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## Spectral dependence of photoemission in multiphoton ionization of NO<sub>2</sub> by femtosecond pulses in the 375–430 nm range.

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We investigate the multiphoton ionization of NO<sub>2</sub> using tuneable (430–375 nm) femtosecond pulses and photoelectron-photoion coincidence momentum spectroscopy. In order to understand the complex electronic and nuclear photodynamics at play following absorption of three to five photons, we also report extended photoionisation calculations using correlated targets and coupled channels. Exploring the multiphoton dissociative (MPDI) and multiphoton ionisation (MPI) processes over such a broad energy range enables us to lend further support to our work carried out around 400 nm of a femtosecond laser [S. Marggi Poullain *et al* *J. Phys. B: At. Mol. Opt. Phys.*, 2014, **47**, 124024]. Two excitation energy regions are identified and discussed in terms of proposed reaction pathways, highlighting the significant role of Rydberg states, such as the [R\*(6a<sub>1</sub>)<sup>-1</sup>, 3pσ] Rydberg state, in the NO<sub>2</sub> multiphoton excitation and photoionization. These new results support our previous assumption that different bent and linear geometries of the NO<sub>2</sub><sup>+</sup>(X<sup>1</sup>Σ<sub>g</sub>) ionic state contribute to the MPDI and to the MPI, consistent with the reported calculations which reveal an important vibronic coupling characterizing the photoemission. Remarkably, the strong anisotropy of the recoil frame photoelectron angular distribution (RFPAD) previously observed at 400 nm appears as a fingerprint across the whole explored photon energy range.

### 1. Introduction

Molecular dynamics in the nitrogen dioxide molecule has attracted much interest in recent years. Despite its apparent simplicity as a triatomic molecule, this non-linear molecule of C<sub>2v</sub> geometry in its (4b<sub>2</sub>)<sup>2</sup>(6a<sub>1</sub>)<sup>1</sup> open-shell ground state presents a very rich photochemistry governed by ultrafast non-adiabatic couplings involving different electronic states, such as vibronic couplings favoured at conical intersections. We refer to the comprehensive review<sup>1</sup> by Wilkinson and Whitaker for the vast literature dedicated to the spectroscopy and photodynamics of NO<sub>2</sub> for excitation energies up to 20 eV, and in particular the extensive work addressing multiphoton photodissociation and photoionization processes in the 400 nm region relevant for the present work. NO<sub>2</sub> is an interesting prototype molecular system to investigate to which extent the methodological approaches such as modelling the recoil frame photoemission in small polyatomic molecules can probe ultrafast molecular dynamics in multiphoton induced photoionization reactions.

In a previous paper<sup>2</sup> referred to as paper I, we reported experimental results for multiphoton dissociative (MPDI) and non-dissociative (MPI) ionization of NO<sub>2</sub> induced by 400 nm femtosecond pulses, obtained using coincident electron-ion momentum spectroscopy, also referred to as vector correlation (VC) method<sup>3,4</sup>. The key observations for the two dominant MPDI and MPI processes, derived from the complete energy and angular analysis of the coincident events involving the (NO<sup>+</sup>, e) fragment and (NO<sub>2</sub><sup>+</sup>, e) parent channels, respectively, were the following: (i) a quite similar photoelectron energy, but (ii) different asymmetry parameters describing the photoemission in the laboratory frame, (iii) a significant ro-vibrational excitation of the NO<sup>+</sup> fragment, (iv) a strong alignment of the NO<sup>+</sup> recoil direction parallel to the laser polarization axis and (v) a remarkable anisotropy of the recoil frame photoelectron emission in the recoil direction of the NO<sup>+</sup> fragment. To facilitate the interpretation of the RFPAD,  $T_{fi}^{(n, \text{RF})}(\theta_e, \phi_e, \chi)$ , where  $\chi$  is the polar angle of the fragment ion recoil direction relative to the light polarization axis and ( $\theta_e, \phi_e$ ) are the polar and azimuthal angles defining the electron emission direction in the recoil frame<sup>2,5</sup>, a formalism was developed to describe a n-photon MPDI process (n=5), involving (n-1)-photon bound-to-bound transitions and one-photon ionization of a molecular excited state of C<sub>2v</sub> symmetry. It was further extended to enable the most tractable comparison with the one-channel and two-channel photoionization calculations also reported in paper I.

Combining the MPDI and MPI results at 400 nm with those obtained for single-photon ionization (SPI)<sup>6</sup> and dissociative ionization (SPDI)<sup>2</sup> using synchrotron radiation of comparable

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total excitation energy, a reaction pathway for the dominant MPDI and MPI processes was tentatively proposed<sup>2</sup> as shown schematically in Figure 1. This figure includes a simplified diagram of the NO<sub>2</sub> energy levels, at the equilibrium geometry: the NO<sub>2</sub>(X<sup>2</sup>A<sub>1</sub>) ground state, the NO<sub>2</sub><sup>+</sup>(X<sup>1</sup>Σ<sub>g</sub><sup>+</sup>) (linear) and the NO<sub>2</sub><sup>+</sup>(a<sup>3</sup>B<sub>2</sub>) (bent) lowest ionic states, and the corresponding Rydberg series [R\*(6a<sub>1</sub>)<sup>-1</sup>] and [R\*(4b<sub>2</sub>)<sup>-1</sup>], as well as the lowest dissociation limits for dissociative ionization (NO<sup>+</sup>(X<sup>2</sup>Π),O(<sup>3</sup>P)) and ion-pair formation (NO<sup>+</sup>(X<sup>2</sup>Π),O(<sup>2</sup>P)). In the proposed reaction pathway, the first four-photon step consists of three bound-to-bound transitions exciting the molecule into a valence state strongly coupled with the [R\*(6a<sub>1</sub>)<sup>-1</sup> 3pσ<sup>2</sup>B<sub>2</sub>, v] Rydberg states, the latter being subsequently ionized into the NO<sub>2</sub><sup>+</sup>(X<sup>1</sup>Σ<sub>g</sub><sup>+</sup>, v) manifold while preserving their initial vibrational quantum number. For the dominant MPDI reaction, an additional (fifth) photon is absorbed leading to the dissociation of the vibrationally excited molecular ion. Due to the Franck-Condon (FC) overlap, this process is expected to be strongly dependent on the ion bending angle.

