

Vector correlations for the investigation of the dynamics of photoionization and photodissociation of small molecules

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Outline

Experimental approach

DPI of D_2 in the region of the Q_1 and Q_2 doubly excited states: dynamics of ionization and dissociation

- * Ion-Electron Kinetic Energy Correlation at 28.5 eV and 32.5 eV comparison with H_2
- * A complete experiment using a single circular polarization of the light
Molecular Frame Photoelectron Angular Distributions

MFPADs probed during photodissociation: a femtosecond time-resolved experiment

J.A. Davies, R.E. Continetti, D.W. Chandler, C. Hayden PRL 2000 Sandia National Laboratories

Vector correlations in DPI of inner-shell photoexcited molecules $(\mathbf{V}_{A+}, \mathbf{V}_{B+}, \mathbf{V}_e, \hat{\mathbf{e}})$

Collaboration with : M. Simon, L. Journel (LCPMR), H. Bergeron (LURE), R. Guillemin, D. Lindle (U. Nevada) line SA22, C. Miron

Conclusion

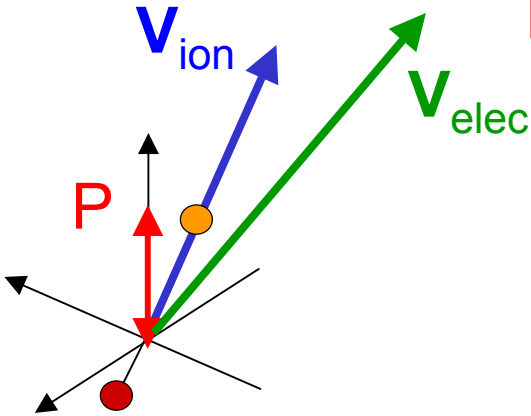
Principle scheme: Double velocity spectrometer

position and time

$$V_x = x/T$$

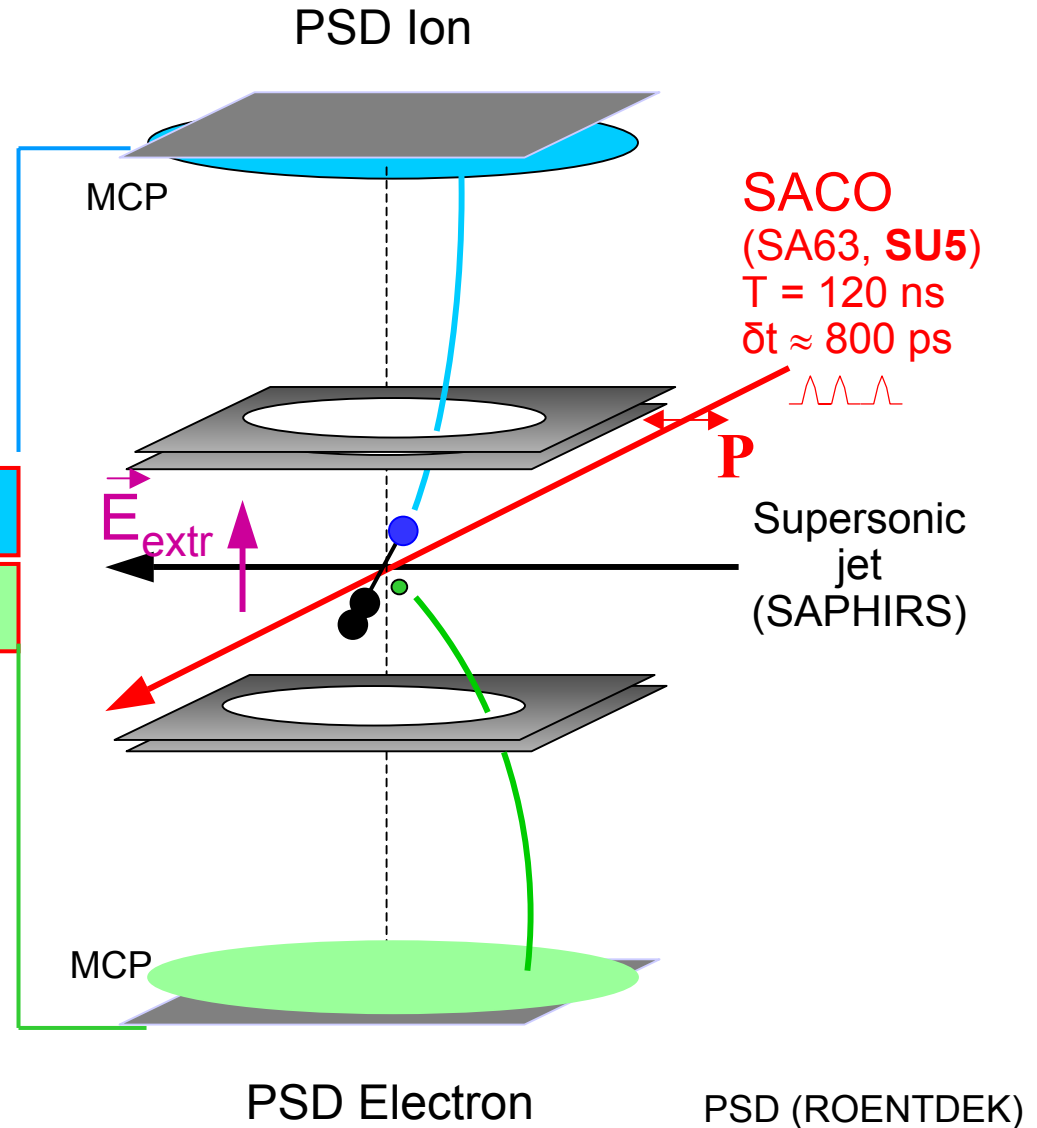
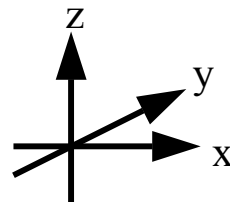
$$V_y = y/T$$

