Electron angular distribution in dissociative photoionization of fixed-in-space D$_2$ molecules induced by circularly polarized light.

D Dowek$^2$, J Fernandez$^1$, M Lebech$^2$, J C Houver$^2$ and F Martin$^1$

1 Departamento de Quimica C-9, Universidad Autonoma de Madrid, 28049 Madrid, Spain

2 Laboratoire des Collisions Atomiques et Moléculaires (UMR Université Paris-Sud et CNRS, N°8625), Bat. 351, Université Paris-Sud, F-91405 Orsay Cedex, France
danielle.dowek@u-psud.fr

Abstract. This work reports new theoretical and experimental results for the circular dichroism in electron angular distribution (CDAD) in the molecular frame of D$_2$ ionized by circularly polarized light in the region involving the resonant excitation of Q$_1$ and Q$_2$ doubly excited states. At the 32.5 eV photon energy, dissociative ionization of D$_2$ into the ground state limit D$^+$ + D(1s) leads to an ion kinetic energy distribution extending over 7 eV, with a continuous energy sharing between the electron and the fragments. On the experimental side we used the vector correlation method to characterize the evolution of the molecular frame photoelectron angular distributions (MFPADs) as a function of the E$_{D^+}$ kinetic energy. The CDAD is quantified by the $\theta_e$ polar angle dependence of the left-right emission asymmetry maximum in the plane perpendicular to the light propagation axis $\mathbf{k}$, for a space fixed molecule orthogonal to $\mathbf{k}$. A remarkable variation of the CDAD is observed along the E$_{D^+}$ energy distribution. The results are compared with the prediction of full four body ab initio calculations.

1. Introduction
Investigation of circular dichroism at the level of photoemission in the molecular frame (MF), i.e. the modification of the photoelectron angular distribution upon the $h = \pm 1$ helicity of the light, is a very sensitive probe of the photoionization (PI) dynamics of molecules. Its occurrence in PI of oriented achiral molecules is a consequence of the spatial non-coplanarity of three vectors: the light propagation vector of elliptically polarized light $\mathbf{k}$, the photoelectron momentum $\mathbf{k}_e$, and the molecular axis $\mathbf{n}$, which creates a handedness for the system [1]. The CDAD observation for randomly oriented achiral molecules has been studied by recording MF photoelectron angular distributions (MFPADs), taking advantage of dissociative photoionization (DPI) induced by absorption of X/VUV circularly polarized synchrotron radiation for inner shell [2-4] and outer shell [5-7] PI. The triplet ($\mathbf{k}_e$, $\mathbf{n}$, $\mathbf{k}$) is identified by measuring in coincidence the initial velocity vectors of the photoion and photoelectron for each DPI event. These studies focused on the dynamics of the PI reaction, along the shape resonance region associated with the ionized orbitals [2,3,5], in the region above the respective ionisation thresholds [4,6], or at resonance with discrete autoionizing states where interferences between resonant and non resonant ionisation occur [7]. They were motivated by the fact that the MFPADs obtained for PI induced by circularly polarized light give the most complete access to the...
precision of the vz component of the electron velocity along the z axis parallel to the extraction field. This region involves autoionization of Q 1 and Q 2 doubly excited states, as previously assigned [8,13].

Components of the Rydberg series \( (\nu \nu \nu) \) doubly excited Rydberg series \( (h\nu \sim 25-35 \text{ eV}) \) leads to a quite original situation since ionization and dissociation occur on a very short time scale. MF photoemission for PI of H 2 and D 2 in this region induced by linearly polarized light [8,9] has demonstrated significant emission asymmetries illustrating symmetry breaking of H 2 dissociation with respect to the electron direction. The MFPADs for a molecule oriented perpendicular to the linear polarization axis, measured as a function of the kinetic energy release (KER) of the fragments, were very well predicted by full four body ab initio calculations based on a quantum treatment of both electrons and protons at \( h\nu = 33.25 \text{ eV} \) [9]. In this frame the emission asymmetry has been explained as the result of the interferences between the two decay channels of the autoionizing Q 2I \( \Pi_d(1) \) lowest state of the Q 2 series, involving the symmetric \( (X^2\Sigma_g^+, 1s\sigma_g) \) and antisymmetric \( (\Sigma_u^+, 2p\sigma_u) \) D + states, for the KER regions where both decay channels contribute.