However, a number of questions remained opened in this study. In particular, the remarkable forward-backward (FW-BW) emission anisotropy observed in the experimental RFPAD –the electron is ejected close to the ion recoil direction– was not well reproduced by the calculations describing photoionization of the Rydberg [R\*(6a<sub>1</sub>)<sup>-1</sup> 3pσ<sup>2</sup>B<sub>2</sub>, v] series. As pointed out in paper I, a similar anisotropy was observed in electron-ion femtosecond time-resolved coincidence studies of dissociative multiphoton ionization<sup>7,8</sup>. Namely, it was reported at a wavelength of 375 nm<sup>7</sup> for a zero delay between the pump and probe beams, and qualitatively attributed to photoionization of the nascent NO(C<sup>2</sup>Π<sub>1/2</sub>) fragment in early stages of the photodissociation<sup>9</sup>, as well as at zero time delay in two-colour experiments employing 400 nm-266 nm<sup>8</sup> for the major MPDI process attributed to three 400nm-photon absorption followed by one 266 nm-photon ionization into the NO<sub>2</sub><sup>+</sup>(a<sup>3</sup>B<sub>2</sub>) dissociative states.

The main goal of the present work is therefore to explore the robustness and the range of applicability of the reaction pathways we proposed in paper I the multiphoton ionization of NO<sub>2</sub> around 400 nm. For this purpose, we have improved the femtosecond laser system in order to obtain an extended tunability between 375 nm and 430 nm wavelengths, shorter pulses and an increase of the repetition rate from 1 kHz to 3 kHz. The new experiments performed using the VC method enable us to observe the evolution of the different dissociative and non-dissociative ionization processes as a function of the excitation wavelength and indeed to identify two different regions in terms of excitation energy corresponding to different reaction pathways. Furthermore, new calculations have been carried out to extend the work published in paper I by including correlated targets and up to five coupled channels to describe the photoionization step.

Finally, we note that (NO<sup>+</sup>,O<sup>-</sup>) ion pair formation has also been recorded in the explored photon excitation energy range and confirmed to be a remarkable channel resulting from 4 photon absorption<sup>10</sup>: these results will be reported separately.

The paper is organized as follows. In section 2, the experimental setup and the computational method are briefly described. In section 3, we report the measured (NO<sup>+</sup>, e) kinetic energy correlation diagrams (KECDs) and photoelectron spectra for MPDI and MPI, respectively, as well as the ion and electron angular distributions in the laboratory frame, as a function of the photon excitation energy. The measured recoil frame photoelectron angular distributions (RFPAD) for the dominant MPDI process are also reported and analysed based on the methodology developed in paper I. In section 4, the computed photoelectron asymmetry parameters β<sub>e</sub> and molecular and recoil frame photoelectron angular distributions (MFPAD and RFPAD) are discussed. In section 5, we conclude with a comparison and discussion the experimental results against the reported calculations. An extended discussion of the theoretical results and their comparison with the measured RFPADs is the subject of a forthcoming paper [in preparation].

## 2. Methods

### 2.a. Experimental

The experiments were carried out at the SOFOCKLE laser facility (LIDYL) which is based on a titanium-sapphire (Ti : Sa) system delivering pulses of 1 mJ at 800 nm, with a 3 kHz repetition rate. A hollow fiber filled with Argon was used to obtain a spectral broadening between 700 nm and 900 nm, based on the self-phase modulation. The output pulses around 800 nm were recompressed to 10 fs with a series of chirped mirrors. The use of a type I BBO crystal of 300 μm thickness for frequency doubling yielded wavelengths between 375 and 430 nm by varying the phase matching angle. Final pulses were characterized by a spectral width varying between 5 and 12 nm and by a duration of 50 fs (±5 fs) for 385-415 nm wavelengths and of 80 fs (±10 fs) for 375-385 and 415-430 nm wavelengths estimated by autocorrelation measurements as well as by self-referenced spectral interferometry measurements<sup>11</sup>. The laser beam is focused at the center of the VC electron-ion double momentum spectrometer by a silica lens of  $f = 44$  cm focal length. The intensity of the laser in the interaction region was estimated to vary between  $\sim 4.5 \times 10^{11}$  Wcm<sup>-2</sup> and  $\sim 9 \times 10^{11}$  Wcm<sup>-2</sup>, considered here as corresponding to weak field conditions.

These measurements were performed using the CELIMENE set-up described in detail previously<sup>12</sup>. CELIMENE, equipped with a supersonic molecular expansion (nozzle  $\phi = 70$  μm and skimmer  $\phi = 1$  mm), hosts a VC electron-ion double momentum spectrometer<sup>3,4</sup> based on two time and position sensitive detectors (PSD)<sup>13</sup> of  $\phi = 80$  mm diameter. The NO<sub>2</sub> molecular beam was produced by expanding 1.5 bars of a gas mixture (5% NO<sub>2</sub> in He). The nozzle was continuously heated at 120 degrees to suppress the N<sub>2</sub>O<sub>4</sub> present at room temperature in the gas mixture. NO<sub>2</sub><sup>+</sup> and NO<sup>+</sup> photoions (*i*) and photoelectrons (*e*) were extracted from the interaction region by a dc uniform electric field fixed between 15 and 30 V/cm such that a 4π collection of electrons and ions guided towards their respective PSD<sup>13</sup> was achieved. For each (*i*, *e*) coincident event, the three components of the emission (**V<sub>i</sub>**, **V<sub>e</sub>**) velocity vectors were

derived from the measured time of flight (TOF) and impact position of the particle on the PSD.

During the VC experiments, the signal rate was controlled and the mean number of events was kept of the order 100 coincidences per second, corresponding to 0.03 events/pulse, in order to ensure a true coincidence acquisition mode.

