Dissociative photoionization of the NO molecule studied by photoelectron–photon coincidence technique

A. Kivimäki¹, J. Alvarez-Ruiz², M. Coreno³, M. de Simone⁴, A. Moise⁵, L. Partanen⁶, R. Richter⁷, M. Stankiewicz⁸

¹CNR-IOM, Laboratorio TASC, 34149 Trieste, Italy

²Departamento de Química Láser, Instituto de Química-Física Rocasolano, Consejo Superior de Investigaciones Científicas, Serrano 119, 28006 Madrid, Spain

³CNR-IMIP, Montelibretti, 00016 Rome, Italy

⁴Sincrotrone Trieste, 34149 Trieste, Italy

⁵Department of Physical Sciences, University of Oulu, P.O. Box 3000, 90014 Oulu, Finland

⁶Instytut Fizyki im. Mariana Smoluchowskiego, Uniwersytet Jagielloński, 30-059 Kraków, Poland

ABSTRACT

Low-energy photoelectron–vacuum ultraviolet (VUV) photon coincidences have been measured using synchrotron radiation excitation in the inner-valence region of the nitric oxide molecule. The capabilities of the coincidence set-up were demonstrated by detecting the $2s^{-1} \rightarrow 2p^{-1}$ radiative transitions in coincidence with the $2s$ photoelectron emission in Ne. In NO, the observed coincidence events are attributed to dissociative photoionization with excitation, whereby photoelectron emission is followed by fragmentation of excited NO^+ ions into $\text{O}^+ + \text{N}^*$ or $\text{N}^+ + \text{O}^*$ and VUV emission from an excited neutral fragment. The highest coincidence rate occurs with the opening of ionization channels which are due to correlation satellites of the 3σ photoionization. The decay time of VUV photon emission was also measured, implying that specific excited states of N atoms contribute significantly to observed VUV emission.

Keywords:

Nitric oxide

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1. Introduction

When a molecule absorbs radiation of energy above the first ionization potential (IP), it can be ionized or it can end up in a highly excited neutral state. The latter is often called a superexcited state. More specifically, superexcited states are either Rydberg excited states converging to higher ionization thresholds of the molecule or multiply excited states, in particular, doubly excited states. Superexcited states can decay in a number of ways, some of which produce neutral excited fragments. Therefore fluorescence emission from neutral fragments has been often used as a probe in the search of superexcited states [1]. Conversely, features observed in the fluorescence excitation functions of fragments are typically attributed to superexcited states (e.g., [2–4]). However, excitation to superexcited states is not the only mechanism that causes fluorescence emission from fragments above the first IP of the molecule, as direct photoionization may also contribute to fluorescence intensity. For example, coincidences between fluorescence photons and N^+ ions have been observed in the inner-valence region of the N_2

molecule [5–7]. They were ascribed to events where photoionization is followed firstly by dissociation of the resulting molecular ion, $\text{N}_2^+ \rightarrow \text{N}^+ + \text{N}^*$, and consecutively by fluorescence emission from the excited neutral fragment N^* . This process is called Dissociative photolionization [with] Excitation (DIE). It was suggested that correlation states related to inner-valence photoionization are doorway states leading to DIE [6,7]. Correlation states exist if a state with an inner-valence hole cannot be described by a single-hole electron configuration but it contains contributions from two-hole one-electron ($2h-1e$) or even higher order states due to configuration mixing ($2h-1e$ states have two holes in outer valence orbitals and an electron in a virtual orbital which is not occupied in the molecular ground state). The effect is manifested in the inner-valence photoelectron spectrum by the appearance of several satellite peaks instead of just one main photoelectron line. Correlation satellites can be populated at all excitation energies above their binding energies. Therefore, if a fluorescence line is due to DIE it displays a continuous intensity distribution as a function of excitation energy. On the contrary, superexcited states yield resonant features in fluorescence excitation functions.