Following these previous works, we study the characteristics of the MFPADs when PI is induced by circularly polarized light, and in particular how the quantum interferences between the decay pathways involving the 1s\( \sigma_g \) and 2p\( \sigma_u \) ionic states may influence the circular dichroism. On the experimental side we use the vector correlation (VC) method providing the generalized \( I(\chi, \theta_e, \phi_e) \) MFPADs in the form of five one dimensional \( F_{1,\lambda}(\theta_e) \) functions [6]. The \( F_{11} \) function governs the CDAD, which quantifies the left-right emission asymmetry maximum in the plane perpendicular to the propagation axis k of the light of defined helicity, for a molecule oriented orthogonal to k. The full four body ab initio calculations [9] have been extended to the case of circularly polarized light and provide computed \( F_{1,\lambda}(\theta_e) \) which are directly comparable with the experiment. A remarkable variation of the CDAD is observed along the E D+ energy distribution: however, although the CDAD for homonuclear molecules usually displays an inversion symmetry with respect to \( \theta_e = 90^\circ \) [10], some regions illustrate a significant symmetry breaking of the CDAD properties. Such a symmetry breaking is also found for the \( F_{21} \) function which, complementary to the \( F_{11} \) function, characterizes the relative phases between the dipole matrix elements for the parallel and perpendicular transitions.

2. Vector correlation method

2.1. Experimental set-up; Electron-ion kinetic energy correlation

The \( (V_D, V_E, \hat{\varepsilon}) \) vector correlation method consists of measuring for each DPI event the three components of the \( V_D \) D + ion and \( V_E \) photoelectron nascent velocity vectors, deduced from the arrival time and position of both particles in the VC double velocity spectrometer [11]. For these experiments, the interaction region was defined at the intersection of a supersonic molecular beam and the polarized light beam delivered by SU5 undulator-based VUV beamline at Super-ACO (LURE, Orsay), operated in the two-bunch mode. Using the Stokes parameters \((s_0, s_1, s_2, s_3)\) the circular polarization rate \( s_3/s_0 \) of the light was higher than 0.95 [12]. Ions and electrons were extracted from the interaction region by a dc electric field \( E \) whose magnitude, here 100V/cm, ensures a 4\pi collection of both particles for the studied processes, and guided to the two delay-line position sensitive detectors through an intermediate region where focusing lens sets are set to control the trajectories [11]. The main resolution limitation was due to the \( \delta t \approx 0.8 \text{ ns} \) time width of the light pulse, affecting mainly the precision of the \( v_z \) component of the electron velocity along the z axis parallel to the extraction field.

In the electron-ion kinetic energy correlation diagram (KECD) derived from the \( (V_D, V_E) \) vector correlation the \( (D^+, e) \) coincident events are found along a diagonal line of slope \( -2 \) [8] which corresponds to a continuous energy sharing between the electron and the \( (D^+ \text{ and } D) \) fragments leading to the \( D^+ + D(1s) \) dissociation channel. We focus the analysis on the events corresponding to energetic D + ions in the range \( 2 \text{ eV} \leq E_{D^+} \leq 8 \text{ eV} \), for which a 4\pi collection of electrons and ions is achieved. This region involves autoionization of Q 1 and Q 2 doubly excited states, as previously assigned [8,13],
and in particular excitation of the Q11Πg(1) lowest state of the Q2 series. In the following, we investigate
the angular properties of MF photoemission as a function of the E\textsubscript{Dg} energy in this diagonal selection.