$$V_z = f(\Delta T)$$

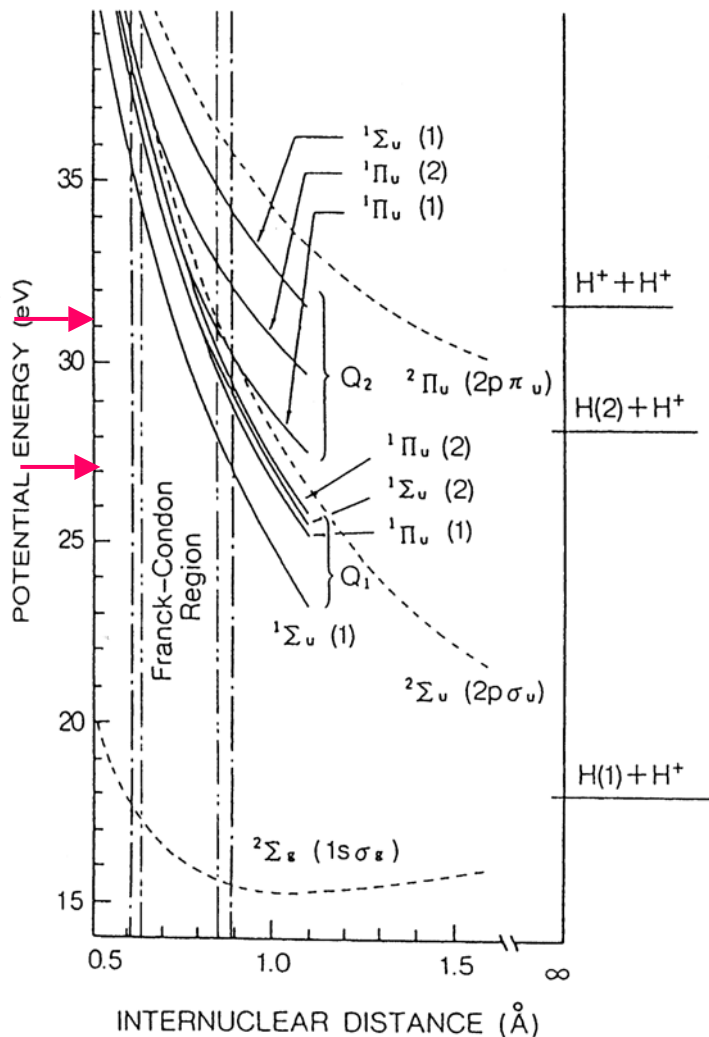


x_i, y_i, T_i

x_e, y_e, T_e



Dissociative photoionization of D₂ and H₂



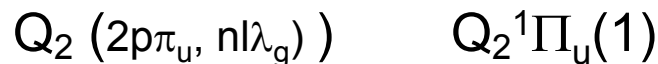
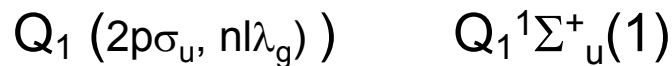
Direct photoionisation in the FC region:



$$0 \leq E_{H^+} \leq 1 \text{ eV} \quad E_e$$



Two series of doubly excited states:



autoionization τ_a / dissociation $\tau_d \sim 5\text{-}10 \text{ fs}$

KED Ito et al JCP 1996, Latimer et al JCP 1995...

DI Ito et al J. Phys.B 2000, Hikosaka and Eland CP 2002

J. Elect. Spectrosc. 2003

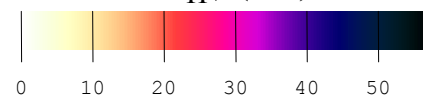
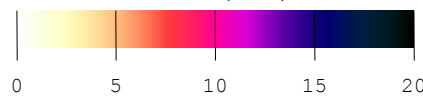
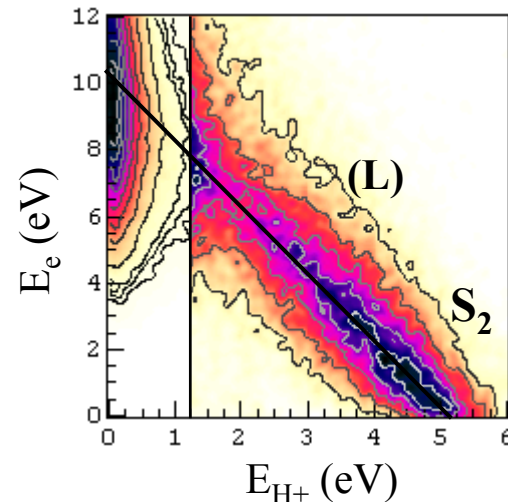
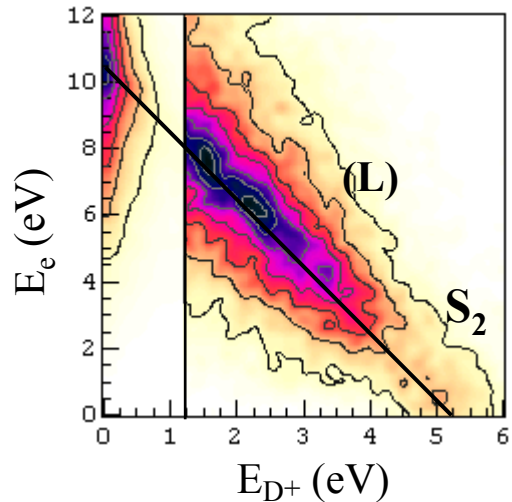
Sanchez and Martin PRL 1997,1999