In the present paper, we have studied dissociation of the nitric oxide (NO) molecule in the inner-valence region by a slightly different coincidence technique as in the above-mentioned

studies of the N_2 molecule [5–7]. Namely, we have observed coincidences between photoelectrons and fluorescence photons. Photoelectron–fluorescence coincidence (PEFCO) technique has earlier been used to determine the radiative lifetimes of the excited ionic states of some molecular ions [8,9]. Bloch and Turner [8] employed a He I photoelectron spectrometer to select a specific molecular ionic state and registered fluorescence emission from that state with a photomultiplier tube (PMT). In the experiments of Biehl et al. [9], a threshold electron analyzer was used to collect threshold electrons in coincidence with fluorescence photons that were detected with a PMT, equipped with a filter to isolate the wavelength windows of interest. In those studies, fluorescence occurred directly after photoionization, i.e., the molecules did not dissociate before fluorescing. More recently, Taylor and Eland [10] have reported electron–fluorescence photon coincidences for a number of diatomic and triatomic molecules in which fluorescence emission occurred in either parent or fragment ions. Their triple coincidence setup hosted a channeltron for electron detection and a PMT for photon detection in the wavelength range 200–500 nm; it also included a time-of-flight (TOF) mass spectrometer to characterize photoions. The same authors have later developed an electron–electron–photon coincidence setup, where a magnetic-bottle electron TOF (e-TOF) spectrometer was used to observe an electron pair resulting from double photoionization and the same PMT (200–500 nm sensitivity range) collected photons emitted by the N_2O^{2+} or CS_2^{2+} dication [11,12]. In the present work, we have exploited yet another electron–photon coincidence scheme: installed at a synchrotron radiation source, a conventional e-TOF spectrometer was used to observe slow electrons in coincidence with VUV photons ($\lambda < 150$ nm) that were collected with a micro-channel plate (MCP).

If we hypothesize that a NO molecule undergoes DIE (as it will be argued later), the electron and photon emissions are separated by dissociation of the molecular ion. For NO, DIE can be written schematically as follows:

where the asterisk (*) indicates an excited species. Photon absorption causes the prompt electron emission, while a fluorescence photon is emitted after the fragmentation of the molecular ion. This type of experiment is therefore affected by two time constants: that of molecular dissociation and that of the lifetime of the emitting state. The dissociation times of molecular unbound states are probably in the fs range [13], while the lifetimes of the possible atomic emitters are typically few ns [14,15]. Molecular dissociation can therefore be considered so fast that it will not affect the temporal distribution of electron–photon coincidences in our measurements. We observe the highest coincidence rate in NO around 41-eV photon energy. The possible mechanisms which can lead to the observed electron–VUV photon coincidences are decay of superexcited states and dissociative photoionization with excitation. Superexcited states have very recently been observed in the inner-valence region of the NO molecule [16], but only DIE can adequately explain our observations.

2. Experimental

The experiments were carried out at the Gas Phase Photoemission beamline [17] at the Elettra synchrotron radiation laboratory in Trieste (Italy). The beamline uses undulator radiation that is monochromatized by a spherical grating monochromator equipped with a planar pre-mirror. After the monochromator, the photon beam can be directed to any of three branch lines. Our experiment

was situated at the branch that operates in the photon energy range of 14–200 eV and that also hosts a Ti:Sapphire laser system for two-color experiments that combine both laser and synchrotron radiation excitation. During the normal multi-bunch operation of the Elettra storage ring, electron bunches are filled in the ring so that synchrotron radiation is emitted every 2 ns, the pulses being ~ 60 ps wide. However, there is a so-called “dark gap” in the filling pattern where no electron bunches are present. The length of this gap is typically 50 ns, while the whole period of the ring is 864 ns. During the present experimental session the storage ring operated in a special filling mode where one (or few) electron bunch (–es) was (were) injected in the dark gap. This allowed us to perform time-resolved experiments where the intensity of the fluorescence emission was measured in coincidence with the storage ring clock (one signal for each period of the electron bunches).

A threshold electron analyzer is an obvious choice for detecting photoelectrons in PEFCO experiments, as it can achieve both high transmission and high-energy resolution. However, a threshold electron analyzer detects only electrons whose kinetic energy is typically less than few meV. Not knowing the cross section of DIE at threshold, we wanted to collect low-energy electrons in a slightly larger energy range. Therefore, an electron time-of-flight (e-TOF) spectrometer was chosen for electron detection. The spectrometer, which was borrowed from the Imperial College (London, UK), was constructed according to the design of Hemmers et al. [18]. It is composed of an electronic lens system and a magnetically shielded drift tube whose length is 244 mm. The e-TOF spectrometer was positioned along the electric vector of the incident synchrotron light. To increase the collection efficiency, photoelectrons were pushed towards the grounded input aperture of the e-TOF by applying a negative voltage on a mesh situated on the opposite side of the interaction region (IR), as it is shown in Fig. 1. An electrically isolated needle was used for the gas inlet. The ambient pressure in the chamber ranged from 2.4×10^{-6} to 1.1×10^{-5} mbar during the measurements, but the pressure in the IR is estimated to be 10–50 times higher. For intensity reasons the needle was brought close (ca. 1 mm) to the IR, which resulted in the perturbation of the electric field. This was partly compensated by applying a potential also to the needle. Voltages were chosen empirically so that transmission was highest for electrons of kinetic energy < 1 eV. Electrons passing through the e-TOF spectrometer were detected with a 40-mm diameter Z-stack micro-channel plate (MCP) detector (set of three stacked MCPs) located after the drift tube (not shown in Fig. 1).