2.2. Molecular frame photoemission: theory of measurements

For linear molecules in the dipole approximation, the I(χ, θ\textsubscript{e}, φ\textsubscript{e}) generalized MFPAD induced by
circularly polarized light of positive helicity (h = 1) has the analytical form [6]:

\[ I_{+}(χ, θ\textsubscript{e}, φ\textsubscript{e}) = F_{00}(θ\textsubscript{e}) - 0.5 F_{20}(θ\textsubscript{e}) P_{1}^{0}(\cos θ\textsubscript{e}) - 0.5 F_{31}(θ\textsubscript{e}) P_{1}^{1}(\cos θ\textsubscript{e}) \cos(ϕ\textsubscript{e}) \]

\[ -0.5 F_{22}(θ\textsubscript{e}) P_{1}^{2}(\cos θ\textsubscript{e}) \cos(2ϕ\textsubscript{e}) + F_{11}(θ\textsubscript{e}) P_{1}^{1}(\cos θ\textsubscript{e}) \sin(ϕ\textsubscript{e}) \]

(1)

where χ is the polar angle referring the orientation of the molecular axis n with respect to the light propagation axis \( k \), and \( (θ\textsubscript{e}, φ\textsubscript{e}) \) characterizes the electron emission direction \( \mathbf{k}_\text{e} \) in the MF defined by
the molecular axis and the light propagation axis. In this expression the dependence on \( φ\textsubscript{e} \) and \( χ \)
through low order analytical functions: the complete dynamical information about the PI reaction is
described by the five one-dimensional \( F_{k\textsubscript{LN}}(θ\textsubscript{e}) \) functions, which give access to the transition moments
between the ionized orbitals and the photoelectron continuum state, their magnitudes and relative
phases. A three angle fit of the \( I_{+}(χ, θ\textsubscript{e}, φ\textsubscript{e}) \) measured distribution provides the five \( F_{k\textsubscript{LN}}(θ\textsubscript{e}) \) functions.

Knowing the \( F_{k\textsubscript{LN}} \) functions, one can plot directly the MFPAD for any well defined orientation of the
molecular axis χ with respect to the propagation axis of circularly polarized light k using equation (1),
or to linearly polarized light P [14].

The most favorable geometry for the observation of circular dichroism in the MF is obtained for a
molecule oriented perpendicular to the light propagation axis (χ = 90\degree). The CDAD is then
characterized by the photoemission left-right asymmetry, maximum in the plane perpendicular to k
(φ\textsubscript{e} = 90\degree/270\degree) as described by the \( \sin(ϕ\textsubscript{e}) \) dependence in equation (1). We defined the dimensionless
CDAD parameter in two equivalent ways, related to the \( F_{k\textsubscript{LN}}(θ\textsubscript{e}) \) functions as follows [6,10]:

\[ \text{CDAD}_{(χ=90,θ\textsubscript{e}=90)} = \frac{I_{+1} - I_{-1}}{I_{+1} + I_{-1}} = \text{CDAD}_{(χ=90,θ\textsubscript{e}=90)} = \frac{I_{90} - I_{270}}{I_{90} + I_{270}} = \frac{2F_{11}}{2F_{00} + \frac{1}{2}F_{20} + 3F_{22}}. \]

(2)

For the reported study of DPI of the D\textsubscript{2} molecules, the \( F_{k\textsubscript{LN}} \) and CDAD parameters are functions of
two variables: the polar angle (θ\textsubscript{e}) and the E\textsubscript{Dg} energy. Although only \( F_{11} \) is characteristic of the circular
dichroism providing the sign of the relative phases between the dipole matrix elements for the
parallel and perpendicular components of the PI transition, we also refer in the text to \( F_{21} \), which carries
complementary information about the magnitude of these relative phases. For PI of homonuclear molecules
both \( F_{11} \) and \( F_{21} \) should display an inversion symmetry with respect to \( θ\textsubscript{e} = 90\degree \)[10 and ref. therein]. The results for \( F_{21}(θ\textsubscript{e}) \) will be reported in another publication.