## 2.b. Theoretical

The calculations reported here for bound and scattering target states were done with the one-electron basis set described in paper I<sup>2</sup> which was based on the standard augmented correlation-consistent polarized valence triple zeta aug-cc-pVTZ basis set<sup>14,15</sup> that was then augmented by diffuse functions. In all calculations the bond length was held constant at its experimental equilibrium<sup>16</sup> value  $R(\text{NO})=1.1945 \text{ \AA}$  with a range of  $\angle\text{ONO}$  angles also being considered. Note that the equilibrium structure of  $\text{NO}_2$  in its ground state has  $\angle\text{ONO} = 133.85^\circ$ .

The transition dipole moments for photoionization were computed using correlated target wave functions and included one, two, and five coupled electronic channels. These calculations are extensions of the results reported earlier<sup>2</sup> where here we have included the full one-electron basis set described above, extended the calculations to include five coupled channels, and also considered one-channel calculations with a correlated target state. They were performed using the complex Kohn method.<sup>17,18</sup>

The orbitals used to represent the bound molecular orbitals were obtained from a state-averaged multi-configuration self-consistent field (SA-MCSCF) calculation<sup>19,20</sup> which are the same as performed previously, with however the improved one-electron basis set as mentioned above. For calculations for ionization from the  $[\text{R}^*(6a_1)^{-1}] 3p\sigma^2 B_2$  state, an additional  $5b_2$  orbital was computed by adding a  $b_2$  orbital to the active orbital set and adding three  $^2B_2$  states to the state average, but freezing the 14 orbitals obtained in the first SA-MCSCF calculation.

In the scattering calculations, one-channel calculations included only the  $X^1A_1$  state of the ion, two-channel calculations added the  $a^3B_2$  ion state, and in the five-channel calculations, three additional low lying  $\text{NO}_2^+$  ion states ( $b^3A_2$ ,  $A^1A_2$ , and  $B^1B_2$ ) were included.

Here we are modelling the dominant MPDI and non-dissociative MPI processes for which the observed photoelectron energy is near 0.5 eV. Thus in the present calculations we considered mainly photoionization from excited Rydberg states of  $\text{NO}_2$  which have an IP of  $\sim 2.6$  eV relative to the  $X^1A_1$  state of  $\text{NO}_2^+$ : one  $\sim 400$  nm photon, with energy of  $h\nu \sim 3.1$  eV, then results in a photoelectron with kinetic energy of  $\sim 0.5$  eV, when vibrational energy is conserved.

To compare efficiently the computed and measured RFPADs, we exploit the method presented in paper I. We consider the principal component analysis of the recoil-frame azimuthal harmonics (PCA-RFAH) of the total RFPAD intensity using the form (see eq.16 of paper I<sup>2</sup>):

$$T_{fi}^{(n,\text{RF})}(\theta_e, \phi_e, \chi) = \sum_{K \lambda=1}^M J_{\lambda}^{(K)}(\chi) G_{\lambda}^{(K)}(\theta_e) \cos(K\phi_e) \quad (1)$$

We have computed the PCA-RFAH expansion for five photon MPDI for the scheme described in paper I, which is equivalent to a  $[2,2,2,2]$  bound-to-bound excitation scheme with a fifth photon leading to ionization. The  $[2,2,2,2]$  pathway refers to four type 2 transitions associated with a transition dipole parallel to the O-O axis, which corresponds to transitions between states of symmetry  $A_1$  and  $B_2$ . For simplicity we assume that the MPDI process can be characterized by two  $\angle\text{ONO}$  angles. The first is the  $\angle\text{ONO}$  angle at the time of the photoionization,  $\theta_p$ , and second angle,  $\theta_r$ , gives the structure of the molecule when it fragments, and thus defines the recoil direction. Calculations performed as a function of these angles show that the dynamical parameters characterizing the one-photon ionization of the  $[\text{R}^*(6a_1)^{-1}]$  Rydberg states vary strongly with  $\theta_p$ . Therefore, both the values of  $\theta_p$  and  $\theta_r$  influence the resulting RFPADs. In the present study we focus on the results for the  $[\text{R}^*(6a_1)^{-1} 3p\sigma^2 B_2]$  Rydberg state and ( $\theta_p = 134^\circ$ ,  $\theta_r = 150^\circ$ ). Other results will be reported and discussed in a forthcoming publication.

## 3. Experimental Results

### 3.a. Electron-ion kinetic energy correlation

The electron-ion kinetic energy correlation diagram (KECD) for the  $(\text{NO}^+, e)$  coincident events corresponding to the dissociative photoionization (MPDI) of  $\text{NO}_2$  are presented in Fig. 2 for several wavelengths in the 430-375 nm range. The dissociation limits deduced from Eq. (2) by energy conservation are also shown in the KECD:

$$nh\nu - E_D^{(l)} = E_{\text{KER}} + E_e \quad (2)$$

where  $n$  is the number of absorbed photons and  $E_D^{(l)}$  represents the dissociation energy for an asymptotic limit ( $l$ ). When five photons are absorbed in the 430-375 nm range, two series of dissociative ionization limits can be populated, labelled  $L_1[5]$  and  $L_2[5]$ , corresponding to  $\text{O}(^3\text{P}) + \text{NO}^+(X^1\Sigma^+, \nu)$  ( $E_D^{(1)} = 12.38$  eV, for  $\nu=0$ ) and  $\text{O}(^1\text{D}) + \text{NO}^+(X^1\Sigma^+, \nu)$  ( $E_D^{(2)} = 14.35$  eV) where the vibrational spacing of  $\text{NO}^+(X^1\Sigma^+, \nu)$  is  $\Delta E_\nu \approx 290$  meV. For a four-photon process, the lowest dissociation limit, labelled  $L_1[4]$ , opens up for wavelengths shorter than 400.5 nm.

The wavelength dependence of the KECDs reveals the existence of two excitation regions: region I ( $\lambda \geq 400.5$  nm) and region II ( $\lambda \leq 400.5$  nm)

For  $\lambda \geq 400.5$  nm (region I), only two broad structures are observed and attributed to MPDI processes due to five photon absorption to reach  $L_1[5]$ , labelled A and B, following the notation introduced in paper I, with a major contribution of peak A (Fig. 2 (a) and (b)). Their main characteristics, a rather well-defined photoelectron energy for each process, varying between 0.2 and 0.8 eV with a maximum around 0.2-0.4 eV (A), and 1.3-1.5 eV (B), are quite similar to those reported previously<sup>2</sup> around 400 nm. The elongation of the A and B

structures along the total KER axis shows that the  $\text{NO}^+(\text{X}^1\Sigma^+, \nu)$  fragment is produced with an extended ro-vibrational energy distribution. For process A the peak of the vibrational distribution of the  $\text{NO}^+(\text{X}^1\Sigma^+, \nu)$  fragment shifts from  $\nu = 2$  at 429 nm, to  $\nu = 6$  at higher excitation energies.

