER dependence

MF circular dichroism CDAD

Isotope effects: $H_2$, $D_2$ and HD

Electron-nuclei motion coupled

Dissociative Photoionization of $H_2$ induced by HH femtosecond pulses

Selection of HHG (H21) (PLFA, SLIC Saclay):

- $\sim 806$ nm
- $\sim 6$ mJ
- $\sim 45$ fs
- $1$ kHz

$E_{H^+} = 5.5$ eV  $H21$ (PLFA)  $SR$ (DESIRS)

Coincident events: $H_2^+$ 15 c/s  $H^+$ $\leq$ 1 c/s
selected KER  $H^+$ $\leq$ 0.25 c/s

MFPADs induced by HH
Remarkable symmetry breaking
MFPADs as a function de $\Delta t$ (HH)
Spectral effect studied at SOLEIL
31–33 eV

Fischer et al PRL 110 213002 (2013)

Control of H$_2$ and D$_2$ dissociative ionization induced by two-VUV-photon excitation using linearly and circularly polarized femtosecond pulses


DPI involving Q$_g$ states, Role of nuclear dynamics
Control the ratio Dissociative Ionization /non-dissociative
Angular distributions of the ion fragments and photoelectrons (VMI)

Clocking ultrafast WP
1 fs XUV-pump-XUV-probe

A. Gonzales-Castrillo, et al
Carpeggiani et al ArXiv 2013

ELI-ALPS
Science
Rich and complex photodynamics, nuclear degrees of freedom
\[ \text{NO}_2 (X) \ldots (1a_2)^2 (4b_2)^2 (6a_1)^1 \]

Extension of the MFPAD approach to non-linear molecules:
Recoil Frame Photoelectron Angular Distribution (RFPADs)

Wörner et al. Science 334 208 (2011)


Time resolved PES and MFPADs:
from WP to observables G. Wu, P. Hocket, A. Stolow PCCP 13 18467 2011, Nat. Phys. 2011
Multiphoton PI of NO$_2$ induced by femtosecond laser 400 nm

\[
\text{NO}_2 (X^2A_1) + 5 \text{ph} \rightarrow \text{NO}^+ + O + e
\]

\[
\text{NO}_2 (X^2A_1) + 4 \text{ph} \rightarrow \text{NO}^+ (1\Sigma_g, v) + O^- (2P)
\]

\[
H(\chi) \propto 1 + \sum_{k=1}^{N} \beta_{2k} P_{2k} (\cos \chi)
\]
Multiphoton / one-photon DPI of NO₂

$$\text{NO}_2 (X^2A_1) + (n) \text{hv} \rightarrow \text{NO}^+ + \text{O} + e$$

Dissociation limits:
- \(L_1\): \(O(^3\text{P}) + \text{NO}^+(X^1S_g^+, \nu = 0)\)
- \(L_2\): \(O(^1\text{D}) + \text{NO}^+(X^1S_g^+, \nu = 0)\)

SOLEIL \(\text{hv} = 15.7 \text{eV}^0\)

Femtosecond laser 5*400 nm (70 fs)

Coupling between Rydberg state series of linear and bent geometry
Conical intersections?
XUV-XUV Pump-probe studies in the femtosecond regime

Marggi Poullain et al (in preparation)
Multiphoton PI of NO$_2$ : General expression of the RFPADs

NO$_2$ ($X^2A_1$) + nhv $\rightarrow$ NO$^+$ + O + e

Four-photon bound-to-bound reaction pathway: $H_v(\chi)$ and one photon ionization

$$T_{fi}^{(n,LPRF)} = \sum_v H_{v}^{(n-1,LP)}(\chi) \sum_{L=0,2} \sum_{N=0}^{L} F_{N,v}^{(L)}(\theta_e) P_L^N(\cos \chi) \cos[(v+N)(\phi_e)]$$

$\chi = 0^\circ$

How to compare the most accurately experiment and theory ? Obtain and compare RFPADs

How to extract most meaningful quantities characterizing photoionization including autoionization of the excited states ?

R. Lucchese  in progress
Marggi Poullain et al (in preparation)

Photoionization of a linear molecule induced by elliptically polarized light: The Stokes parameters are encoded in the MFPAD

\[ I_{\mu_0} = \pm (\chi, \theta_e, \phi_e) = F_{00}(\theta_e) - 0.5 F_{20}(\theta_e) P_{20}(\cos \chi) - 0.5 F_{21}(\theta_e) P_{21}(\cos \chi) \cos(\phi_e) - 0.5 F_{22}(\theta_e) P_{22}(\cos \chi) \cos(2\phi_e) \pm s_3 F_{11}(\theta_e) P_{11}(\cos \chi) \sin(\phi_e) \]

Lebech et al JCP 118 9653 (2003)
Molecular frame photoemission is a sensitive probe of the wave function of the ionized molecular state. MFPAD observables including the circular dichroism provide knowledge for symmetry and lifetime of autoionizing states, couplings between electronic excited states as well as electronic and nuclear motions. 

MFPADs can be completely determined by 3D imaging coincident electron-ion momentum spectroscopy taking advantage of dissociative photoionization.

MFPAD electron-ion momentum spectroscopy extended from synchrotron radiation to fs lasers and sub-fs VUV light sources (kHz): complementarity

MFPADs: DPI of H₂ and D₂ induced by HHG (SLICS, CEA, Saclay): Two VUV photon ionization and XUV-pump-XUV-probe of the role of nuclear dynamics.

RFPADs: NO₂ prototype for multi-photon ionization probing electron-nuclear couplings

Extension of the analytical description

Pump-probe schemes at the subfemtosecond scale: electronic and nuclear dynamics at conical intersections and through Rydberg series.

Complementarity between time and spectrally resolved studies...
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