Prior et al Int. Symp. e-2e.... 2003

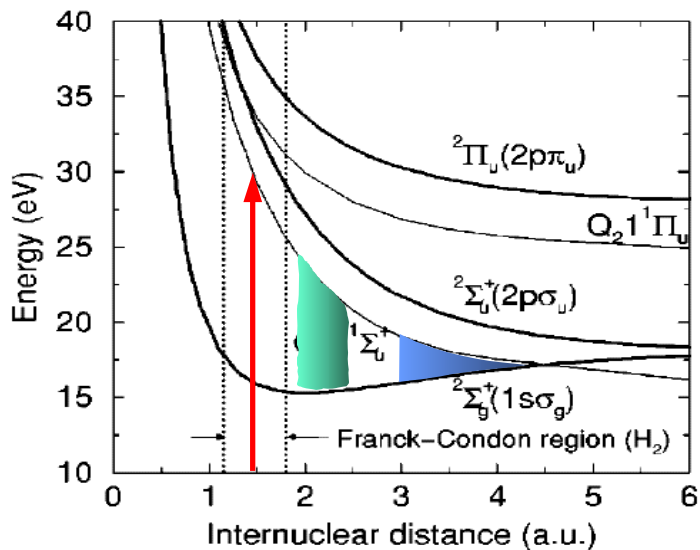
M. Glass-Maujean JCP 1986,1988

Ion-electron kinetic energy correlation (D^+, e) events

$h\nu = 28.5 \text{ eV}$

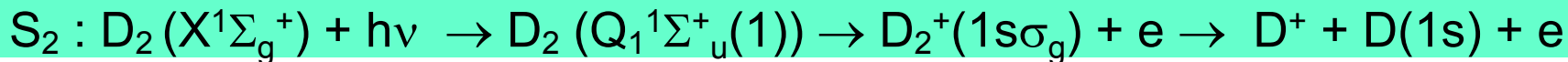


$$\beta_{S_2} \approx 1.8 \text{ (D}^+, \text{H}^+)$$



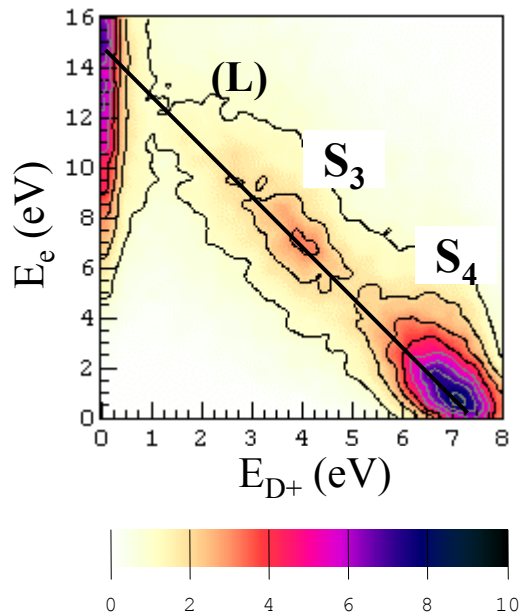
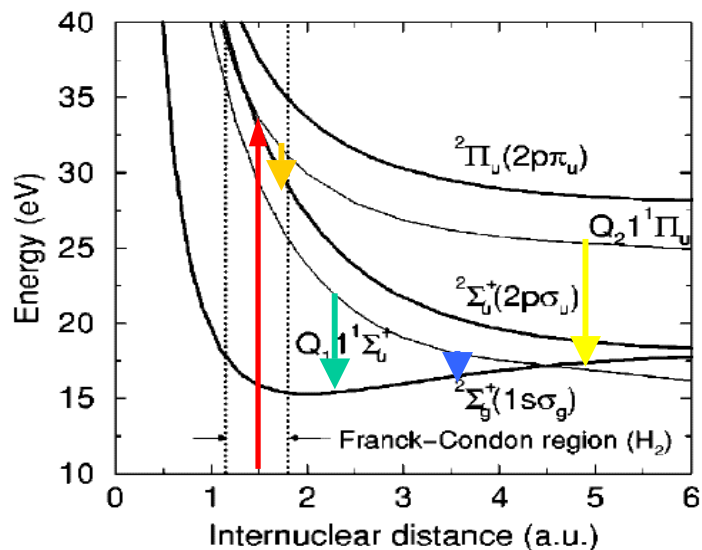
Electron emission D_2