The detailed analysis of the process A reveals indeed a correlation between the vibrational excitation of the  $\text{NO}^+(\text{X}^1\Sigma^+, \nu)$  fragment ion and the one of the  $\text{NO}_2^+(\text{X}^1\Sigma_g, \nu_1, \nu_2, \nu_3)$  parent ion produced prior photodissociation -reflected in the  $E_e$  energy distribution-. This correlation evolves with the excitation wavelength (see insets Fig 2 (b) and (c) for an example). Although neither the  $\text{NO}^+(\text{X}^1\Sigma^+, \nu)$  vibrational spacing in the KER distribution ( $\sim 290$  meV), nor those of the  $\text{NO}_2^+(\text{X}^1\Sigma_g, \nu_1, \nu_2, \nu_3)$  state (175 meV,  $\sim 77$  meV, and 296 meV, respectively) in the  $E_e$  distribution, are well resolved, a filtering of events enabling better electron energy resolution shows that ionization takes place into the  $\text{NO}_2^+(\text{X}^1\Sigma_g)$  molecular ion, where different vibrationally excited levels in the bending mode and/or in the symmetric stretching mode are correlated to a different  $\text{NO}^+$  vibrational excitation. Such a complex pattern reflects the complex vibronic dynamics involved.

At  $\lambda = 400$  nm, the four-photon excitation energy becomes enough to reach the first dissociation limit  $L_1[4]$  and a new process (D) appears in the KECD. This process may be interpreted as an ionisation into vibrationally excited  $\text{NO}_2^+(\text{X}^1\Sigma_g, \nu_1, \nu_2, \nu_3)$  followed by quasi-resonant dissociation with no excess of energy to the ground state limit  $L_1$  ( $\text{NO}^+(\text{X}^2\Pi)$ ,  $\text{O}(\text{P})$ ). We note that such a reaction necessarily involves an intersystem crossing mechanism<sup>21</sup>. Large spin-orbit coupling values are indeed found in the CASPT2 calculations<sup>21</sup> in particular between the  $\text{NO}_2^+(\text{X}^1\text{A}_1)$  and ( $\text{a}^3\text{B}_2$ ) ionic states.

Process D is observed over the whole 375–400 nm range (region II) and becomes dominant for  $\lambda \leq 380$  nm with a significant increase of the total MPDI probability, from  $\sim 65$  % in the 430–400 nm range up to  $\sim 90$  % of the total PI probability at  $\lambda = 375$  nm (see the supplementary material). At  $\lambda \approx 375$  nm a small amount of excess energy is released into translational energy of the fragments ( $\text{KER} \leq 0.3$  eV).

### 3.b. Photoelectron Energy Spectra

Figure 3 displays the PE spectra for the MPDI channel compared to those measured for non-dissociative MPI at the same wavelengths and attributed to PI into the  $\text{NO}_2^+(\text{X}^1\Sigma_g)$  ionic state. The amplitudes of the peaks A (MPDI) and  $\alpha$  (MPI) are adjusted to facilitate the comparison of their energy profile. In region I ( $430 \leq \lambda \leq 400$  nm, Fig. 3 (a)-(c)), both PE spectra show a dominant structure corresponding to processes A for MPDI and  $\alpha$  for MPI, observed at similar values of the photoelectron energy  $E_e$  but with a different energy width, and a second peak attributed to process B for MPDI and process  $\beta$  for non-dissociative MPI. These similarities support a common interpretation of the PI reactions as proposed in paper I. Three-photon absorption to an excited valence state strongly mixed with a  $[\text{R}^*(6\text{a}_1)^{-1}]$  Rydberg state followed by one-photon ionization to the  $\text{NO}_2^+(\text{X}^1\Sigma_g, \nu_1, \nu_2, \nu_3)$  state leads to processes  $\alpha$  and  $\beta$ , while subsequent dissociation after absorption of a fifth photon leads to processes A and B.

The widths associated with processes A (350 meV FWHM) and  $\alpha$  (150 meV FWHM) reflect a different vibrational distribution, although centred around a similar  $E_e$  value, of the  $\text{NO}_2^+(\text{X}^1\Sigma_g, \nu_1, \nu_2, \nu_3)$  ion responsible of the MPDI and MPI, respectively. Process  $\alpha$  appears to be more selective in terms of internal excitation than process A (MPDI). In Fig. 3 c (400 nm) two weaker structures, labelled  $\gamma$  and  $\delta$ , are visible and assigned to  $\nu_1$  symmetric stretching vibrational excitation.

In region II ( $375 \leq \lambda \leq 400$  nm, Fig. 3 (d)-(f)), two trends can be identified in the photoelectron spectra characterized by the position of the  $E_B^{(4)}$  binding energy with respect to the  $E_D^{(1)}$  dissociation limit, where the binding energy is defined as the difference between the excitation energy (with  $n = 4$  here) and the photoelectron energy:  $E_B^{(n)} = nh\nu - E_e$ . For  $383 \leq \lambda \leq 400$  nm, processes A and  $\alpha$  are still observed at similar  $E_e$  position as illustrated in Fig. 3 (d), and they correspond to  $E_B^{(4)} < E_D^{(1)}$ , while process D assigned to four-photon MPDI corresponds to  $E_B^{(4)} \approx E_D^{(1)}$ . In contrast, for  $375 \leq \lambda \leq 383$  nm, the condition  $E_B^{(4)} \geq E_D^{(1)}$  is true for all the identified processes. The process D which becomes the dominant structure in the PE spectrum, corresponds now to a  $E_e$  value close to that of process  $\alpha$  while process A vanishes (see the suppl. material). At the highest photon energy,  $\lambda = 375$  nm (Fig. 3 (h)), the relative contribution of ( $\text{NO}_2^+$ , e) MPI is strongly reduced (10 %) and it includes a new contribution through a second resolved peak, assigned to excitation of the  $\nu_3$  asymmetric stretching vibrational mode.