3. Theory

We have made use of the dipole approximation and Dill’s formula [15] to evaluate PI cross sections
and related \( F_{k\textsubscript{LN}}(θ\textsubscript{e}) \) functions corresponding to leaving the residual molecular ion in a specific
electronic state α, differential in i) the photoelectron energy ε, ii) the photoelectron emission direction
in the MF \( φ\textsubscript{e} = (θ\textsubscript{e}, φ\textsubscript{e}) \) and iii) the polarization direction with respect to the molecular axis. The
transition matrix element involves the ground molecular state of energy \( W_{\textit{g},\textit{e}} \) and the final molecular state of energy \( W_{\textit{α},\textit{e}} + ε \) representing a molecular ion in the \( v_{\textit{α}} \) vibronic state (either dissociative or non
dissociative) and an emitted electron of energy ε. Energy conservation dictates that \( W_{\textit{g},\textit{e}} + hν = W_{\textit{α},\textit{e}} + ε \). The two wave functions are connected by the dipole operator and are evaluated, neglecting
rotational effects, in the adiabatic approximation [16] (see also equations 42 and 60 of [17]).

Briefly, the final state comes from a close-coupling calculation incorporating contributions from the
two lowest ionization thresholds of H\textsubscript{2} or D\textsubscript{2} [X \Sigma\text{g} \text{g}(1s\sigma\textsubscript{g}) 2Σ\text{g} \text{u}(2p\sigma\textsubscript{u})], the six lowest doubly excited
states of the Q\textsubscript{1} and Q\textsubscript{2} series, for both \( Σ\text{u} \) and \( Π\text{u} \) symmetries, as well as the corresponding vibrational
and dissociative states. As shown in [17], the theory includes the possibility of autoionization decay as
the molecule dissociates as well as interferences among the various electronic and nuclear channels. B-spline functions were used to obtain the electronic and vibrational wave functions.

4. Molecular frame photoemission induced by circularly polarized light: $E_{D^+}$ dependence of the $\theta_e$ angle integrated $F_{LN}$ functions

In this section we compare the $E_{D^+}$ dependence of selected experimental and theoretical results at the level of $\theta_e$ integral $F_{LN}$ functions.

In the experimental side the data analysis is as follows: taking into account the $D^+$ energy resolution of the order of 0.5 eV, and the statistics enabling the extraction of the $F_{LN}(\theta_e)$ functions for each $E_{D^+}$ selection, the $F_{LN}(\theta_e)$ functions are first determined for sets of events lying along the diagonal in the KECD, included between the two straight lines of slope $-2$ representing pseudo-dissociation limits at 15 eV and 21 eV, in intervals of $\Delta E_{D^+} = 0.5$ eV, by steps of 0.25 eV.

**Figure 1.** Selected angle integrated $F_{LN}$s as a function of the $E_{D^+}$ energy: theory (full line), convoluted theory (dashed line), experiment (dots).

The five integral functions $IntF_{LN}(E_{D^+})$ are obtained as:

$$IntF_{LN}(E_{D^+}) = \int_0^\pi d\theta_e \sin(\theta_e) F_{LN}(\theta_e,E_{D^+}) .$$

In figure 1 we display the $E_{D^+}$ dependence of $IntF_{00}$, $IntF_{20}$, $IntF_{11}$ and the normalized ratio $IntF_{11}/IntF_{00}$ for (i) the present calculations (ii) the calculations convoluted with the apparatus function using a Monte Carlo simulation of the trajectories in the VC spectrometer, and analyzed according to the same procedure as the experimental data in intervals of 0.5 eV (iii) the experimental results. Experiment is normalized to theory such that the integral PI cross section over the studied $E_{D^+}$ energy range is identical. Figures 1 (a) and (b) show that the effect of convolution on the $IntF_{00}$ and $IntF_{20}$ $E_{D^+}$ dependence is small and that a good agreement between theory and experiment is achieved. $IntF_{00}$ represents the integral PI cross section, in good agreement with previous measurements and calculations [13,17]. The sign inversion of $IntF_{20}$ for $E_{D^+} \approx 5.5$ eV corresponds to the change from a dominant parallel transition for low $D^+$ energies ($\beta_{D^+} \approx 0.5$ along the 2-4 eV plateau) to a dominant perpendicular transition for $E_{D^+} > 5.5$ eV ($\beta_{D^+} \approx -0.5$ in the range 6-7 eV). The same good agreement is obtained when comparing the computed and measured $IntF_{22}$.