Electron emission H_2



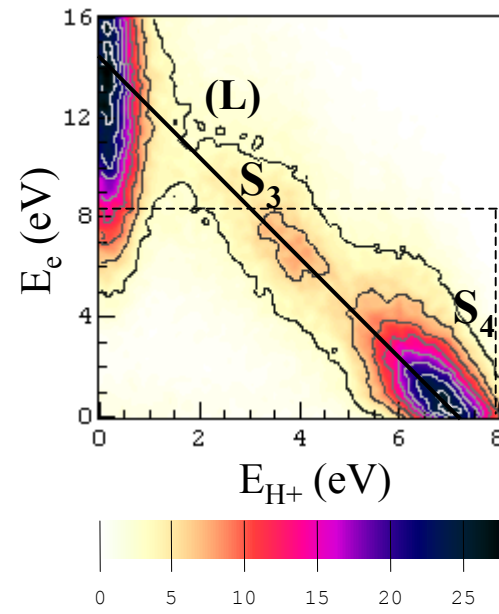
Ion-electron kinetic energy correlation (D^+, e) events

$h\nu = 32.5 \text{ eV}$



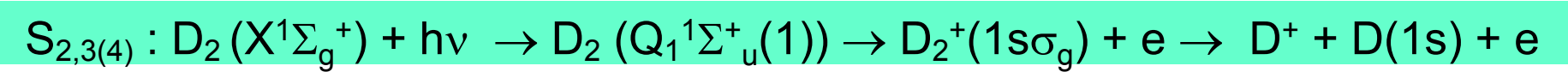
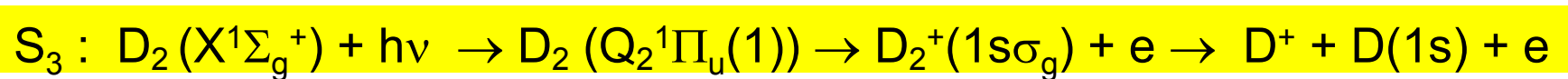
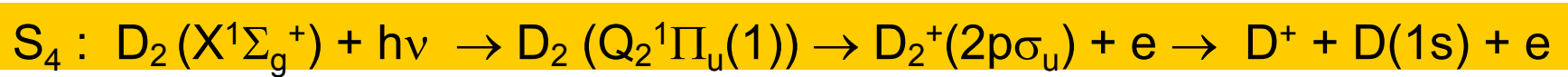
$$\beta_{S_3} \approx 0.5 \text{ (D}^+)$$

$$\beta_{S_4} \approx -0.2 \text{ (D}^+)$$



$$\beta_{S_3} \approx 0 \text{ (H}^+)$$

$$\beta_{S_4} \approx 0.25 \text{ (H}^+)$$



Molecular Frame Photoelectron Angular Distributions

$$I(\chi_{A+}, \theta_e, \phi_e)$$

Generalized MFPAD for circularly polarized light (Lucchese et al PRA 2002, Lafosse et al JCP 2002)

$$I_{\mu=\pm 1}(\theta_e, \phi_e, \chi_{A+}) = F_{00}(\theta_e) - 0.5 F_{20}(\theta_e) P_{20}(\cos \chi_{A+}) - 0.5 F_{21}(\theta_e) P_{21}(\cos \chi_{A+}) \cos(\phi_e) \\ - 0.5 F_{22}(\theta_e) P_{22}(\cos \chi_{A+}) \cos(2\phi_e) \\ \pm F_{11}(\theta_e) P_{11}(\cos \chi_{A+}) \sin(\phi_e)$$

where: $F_{LN}(\theta_e) = \sum_{L'} C_{L'LN} P_{L'N}(\cos \theta_e)$ $L = 0 \text{ or } 2, N = 0, 1..L$

MFPADs for any fixed molecular orientation in space

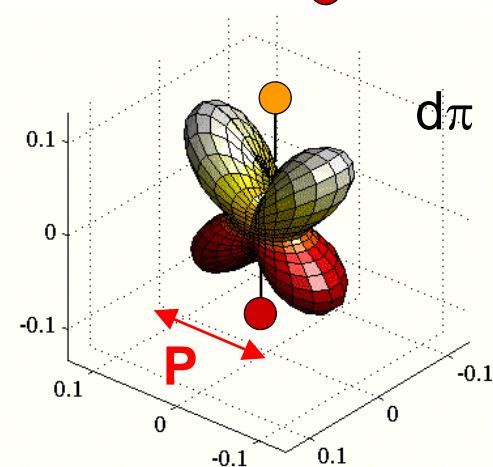
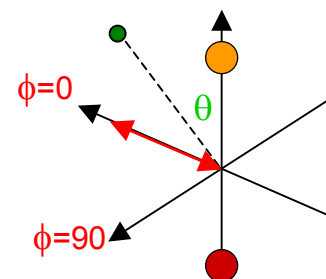
$$I_{0^\circ}(\theta_e) = F_{00}(\theta_e) + F_{20}(\theta_e)$$

$$I_{54.7^\circ}(\theta_e, \phi_e) = F_{00}(\theta_e) + 2^{1/2} F_{21}(\theta_e) \cos(\phi_e) + 2 F_{22}(\theta_e) \cos(2\phi_e)$$