The contribution of processes  $\beta$  and B amounts to  $\sim 15$ –20 % of the MPI and MPDI channels, respectively, for  $\lambda$  values around 383–400 nm and vanishes for  $\lambda \leq 380$  nm.

Figure 4 presents the dependence of the peak position in the PE spectrum for processes A, D and  $\alpha$  as a function of the photon energy in eV and their fit by linear regression. For a vertical PI process at fixed geometry of the molecule, this slope should reflect the number of absorbed photons. However it is found that for MPDI process A and MPI process  $\alpha$ , in the whole explored  $\lambda$  range the peak shift is well described by a straight line of slope close to 1, *i.e.* it varies as the energy of one absorbed photon, the excess energy being therefore transferred into internal energy of the ionic state. This behaviour is the signature of a reaction pathway involving PI of a Rydberg state converging to the  $\text{NO}_2^+(\text{X}^1\Sigma_g)$  state<sup>2</sup>, which preserves the  $E_{\text{vib}}$  internal excitation of the molecule<sup>22</sup>. For process D, the results are shown for  $375 \leq \lambda \leq 383$  nm, where the energy shift is also close to the energy of one photon absorbed.

### 3.c. Laboratory Frame Angular Distributions

The laboratory frame angular distribution of both ion fragments and photoelectrons emitted in a  $n$ -photon MPDI process can be expanded as:

$$H(\chi) \propto 1 + \sum_{k=1}^n \beta_{2k} P_{2k}(\cos \chi) \quad (3)$$

where  $\beta_{2k}$  are the asymmetry parameters and  $P_{2k}(\cos \chi)$  the Legendre polynomials.

The measured  $\beta_{2k,NO^+}$  asymmetry parameters for process A are reported in Table 1 for different wavelengths in the explored range. The  $NO^+$  ion fragment angular distributions are characterized by two or three asymmetry parameters, consistent with the absorption of at least three photons prior to the dissociation step. The positive and significant values of  $\beta_{2k,NO^+}$  parameters reflect the strong alignment of the  $NO^+$  recoil direction along the polarization axis, remaining quite stable as a function of the excitation wavelength.

Referring to the reaction pathway proposed in paper I, the ion fragment angular distribution in the  $n$ -photon MPDI process results from the  $(n-1)$  one-photon bound-to-bound transitions between near resonant states, plus one-photon ionization step. Using here a similar representation for the bound-to-bound transitions depending on the orientation of the transition dipole moments<sup>2,10</sup>, the A process can be described by a reaction scheme labelled [2,2,2,2] which involves four bound-to-bound transitions of type-2 with the molecule at a geometry close to equilibrium.

Extraction of the  $NO^+$  angular distribution for process D is subject to larger uncertainties due to the small emission velocities of the ion fragments, which results in narrow position and TOF distributions using the extraction fields required for a complete collection of all processes. Therefore the measured asymmetry parameters for this process are rather indicative: the  $NO^+$  angular distribution is there characterized by two asymmetry parameters varying around  $\beta_2 \approx 1.5$  and  $\beta_4 \approx 0.5$ , rather consistent with a three photon absorption pathway labelled [2,2,2].

For the A (MPDI) and  $\alpha$  (MPI) processes, the photoelectron angular distributions are mainly characterized by a single  $\beta_{2k,e}$  asymmetry parameter, which supports the description of a reaction pathway involving the ionization of a Rydberg state<sup>2</sup>. Figure 5 displays the evolution of  $\beta_{2,e}$  as a function of the excitation wavelength for these two processes which reveals two distinct behaviours. For  $E_B^{(4)} \leq E_D^{(1)}$ , processes A and  $\alpha$  are characterized by quite different  $\beta_{2,e}$  values, around 0.9 for the A process and around 0.4 for the  $\alpha$  process, which remain rather constant as a function of the excitation wavelength (for  $\lambda \geq 385$  nm), and are consistent with the  $\beta_{2,e} \approx 1$  and  $\beta_{2,e} \approx 0.3$  for  $\lambda \approx 400$  nm, respectively, reported in paper I. This difference in  $\beta_{2,e}$  values between A and  $\alpha$  for a PI reaction involving the same electronic state can be interpreted as reflecting the contribution of two geometries in the ionization reaction (as shown later in sect. 4.) and thus in the populated  $NO_2^+$  ( $X^1\Sigma_g^+, \nu_1, \nu_2, \nu_3$ ) manifold, leading either to MPDI (bent case) after absorption of the fifth photon or to MPI (linear case).

For  $E_B^{(4)} \geq E_D^{(1)}$ , the  $\beta_{2,e}$  values for A, D and  $\alpha$  processes are similar and increase from  $\sim 0.6$  up to  $\sim 0.9$  with the excitation energy (for  $\lambda \leq 385$  nm). We note that for the shorter wavelengths, the  $\beta_{4,e}$  parameter amounts to  $-0.2$  for processes D and  $\alpha$ . At  $\lambda = 375$  nm, the second peak resolved in the MPI photoelectron spectrum (Fig. 3h) and assigned to excitation of the  $\nu_3$  asymmetric stretching vibrational mode corresponds to larger  $\beta_{2,e}$  parameters ( $\sim 1.2$  for  $\nu_3 = 1$  vs.  $0.7$  for  $\nu_3 = 0$ ).

### 3.d. Recoil Frame Angular Distributions

Figure 6 (a-e) presents the RFPADs measured for MPDI process A at several excitation wavelengths, selecting only the dominant parallel orientation. For the whole range of wavelengths, RFPADs for a perpendicular orientation have an almost zero intensity, consistently with the [2,2,2,2] “parallel” reaction pathway. The remarkable FW-BW asymmetry reflecting the favoured photoelectron emission in a direction around the  $NO^+$  ion recoil axis is shown to be a striking robust feature in the whole explored range of excitation energies. Some differences are nevertheless observed in the shape of the RFPAD: the “conical” angle which characterizes the photoemission lobe of the emitted electron is found to increase from  $\theta_e \sim 10^\circ$  to about  $35^\circ$  when the wavelength decreases from 429 nm to 380 nm. We note that two lobes around  $\theta_e = 30^\circ$  are observed at 400 nm and lower wavelengths, similar to the results reported in paper I at 397 nm.