However the situation is different for the $E_{D^+}$ variation of $IntF_{11}$ shown in figure 1 (c) (as well as that of $IntF_{21}$ not shown): the computed $IntF_{11}$ and $IntF_{21}$ lie close to zero for low $D^+$ energies $2 \leq E_{D^+} \leq 4$ eV and display strong positive and negative oscillations in the range $4 \leq E_{D^+} \leq 7.5$ eV, with a half-period of the order of 0.5 eV. This result is the first fingerprint that, for the higher $E_{D^+}$ range, the CDAD does not display the inversion symmetry expected for PI of homonuclear molecules, which
would imply that both \( IntF_{11} \) and \( IntF_{21} \) would remain about zero. The effect of convolution strongly attenuates the contrast of these oscillations. The experimental result is in qualitative agreement with the theoretical prediction in the sense that \( IntF_{11} \) and \( IntF_{21} \) are close to zero in the \( 2 \leq E_{D^+} \leq 4 \) eV range, take non-zero values for \( 4 \leq E_{D^+} \leq 6 \) eV of comparable amplitude with the convoluted theory, and decrease to zero again for higher energies. However the sign of the measured \( IntF_{11} \) is negative in the region where theory predicts positive values, and the opposite is true for the evolution of \( IntF_{21} \).

5. Molecular frame photoemission induced by circularly polarized light: \( F_{LA}(\theta) \) functions and MFPADs

We report \( F_{LA}(\theta) \) functions and related MFPADs for two specific \( D^+ \) energy selections: the first one, \( 5.5 \leq E_{D^+} \leq 6.5 \) eV (figure 2(a)), in the region of the maximum of the cross section where the integral CDAD is close to zero, and the second one, \( 4.5 \leq E_{D^+} \leq 5.5 \) eV (figure 2(b)), in the region where the computed and measured \( IntF_{11} \) (and \( IntF_{21} \)) are of significant magnitude.

For both examples we present here the experimental and theoretical results in terms of (i) \( F_{LA}(\theta) \), (ii) the CDAD parameter according to equation (2), and (iii) the cuts of the MFPAD induced by polarized light of helicity +1 for a \( D_2 \) molecule oriented perpendicular to the \( k \) propagation axis corresponding to electron emission at \( \phi = 90^\circ/270^\circ \) (left/right side): convol. theory (line), exp. (dots).

\[ \text{Figure 2. For (a) } 5.5 \leq E_{D^+} \leq 6.5 \text{ eV and (b) } 4.5 \leq E_{D^+} \leq 5.5 \text{ eV : left column: } F_{LA}, \text{ CDAD: theory (full line), convol. theory (dashed line), exp. (dots); right column: cut of the MFPAD induced by } h=+1 \text{ polarized light for } D_2 \text{ oriented perpendicular to } k \ (\chi = 90^\circ) \text{ corresponding to electron emission at } \phi = 90^\circ/270^\circ \text{ (left/right side): convol. theory (line), exp. (dots).} \]