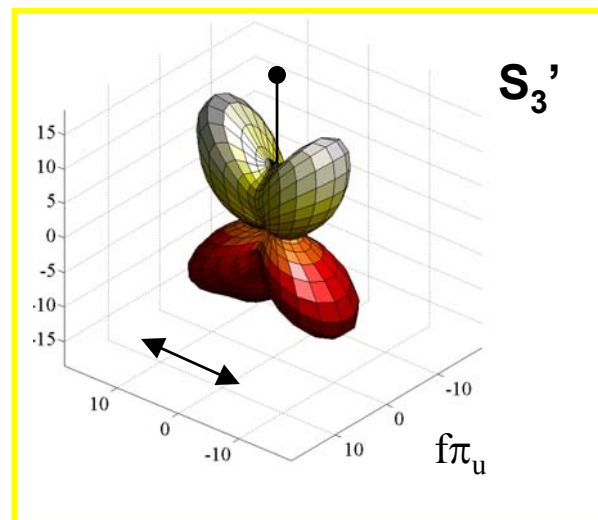
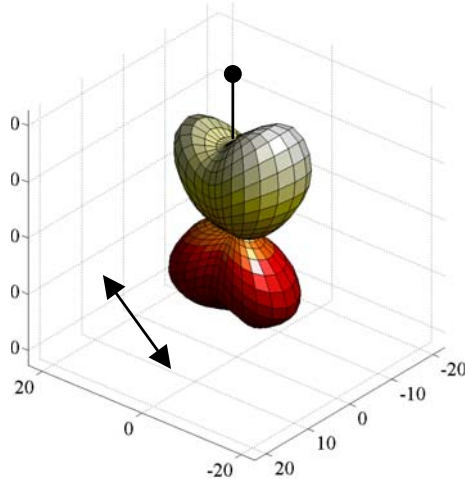
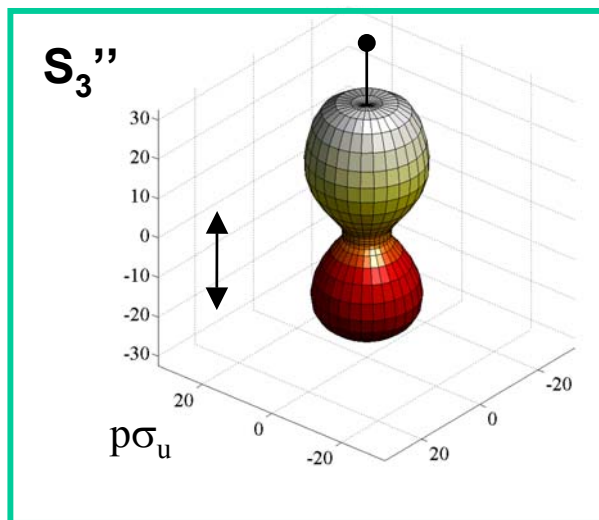
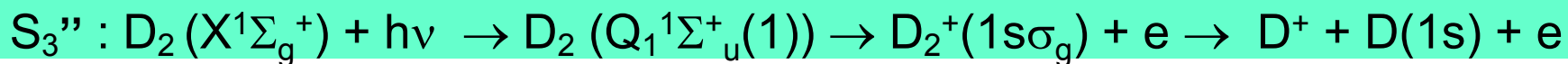
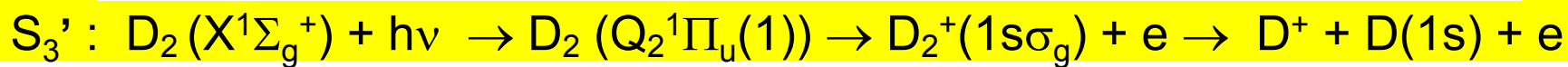
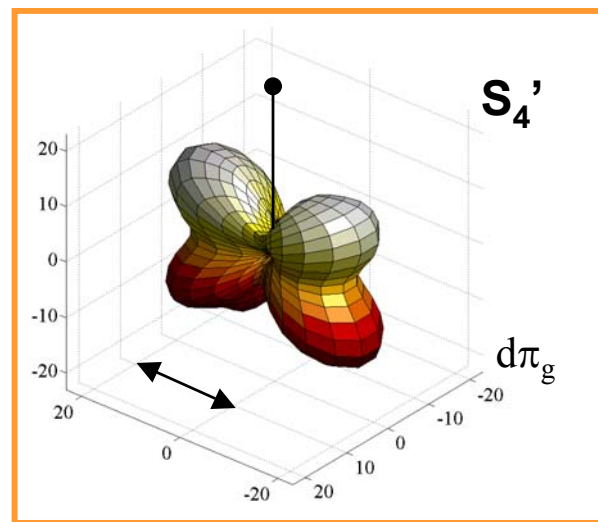
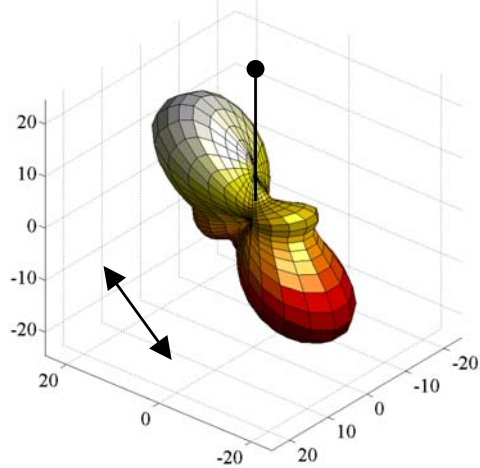
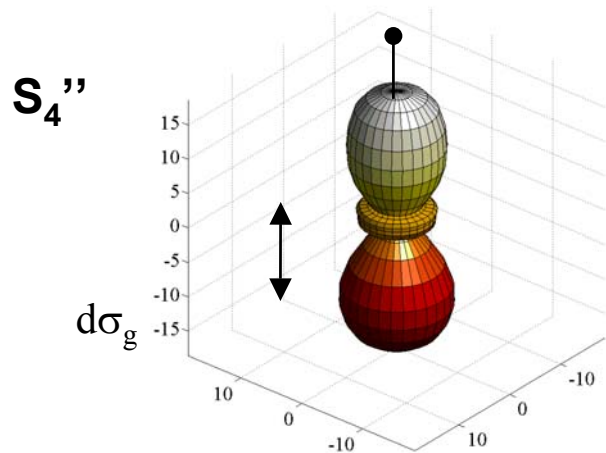
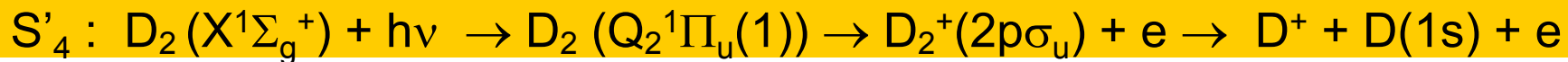
$$I_{90^\circ}(\theta_e, \phi_e) = F_{00}(\theta_e) - 0.5 F_{20}(\theta_e) + 3 F_{22}(\theta_e) \cos(2\phi_e)$$