For photon detection, the experimental setup included another MCP detector with a 25-mm diameter (a chevron configuration –

Fig. 1. Schematic presentation of the experimental arrangement around the interaction region (IR). Typical potentials applied to the meshes, the needle and the cup surrounding the MCP are given in parentheses. Synchrotron light comes perpendicularly from the back side of the paper. The distance between the nose of the e-TOF spectrometer and the IR was 20 mm.

stack of two MCPs). It was installed opposite to the e-TOF spectrometer (Fig. 1), also in the direction of the light polarization vector. This MCP detector was shielded from the sides and back to screen it from stray photons. There was a mesh (90% transmission) in front of the MCP. Application of a positive potential on it prevented positive ions from entering the detector. The front of the MCP was set at -2.8 kV (this assured that any electrons were repelled and did not contribute to the signal), while the back was at ground. The use of a standard MCP as a photon detector is limited to wavelengths below 150 nm. Our MCP detector could measure the yield of Lyman- α photons (121.6 nm) from methane [19] but the intensity appeared weak, so the upper sensitivity limit is probably well below 150 nm.

It was found that a part of the measured photon signal was due to scattering and reflection of the incident synchrotron light. The major cause of the reflected light was the chamber's glass window which was installed for the entrance of the laser beam in order to perform possible two-color experiments. Our efforts to reduce the reflections by masking the window with the diagnostics photo diode already mounted inside the chamber on a manipulator only worsened the situation. However, in electron-fluorescence photon coincidence measurements the scattered light contributed only to the increased level of uniform background. On the other hand, it created distinct peaks in the experiments where the arrival times of photons were recorded in coincidence with the storage ring clock.

The signals from the detectors were fed into a Time-to-Digital Converter (TDC) system (TMD-GPX from ACAM [20]) in order to record the arrival times. The TDC was configured to provide 81 -ps resolution. Even though the photon in our experiment was emitted after the correlated photoelectron, it was actually detected first because it takes some tens of ns for the electrons to pass through the e-TOF spectrometer before reaching the detector. In the electron-fluorescence photon coincidence measurements performed, the photon detector provided the start signal and the e-TOF the stop signal.

3. Test experiments with Ne

Performance of the fluorescence photon-slow electron coincidence apparatus was tested with Ne atoms. The incident photon energy was scanned with a step of ~ 25 meV across the Ne $2s$ threshold (48.475 eV [21]) and coincidences were measured between VUV photons and electrons. These coincidences, shown in the spectra of Fig. 2, come either from direct Ne $2s$ photoionization, which is followed by $2s^{-1} \rightarrow 2p^{-1}$ radiative decay with fluorescence emission at ~ 46 nm [21], or from Ne $2s \rightarrow np$ Rydberg excitations that converge to the $2s$ IP [22]. In the latter case, the excited Rydberg states were found to decay by fluorescence (~ 27 eV photons) to the $2s^2 2p^5(^2P_{1/2}) n'p$ states which further decayed by autoionization to the Ne $^+ 2s^2 2p^5(^2P_{3/2})$ state, releasing an electron with kinetic energy of less than 97 meV. Exciting photon energies were calibrated by comparing our VUV yield to that published in Ref. [22]. However, there remains an uncertainty of 15 meV (or about half of the used step size) in the photon energy scale.

We can clearly see that an electron-VUV photon coincidence peak arises at the time of ~ 32 ns, when the exciting photon energy crosses the Ne $2s$ threshold. Below the $2s$ IP, we observe only hints of weak intensity, particularly in the second and third lowermost spectra in Fig. 2. In the former, the incident photon beam induced the Ne $2s \rightarrow 15p$ and $16p$ transitions, while still higher Rydberg orbitals ($n \approx 18$) were excited in the latter. A prominent intensity increase occurs when the photon energy exceeds the Ne $2s$ IP. The coincidence peak is narrowest just above the threshold. It then splits in two components whose time difference increases with the excess energy above the Ne $2s$ IP. The two peaks originate from the

Fig. 2. Electron-VUV photon coincidence measurements at the Ne $2s$ ionization threshold. Acquisition time was 200 s per spectrum. The base levels of the spectra have been shifted for clarity; the real base lines are ~ 1 count in each spectrum. Photon energy resolution of the incident radiation was about 15 meV. Photon energies are given on the right side of each spectrum in the units of meV relative to the Ne $2s$ IP (48.475 eV). The uncertainty in the energies is ± 15 meV.

photoelectrons that are emitted towards and away from the e-TOF spectrometer. The angular anisotropy parameter, β , is 2 for Ne $2s$ photoionization, which means that the photoelectrons are emitted preferentially along the electric vector of the linearly polarized light. The e-TOF spectrometer was positioned in that direction.