The RFPADs for process D at  $\lambda = 380$  nm and 375 nm are also reported in Figure 6 (f-g). The FW-BW asymmetry, observed for process A for a parallel orientation, appears here. We remark that for this process, the perpendicular component amounts about 20 % contrary to the findings for process A, thus RFPADs for other orientations (not shown here) also contain information on the PI process. For all wavelengths, the FW-BW asymmetry is recovered, even though the asymmetry is stronger at higher photon energies. At 375 nm, two lobes for  $\theta_e$  emission angles around  $40^\circ$  are observed in fair agreement with previous RFPADs measured by Davies and co-workers<sup>7</sup>.

In paper I, we have introduced the method of the principal component analysis (PCA) based on RFPAD development in terms of  $R_K(\chi, \theta_e)$  recoil frame azimuthal harmonics (RFAHs). The PCA allows us to extract the fingerprints for each RFAH of order  $K$  in the RFPAD expansion in  $\phi_e$ . Therefore, it permits an efficient quantitative comparison of the experimental results with the calculations as well as, comparisons between different experiments or calculations. We report in Figure 7, experimental results for three selected reactions: process A at 416 nm and 383 nm, and process D at 380 nm, focusing on the lowest  $K$  orders i.e., on the  $R_{K=0}(\chi, \theta_e)$  and  $R_{K=1}(\chi, \theta_e)$  RFAHs. Here we display the  $J_{u,\lambda^{(K)}}(\chi)$  and  $G_{u,\lambda^{(K)}}(\theta_e)$  unitary eigenvectors of the covariance matrix, ordered and weighted by the  $\Lambda_\lambda$  eigenvalues, limited to the first and second orders ( $\lambda = 1, 2$ ). In the following we omit the  $u$  index for sake of simplicity. In this description, the first order  $J_{\lambda=1^{(K)}}(\chi)$  functions describe the main features of the reaction pathway for the most effective  $\theta_e$  MF angular profile, while the  $G_{\lambda=1^{(K)}}(\theta_e)$  functions account for those of the MF emission profile, for the most effective  $\chi$  recoil angle distribution.

Figures 7 (a and c) show that  $R_{K=0}(\chi, \theta_e)$  is indeed mainly characterized by the first order  $J_{\lambda=1^{(0)}}(\chi)$  and  $G_{\lambda=1^{(0)}}(\theta_e)$  functions.  $J_{\lambda=1^{(0)}}(\chi)$  has a similar shape for both processes A and D in the whole range of energies, close to the measured photoion angular distribution in the laboratory frame, consistent with a [2,2,2,2] or [2,2,2] reaction pathway, respectively. The  $G_{\lambda=1^{(0)}}(\theta_e)$  function reflects the strong FW-BW asymmetry observed. For process A, a single maximum at  $0^\circ$  is observed, reflecting the FW peaked shape of the RFPAD for a parallel orientation. For process D the FW-BW asymmetry is

structured differently, with a relative maximum at  $30^\circ$  reflecting the two observed lobes in the corresponding RFPAD. For  $R_{K=1}(\chi, \theta_e)$ ,  $J_{\lambda=I^{(1)}}(\chi)$ , antisymmetric relative to  $90^\circ$ , remains stable as a function of the process or the excitation energy.  $G_{\lambda=I^{(1)}}(\theta_e)$  also displays a similar shape observed for both A and D processes in the whole range of excitation energies, however the intensity of the maximum at  $45^\circ$  varies, as well as the observed minimum around  $15^\circ$ .

#### 4. Theoretical Results

Theoretical results are presented in terms of the  $\beta_{2k,e}$  asymmetry parameters and RFPAD observables for five-photon MPDI, in order to probe the proposed reaction scheme. The angular distribution of the ion fragments is interpreted as a signature of the orientation of the transition moment for the three or four-photon bound-to-bound excitation pathway plus the photoionization step, as discussed earlier.

PI calculations have been performed considering different parameters: (i) the single-configuration or correlated description of the  $\text{NO}_2^+$  target (ii) the number of channels implied in the scattering process (iii) the electronic character of the ionized  $[\text{R}^*(6a_1)^{-1}] 3p\pi^2B_1$ ,  $[\text{R}^*(6a_1)^{-1}] 3p\pi^2A_1$  and the  $[\text{R}^*(6a_1)^{-1}] 3p\sigma^2B_2$  Rydberg states, as well as (iv) a set of ( $\theta_p$ ) and ( $\theta_R$ )  $\angle\text{ONO}$  PI and recoil angles, which all influence the photoelectron angular distributions. Here we consider PI of the  $[\text{R}^*(6a_1)^{-1}] 3p\sigma^2B_2$  Rydberg state, and we focus on the effect of electronic correlation in the ground state of  $\text{NO}_2^+$  which is dominant here, and is found to be more important than the dynamical electronic correlation included when the calculation is extended from one-channel to five-channel –involved in the scattering process– [see *e.g.* discussion in ref <sup>23</sup>], except in the vicinity of autoionizing resonances. We also found that in the more detailed PCA-RFHA calculations, the results were not significantly changed when we went beyond the one-channel correlated-target calculations. Thus one-channel calculations with correlated targets are a good representation of the photoionization step and will be the primary type of calculation considered here.