$F_{11}(\theta_e) \rightarrow$ circular dichroism

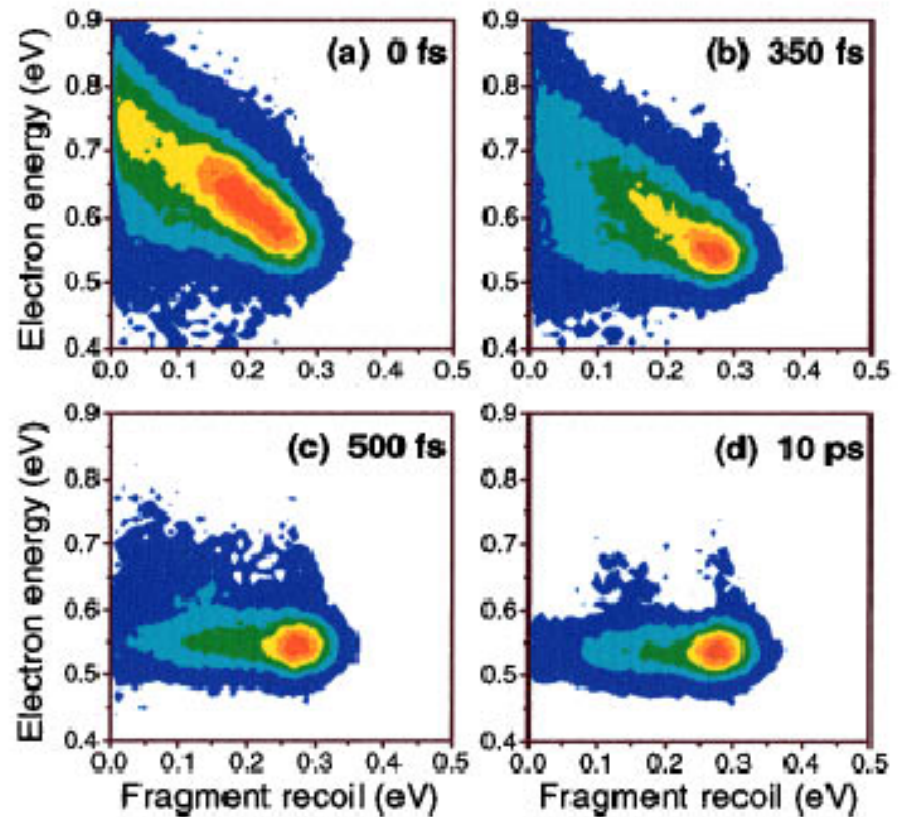
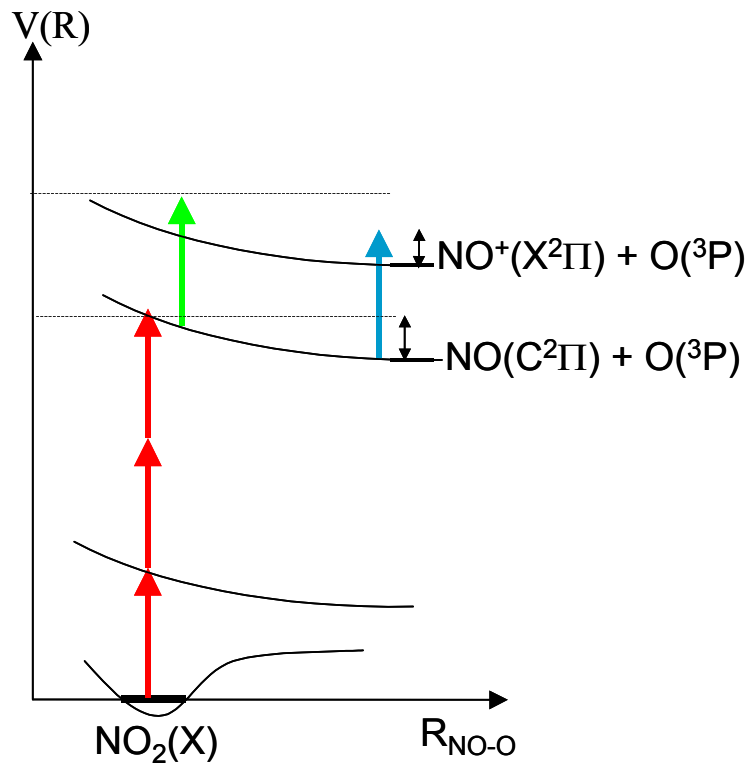
poster users meeting