We do not observe any electron-VUV photon coincidences at the photon energies below 48.38 eV (the lowermost spectrum in Fig. 2). This also implies that Ne $2s$ photoionization caused by the second-order and higher order radiation, which is known to be present to some extent in the photon beam after the monochromator, does not disturb this particular experiment. The reason is the reduced TOF collection efficiency for fast electrons. Electrons emitted directly towards the entrance aperture of the e-TOF spectrometer should be detected no matter what is their kinetic energy but the TOF acceptance solid angle is very small (0.06% of 4π) for the used geometry (TOF input aperture has a 2 -mm diameter and it is 20 mm apart from the IR). (For low-energy electrons the collection efficiency is largely increased by application of the external electric field, reaching 100% for zero kinetic energy electrons.) Indeed, no structure is observed at time of flights shorter than 32 ns, where high-energy photoelectron-VUV photon coincidences originating from second or higher order radiation are expected. In contrast, there is a weak structure at a time slightly longer than that of the main peak (for instance, at ~ 34 ns with 61 meV excess energy). It seems to be connected to electron-VUV photon coincidences. This "side" peak is most likely due to the ringing signal in the electron detector or amplifier.

Fig. 3. (a) The total VUV fluorescence yield and (b) the total low-energy electron yield of NO as a function of exciting photon energy. The sharp peak at 21.68 eV in (a) is due to metastable fragments [23]. The lower curves in each panel correspond to the same measurements without gas. The results have been normalized to the photodiode current.

4. Experiments with NO

The “total” fluorescence (limited to VUV photons) and photoelectron (low energy – see collection efficiency discussion above) yields of the NO molecule were first measured in single spectra, by registering the signals coming from the detectors without any restriction on their arrival times. The reference spectra were measured without the sample gas. These results are shown in Fig. 3. It is clear that, in the fluorescence yield measurement, most of the intensity at photon energies below 35 eV is due to scattered light because the reference spectrum is very similar to the spectrum measured with the NO gas. However, the fluorescence yield from NO shows a sharp peak at 21.68 eV. This peak is actually not due to fluorescence, but due to metastable fragments that have been observed just before the $c^3\Pi$ threshold of NO^+ [23]. Metastable fragments, drifting in all directions, can have enough internal energy to be detected when they hit the MCP. At photon energies above 35 eV, the fluorescence yield measured with the sample gas begins to have more intensity than the reference spectrum without gas, indicating that VUV emission of the NO molecule increases significantly at these excitation energies. Dispersed VUV emission in the NO molecule has been observed, for instance, at wavelengths 118–142 nm following the photoexcitation of the N 1s and O 1s electrons to the antibonding 2π orbital [24] and at wavelengths 110–180 nm using electron impact at 100-eV energy [25], but, to our knowledge, not after direct inner-valence photoionization. The two spectra [24,25] display quite similar intensity ratios between the vibrational bands in the $\text{NO}^+ A^1\Pi \rightarrow X^1\Sigma^+$ emission

system and the emission lines due to excited neutral nitrogen and oxygen fragments.

In contrast to the reference fluorescence yield, the electron signal is almost negligible in the reference measurement without gas (Fig. 3b). Most of the electrons in the IR therefore originate from the sample gas. The measured electron yield rises rapidly at 21.7 eV, at an energy that is immediately after the resonance peak due to the metastable fragments in Fig. 3a. This rise can be attributed to the opening of a new photoionization channel that leads to the $c^3\Pi$ state of the NO^+ ion. In other words, when photon energy barely exceeds the $c^3\Pi$ ionization potential (21.7 eV [26]), very slow electrons are emitted and efficiently collected by the e-TOF spectrometer. The threshold photoelectron spectrum (PES) of NO [27] does not show any features immediately after the threshold of $c^3\Pi$ photoionization. Therefore, the shape of this peak in our electron yield spectrum is concluded to represent approximately the transmission of the e-TOF spectrometer in the present measuring conditions. The FWHM of the peak is about 0.42 eV and the total width at the base level is about 1.1 eV. Thus, the collected electrons mostly have kinetic energies less than 1 eV in our experiments. Because of this modest electron resolution, all the sharp features that were observed in the threshold PES of NO [27] are smeared out in our spectrum. The electron yield displays a high background, which is due to slow electrons that can be created when photoelectrons lose energy when colliding with molecules, walls or other surfaces in the chamber. These secondary electrons, however, are not correlated with VUV emission and therefore do not create peaks in the coincidence spectrum. The high background (like in Fig. 3b) can be tolerated in the electron yield, as the enhanced transmission achieved should help to decrease considerably the measuring time in coincidence measurements.