The  $\beta_{2,e}$  photoelectron asymmetry parameters computed for the one-photon PI of this  $3p\sigma$  Rydberg state as well as taking into account the previous three photon absorption considering a [2,2,2] pathway are reported in Fig. 8 as a function of the  $\theta_p$  angle, selecting here the condition  $\theta_p = \theta_R$ . A strong dependence of  $\beta_{2,e}$  on angle is observed, with values varying from 1.2 at smaller  $\theta_p$  angles to about 0 or slightly negative values near  $180^\circ$ , comparable to the difference in  $\beta_{2,e}$  observed for the  $\alpha$  MPI and A MPDI processes, assigned to quasi-linear or bent geometries of the  $\text{NO}_2^+$  molecular ion in the proposed reaction scheme, respectively. This significant dependence indeed features the role of vibronic coupling in the  $\text{NO}_2^+$  ( $X^1A_1, \nu_1, \nu_2, \nu_3$ ) ionic state i.e., a coupling between electronic and nuclear vibrational motion. This occurrence when ascribed to an intrachannel effect is referred to as “type (a)” vibronic interaction<sup>24</sup>. We remark that  $\beta_{4,e}$  and  $\beta_{6,e}$  computed values (not shown here) are almost zero at the  $\angle\text{ONO}$  angles considered here in agreement with the photoelectron angular distributions

measured for the  $\alpha$  and A processes mostly characterized by a single  $\beta_{2,e}$ .

Figure 8 also illustrates the key feature of the PI calculations mentioned above, i.e., the fact that the one-channel  $\beta_e$  computed using Hartree-Fock type wave functions are significantly different from all results obtained using correlated targets<sup>2</sup>, whether the latter correspond to one-channel or few-channel scattering calculations. The most important source of the observed qualitative differences among computed observables is the fact that the Hartree-Fock wave function and the configuration interaction (CI) wave function for the  $\text{NO}_2^+$  ground state correspond to significantly different electronic density distributions. This will be discussed in more detail in the forthcoming publication.

In Fig 9, we display the computed MFPADs for the three most relevant transitions (type 3 ( $z_{\text{MF}}$ , (a)), type 2 ( $y_{\text{MF}}$ , (b)) and type 4, (parallel to an NO bond, (c))) in one-photon PI of this  $[\text{R}^*(6a_1)^{-1}] 3p\sigma^2B_2$  state, computed for  $\theta_p \approx 134^\circ$  (a, b, c) (one-channel correlated calculation), as well as the RFPAD corresponding to a polarization axis parallel to the recoil direction ( $\chi = 0^\circ$ ), for a recoil angle  $\theta_R \approx 150^\circ$  (d). The RFPAD is obtained after integration over the  $\gamma_R$  Euler angle of the MFPAD expressed in the R-MF reference frame whose z axis is parallel to the  $\text{NO}^+$  ion fragment recoil velocity [see paper I]. Figure 9, compared with Figure 11 of paper I, illustrates the major differences at the level of MFPADs between the HF and the correlated one-channel PI calculations for the  $\theta_p \approx 134^\circ$  PI angle, which lead in particular to a different interpretation of the observed FW-BW recoil frame photoemission anisotropy. In the correlated calculation, PI is strongly favoured for the  $3p\sigma b_2 \rightarrow kb_2$  type 3 transition which corresponds to a well structured MFPAD, while the  $3p\sigma b_2 \rightarrow ka_1$  type 2 transition, which is dominant in the HF calculation, is here significantly reduced and displays a blurred structure MFPAD. In the present case, the RFPAD asymmetry displayed in Fig.9 (d), consistent with the behaviour discussed earlier in terms of PCA-RFAH, originates mostly from the contribution of the dominant type 3 transition to the MFPAD associated with a type 4 transition, where the transition moment is parallel to the NO breaking bond. Combined with a [2,2,2] pathway, a similar FW-BW is nevertheless preserved in the RFPAD.

#### 5. Discussion and conclusion

The results for MPDI and MPI processes following excitation at wavelengths between 430 and 375 nm reveal two different excitation regions. In region (I),  $430 \leq \lambda \leq 400$  nm, a progressive evolution of the MPDI processes, A and B, and the MPI processes,  $\alpha$  and  $\beta$ , attributed to different components of the PI to the  $\text{NO}_2^+$  ( $X^1\Sigma_g$ ) state is observed. For wavelengths between  $375 \leq \lambda \leq 400$  nm (region (II)), a new four-photon process D is observed which branching ratio increases when the wavelength decreases becoming dominant for wavelengths below  $\lambda \leq 386$  nm.

The measured RFPADs for A and then D processes show that the remarkable electron emission anisotropy, strongly favouring photoemission in the  $\text{NO}^+$  recoil direction, parallel to



the polarization axis, or at small  $\theta_e$  emission angles ( $\theta_e \leq 30^\circ$ ), is a fingerprint of MPDI in the whole explored wavelength range. Relying on the expansion of the RFPAD in terms of the recoil-frame azimuthal harmonics and the related principal component analysis (PCA-RFAH), the comparison between experimental and theoretical RFPADs, leads us to the conclusion that the  $[R^*(6a_1)^{-1}, 3p\sigma b_2]$  Rydberg state is the most likely populated excited state after three-photon absorption, with preferred geometries around ( $\theta_p = 134^\circ$ ,  $\theta_R = 150^\circ$ ) at the moment of PI and dissociation, respectively. Furthermore, this comparison emphasizes the importance of electronic correlation of the  $NO_2^+$  ( $X^1\Sigma_g$ ) ground state, which plays a major role in the description of the PI process. The calculation for PI of the  $[R^*(6a_1)^{-1}, 3p\sigma b_2]$  Rydberg state reproduces the values of the  $\beta_{2,e}$  asymmetry parameters measured for MPDI and MPI processes, if the  $\alpha$  MPI process is assigned to PI of the  $3p\sigma b_2$  Rydberg state, at a geometry closer to the linear conformation  $\theta_p \approx 180^\circ$ .

The different reaction mechanisms proposed in paper I<sup>2</sup> are shown in Fig. 1 and discussed below in the light of the new experimental and theoretical results presented herein.

In region (I), the reaction pathway proposed for the excitation with  $\lambda \approx 400$  nm<sup>2</sup> is confirmed by the results obtained for the whole explored range of wavelengths. In this scheme, the three-photon absorption excites the molecule to a state strongly coupled to the  $[R^*(6a_1)^{-1}]$  Rydberg series, favouring the  $[R^*(6a_1)^{-1}] 3p\sigma^2 B_2$  state in an excited vibrational state with a large degree of bending mode excitation. The absorption of a fourth photon by these Rydberg states bringing the molecule to the ionization continuum between 11.5 and 12.4 eV, results in the population of  $NO_2^+$  ( $X^1\Sigma_g, v_1, v_2, v_3$ ) by direct ionization, possibly influenced by autoionization involving the  $[R^*(4b_2)^{-1}]$  Rydberg states. The potential surfaces of the  $[R^*(6a_1)^{-1}]$  Rydberg states closely resemble that of the ionic state  $NO_2^+$  ( $X^1\Sigma_g$ ), to which these states converge leading to the conservation of the vibrational quantum numbers during ionization, a fingerprint of PI of Rydberg states<sup>22</sup>. This mechanism is supported by the single photon dependence of the peak energies in the photoelectron spectrum associated to A and  $\alpha$  processes, as a function of the excitation wavelength (Fig. 3).