$$F_{22}(\theta_e) > 0 \quad \Sigma^+ \rightarrow \Sigma^+$$

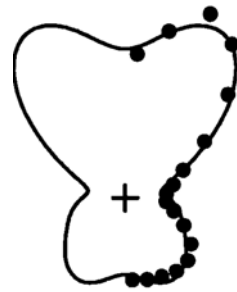


Dissociative Multiphoton Ionization: femtosecond time resolved vector correlations

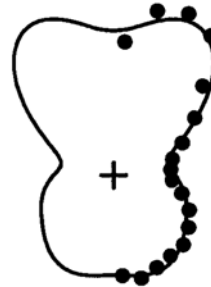


Ti-Sa 2.2 kHz 100fs
 $h\nu = (375 \text{ nm})$

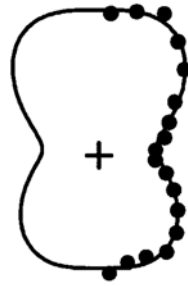
MFPADs probed during photodissociation



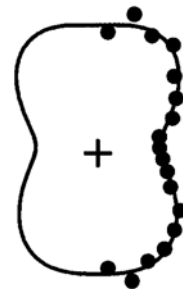
(a) 0 fs



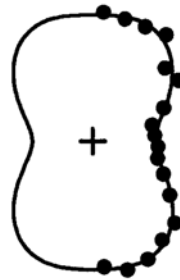
(b) 350 fs



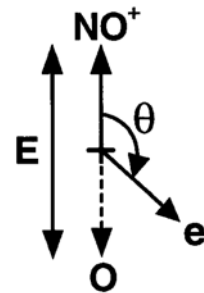
(c) 500 fs



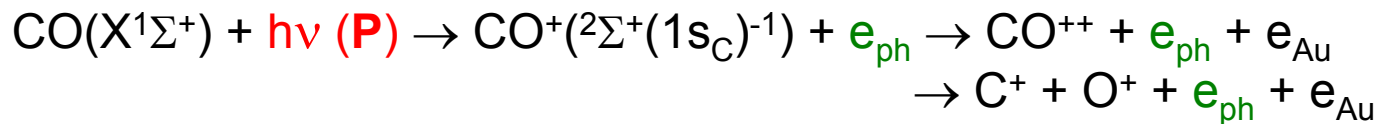
(d) 1 ps



(e) 10 ps

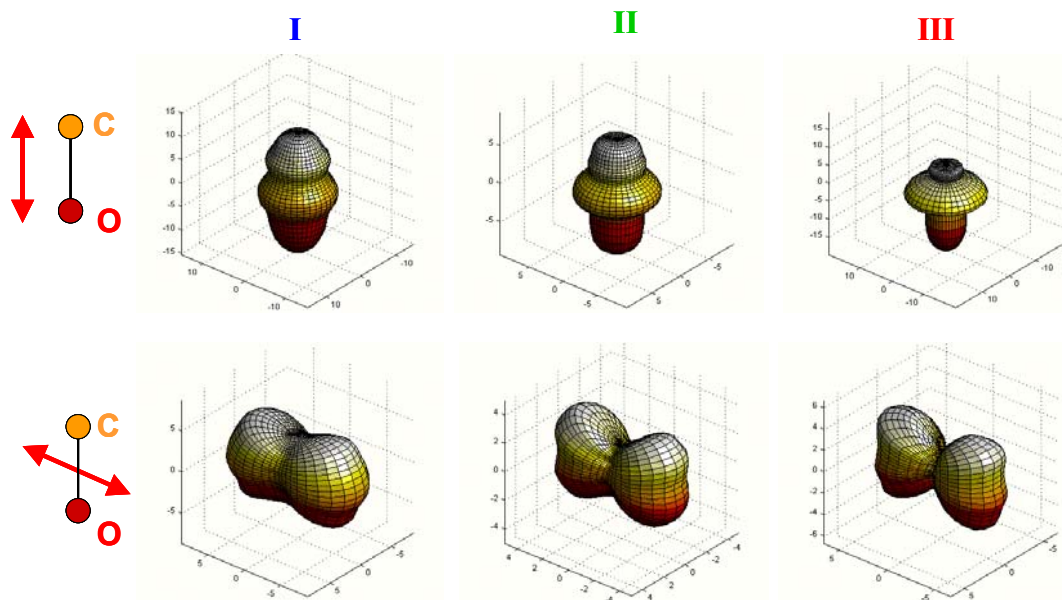
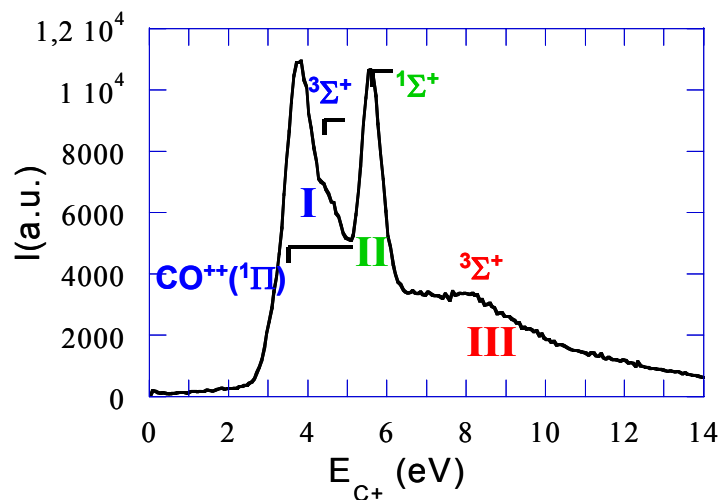


Vector correlations in DPI of inner-shell photoexcited molecules : CO



$h\nu = 302 \text{ eV}$
 $E_{\text{eph}} \approx 6 \text{ eV}$

$(\mathbf{V}_{\text{C}^+}, \mathbf{V}_{\text{O}^+}, \mathbf{V}_e, \mathbf{P})$



Weber et al J. Phys.B **34** 3669 (2001); Shigemasa et al PRL **80** 1622 (1998); Heiser et al PRL **79** 2435 (1997); Guillemin et al PRL **87** 203001 (2001)... Simon et al PRL **79** 3857 (1997)

Conclusion, perspectives

Combining time-of-flight resolved coincidence and imaging techniques is a powerful method for the investigation of the dynamics of photofragmentation of molecules induced by synchrotron radiation polarized light, ionization and dissociation, in the VUV and soft X ray range.