6. Conclusion
We have reported selected results of a comparative theoretical and experimental study of MF photoemission in PI of D₂ induced by circularly polarized light. The remarkable evolution of the CDAD predicted by the full four body calculations is in qualitative agreement with the experimental results in the sense that both demonstrate a strong evolution of the CDAD as a function of E_D+, with a violation of the inversion symmetry with respect to $\theta = 90^\circ$ that characterizes MF circular dichroism in PI of homonuclear molecules, for D+ energies $E_{D+} \geq 3.5$ eV. We interpret this feature as due to interferences between the $Q_2^1\Pi_u(1)$ state decay channels involving the $(X^2\Sigma_g^+, 1s\sigma_g)$ and $(\Sigma_u^+, 2p\sigma_u)$ D₂⁺ states, in the KER regions where both channels contribute. Indeed the $E_{D+} \geq 3.5$ eV region corresponds to the one where the observed strong asymmetries in electron emission induced by linearly polarized light have been assigned to such interference effects [9]. The quantitative disagreement remaining between theory and experiment at the level of the $F_{11}$ and $F_{21}$ most sensitive parameters characterizing the relative phases of the dipole matrix elements shows that progress can still be achieved in the theoretical description. In particular, inclusion of additional Q states seems to be necessary. In parallel, complementary experiments with circularly polarized light are planned on a short term on the beamline DESIRS at SOLEIL where the 3rd generation characteristics of the light beam should enable a significant improvement of the $F_{1N}(\theta_e, E_{D+})$ resolution.

Acknowledgments

DD, ML and JCH acknowledge the support of L. Nahon, beamline scientist for SU5 at Super-ACO, B. Pilette for technical assistance, as well as the machine staff for operating Super-ACO (LURE).

References

[1] Cherepkov N A, Kuznetsov V V 1987 Z. Phys. D 7 271; Schönhense G 1990 Physica Scripta T31 255.
[2] Motoki S, Adachi J, Ito K, Ishii K, Soejima K, Yagishita A, Semenov S K, and Cherepkov N A 2002 Phys. Rev. Lett. 88 063003.
[3] Jahneke T et al 2002 Phys. Rev. Lett. 88 073002.
[4] Li W B, Houver J C, Haouas A, Catoire F, Elkharrat C, Guillemin R, Journel L, Montuoro R, Lucchese R R, Simon M, and Dowek D 2007 J. Electron Spectrosc. Relat. Phenom. 156-158, 30.
[5] Gessner O, Hikosaka Y, Zimmermann B, Hempelmann A, Lucchese R R, Eland J H D, Guyon P M, and Becker U 2002 Phys. Rev. Lett. 88, 193002.
[6] Lebech M, Houver J C, Lafosse A, Alcaraz C, Nahon L, Lucchese R R and Dowek D 2003 J. Chem. Phys. 118, 9653.
[7] Lebech M, Houver J C, Dowek D and Lucchese R R. 2006 Phys. Rev. Lett. 96, 073001.
[8] Lafosse A, Lebech M, Brenot J C, Guyon P M, Spielberger L, Jagutzki O, Houver J C and Dowek D 2003 J. Phys. B: At. Mol. Phys. 36 4683; Dowek D, Lebech M and Houver J C Proc. of the XXIV ICPEAC 20-26 July 2005 Rosario Argentina (ed. P D Fainstein et al World Scientific Pub. 2006) p214
[9] Martin F et al 2007 Science 315 629
[10] Dowek D, Lebech M, Houver J C and Lucchese R R, Molecular Physics (in press).
[11] Lebech M, Houver J C and Dowek D 2002 Rev. Sci. Instrum. 73, 1866
[12] Nahon L and Alcaraz C 2004 Applied Optics, 43, 1024.
[13] Strathdee S and Browning R 1979 J. Phys. B: At. Mol. Phys. 12, 1789; Ito K, Hall R and Ukai M 1996 J. Chem. Phys. 104, 8449; Latimer C J, Geddes J, MacDonald M A, Kouchi N and Dunn K F 1996 J. Phys. B: At. Mol. Phys. 29, 6113.
[14] Lucchese R R, Lafosse A, Brenot J C, Guyon P M, Houver J C, Lebech M, Raseev G and Dowek D 2002 Phys. Rev. A 65, 020702-1.
[15] Dill D 1976 J. Chem. Phys. 65, 1130.
[16] Sanchez I and Martin F 1999 Phys. Rev. Lett. 82, 3775.
[17] Martin F 1999 J. Phys. B 32, R197.