This complex ionization mechanism involving an important vibronic coupling may create a bimodal distribution in the  $NO_2^+$  ( $X^1\Sigma_g, v_1, v_2, v_3$ ) population, associated with two geometries the molecule: linear and bent, and thereby leading to two values of  $\beta_{2,e}$ , as discussed previously<sup>2</sup>. In this scheme, the selective photodissociation of preferably bent  $NO_2^+$  ( $X^1\Sigma_g, v_1, v_2, v_3$ ) molecular ions, by the fifth photon absorption leads to the population of a dissociative excited state of  $NO_2^+$ , such as the  $NO_2^+$  ( $A^1A_1$  or  $B^1B_2$ ) states, while the population associated with a linear geometry remains in the  $NO_2^+$  ground state. This selective photodissociation acts thus as a sorting between these two populations. The dissociation of the  $A^1A_1$  or  $B^1B_2$  excited state to the  $L_1$  limit occurs through intersystem crossing mechanism<sup>21</sup>, which is expected to occur on a time scale shorter than the molecular rotation or bending, preserving thus the validity of the axial recoil approximation. The stability of the two  $\beta_{2,e}$  values characterizing the MPDI and non-dissociative MPI in

the entire region (I) supports this proposed reaction mechanism for the whole excitation energy range. For the A MPDI process, the translational versus internal energy sharing of the fragments, leading to an extended  $v=0-6$  vibrational distribution of the  $NO^+$  ( $\Sigma^1X$ ) molecular ion is then attributed to the photodissociation step induced by the fifth photon absorption.

In region (II),  $\lambda < 400$  nm, the total excitation energy corresponding to a four-photon absorption is higher than the adiabatic MPDI threshold, located at 12.38eV ( $L_1$ ). The reaction mechanism involving the ionization of the  $[R^*(6a_1)^{-1}, 3p\sigma b_2]$  Rydberg state to the  $NO_2^+$  ( $X^1\Sigma_g$ ), preserving the  $E_{vib}$  internal excitation *i.e.* the vibrational quantum number in the ionization step, can also be proposed to interpret the MPDI process A and MPI process  $\alpha$ . For the four-photon MPDI process D, a similar scheme applies for wavelengths  $\lambda \leq 383$  nm, where conservation of vibrational excitation of the  $[R^*(6a_1)^{-1}, 3p\sigma b_2]$  Rydberg state in the ionization steps leads to the population of the  $NO_2^+$  ( $X^1\Sigma_g, v_1, v_2, v_3$ ) manifold around the  $NO^+$  ( $\Sigma^1X$ ) + O( $^3P$ ) dissociation threshold, or directly into the dissociative continuum, at shorter  $\lambda$  values. The probability for the A process becomes negligible for an  $E_B^{(4)}$  energy above the  $E_D^{(1)}$  dissociation energy. The characteristics of the MPI process  $\alpha$ , similar to those of the MPDI process A for  $E_B^{(4)} \leq E_D^{(1)}$ , become very similar to those of process D for  $E_B^{(4)} \geq E_D^{(1)}$ .

A remarkably similar value of the  $\beta_{2,e}$  asymmetry parameter ( $\beta_{2,e} \sim 0.9$ ) characterizes the three processes A,  $\alpha$  and D in region (II). This suggests that both the non-dissociative and dissociative ionization reactions now involve the same population in terms of vibrational states of the  $NO_2^+$  ( $X^1\Sigma_g, v_1, v_2, v_3$ ) ion. This may then correspond either to a single geometry of the molecule, or to a composite population involving a few geometries, but no longer discriminated in the photodissociation step.

At shorter wavelengths, in particular for  $\lambda = 375$  nm, other Rydberg states, such as the  $[R^*(6a_1)^{-1}] 3p\pi^2 A_1$ , may be involved in the PI step associated with process D as it will be discussed in the forthcoming publication. Moreover, we remark that the reaction pathway proposed here for  $\lambda = 375$  nm does not contradict the interpretation by Davies *et al*<sup>7</sup> in their time-resolved study: at  $\Delta t=0$ , the dominant contribution is the ionization of the Rydberg state (which may include a nascent dissociation of the  $NO_2$  excited state) while at longer pump-probe delays, dissociation through the Rydberg state may occur prior ionization probing the dissociation process as proposed in Davies *et al*<sup>7,9</sup>. Their determined dissociation time<sup>9</sup> around 500 fs is indeed coherent with the lifetimes around 600 fs for  $[R^*(6a_1)^{-1}]$  Rydberg states lying around 9.3 nm previously reported by both López-Martens *et al*<sup>25</sup> and Blanchet and coworkers<sup>26</sup>. Such lifetimes support our proposed reaction pathways: photodissociation after three-photon absorption within the shorter duration of our laser pulse is not possible.

Finally, we note as in paper I, that the characteristics of peak B in the KECD are consistent with one-photon photodetachment of O $\cdot$  following  $NO^+-O\cdot$  ion pair formation: (i) the full width of the KER distribution for this process is

comparable to that of the ion-pair reaction at comparable photon excitation energy (ii) the photoelectron distribution peaks at 1.6 eV for  $\lambda \sim 400$  nm as expected for such process, taking into account that the electron affinity of  $O^-$  is equal to 1.47 eV. We also note that peak B vanishes when ion-pair becomes negligible.

Further investigation of the proposed reaction scheme would benefit from femtosecond pump-probe experiments at shorter time scale, where one VUV photon excites the  $[R^*(6a_1)^{-1}] NO_2$  Rydberg states around the 9.3 eV which are then probed by a delayed 400 nm laser pulse.

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