Femtosecond time-resolved light sources: follow the dissociation dynamics in real time

Ion-electron kinetic energy correlation

- Identification of the processes : reaction pathway
- Branching ratios
- Selection of one process

Molecular frame photoelectron angular distributions

→ $I(\theta_e, \phi_e, \chi_{A^+})$ MFPADs: detailed information, spectroscopy and dynamics and comparison with theory at the most fundamental level

electronic correlation, characterization of the ionization continuum: autoionizing states, shape resonances, coupling of ionization and dissociation

- axial recoil approximation, molecular rotation, bending
- Scheme for complete experiments with a single circular polarization of the light
- Importance of the circular dichroism

Perspectives:

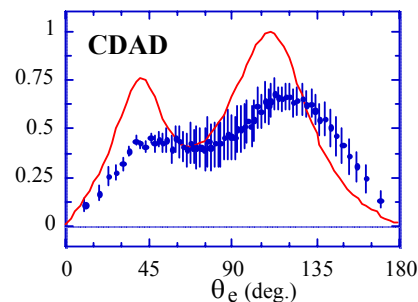
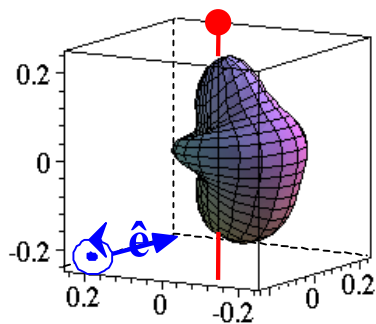
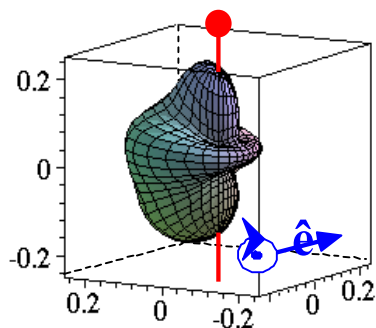
- breaking of a molecular bond in non-linear molecules and more complex molecular systems
- time - resolved vector correlation studies
- reaction dynamics

X-VUV time-resolved polarized light sources



Circular polarization and circular Dichroism

$$\mathbf{I}_{\pm 90^\circ}(\theta_e, \phi_e) = \mathbf{F}_{00}(\theta_e) - 0.5 \mathbf{F}_{20}(\theta_e) - 0.5 \mathbf{F}_{21}(\theta_e) \cos(\phi_e) - 0.5 \mathbf{F}_{22}(\theta_e) \cos(2\phi_e) \pm \mathbf{F}_{11}(\theta_e) \sin(\phi_e)$$



Lebech et al JCP june 2003

MFPAD D2
32.5 circ