Coincidences between VUV photons and slow electrons were measured at various photon energies in the valence region; the spectra are shown in Fig. 4. The coincidence peak forms at 29 ns when photon energy is increased. The slightly different position of the maximum as compared to the Ne measurements shown in Fig. 2 was caused by a small adjustment of the operating voltages of the e-TOF spectrometer. The measurements at 25 and 30-eV photon energy show no peaks above noise level. In contrast, at 35-eV photon energy a very narrow peak with weak intensity appears at the correct position for electron-VUV photon coincidences. At 38-eV photon energy, the coincidence peak becomes more intense and broader. This indicates that a threshold, which leads to both electron and VUV photon emissions, has been exceeded and the electrons detected can also have a small amount of kinetic energy. The coincidence rate increases substantially when going from 38- to 41-eV photon energy. At the latter energy, we observed about 4 coincidences/minute within a 1-ns wide window at the peak maximum, while the background level was ~ 0.3 counts/min. (These spectra have been binned from the original data.) At 50-eV photon energy, the coincidence rate decreases at the maximum and the peak profile becomes broader. This is obviously caused by the increase in the average kinetic energy of the photoelectrons detected.

The temporal profile of VUV emission was measured at the photon energy of 41.5 eV. The time measurement was started by a photon hitting the MCP and stopped by the ring clock, which leads to a reversed time axis in the spectrum. The temporal distribution of detected photons with and without NO gas are shown in Fig. 5 for the time region where the extra electron bunches were inserted in the dark gap (the position of the origin of the time axis, 0 ns, is irrelevant). The inset shows the spectrum without gas in a wider time region. It demonstrates that there were no electron bunches between 210 and 180 ns until the three electron bunches inserted in the dark gap arrived (at 181.3, 179.3 and 173.3 ns). These measurements did not involve electron detection, hence the result obtained

Fig. 4. The photoelectron-VUV photon coincidence spectra of NO measured at the photon energies of 50, 41, 38, 35, 30, and 25 eV (traces from top to bottom). The spectra have been normalized to the photon flux measured with a photodiode. Measuring time was 10 min for each spectrum. The base levels of spectra have been raised for clarity as follows: at 50 eV by 40 counts, at 41 eV by 25 counts, at 38 eV by 20 counts, at 35 eV by 13 counts and at 30 eV by 9 counts.

does not necessarily relate to the coincidence events observed in Fig. 4, but to the most intense VUV emission detected by the MCP. The measurement without gas shows that there is a significant contribution of scattered SR light (probably from the needle). This can be deduced from the appearance of the peaks which fit the electron

Fig. 5. VUV photon-ring clock coincidence spectra measured with and without NO gas. The inset shows the spectrum without gas in a wider region, demonstrating the electron bunch structure and the dark gap that begins at ~ 210 ns and ends at ~ 270 ns. Note that the real time axis runs from right to left. Measurement time was 60 min for each spectrum. Photon energy was 41.5 eV.

Fig. 6. The decay time analysis of VUV fluorescence emission in the NO molecule. The “instrumental” profile (see text for details) was convoluted by the exponential decay curve, characterized by the lifetimes of 1.82 ns (red curve) and 2.4 ns (black curve), and adjusted on the experimental spectrum (points connected with line), which is the difference of the two curves in Fig. 5. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

bunch time structure of the Elettra storage ring (pulse every 2.0 ns). However, there were also some peaks whose intervals (2.3 ns in Fig. 5) did not follow the 2.0-ns bunch structure of the ring. As those peaks shifted upon the insertion of the photodiode in front of the glass exit window, they should be caused by the reflection of the incident SR beam when it hits the end of the beam line, i.e., the photodiode or the exit window. They are labeled as “reflection” in Fig. 5. The origin of the peak, which is provided with a question mark, is not clear.

The most intense peak at ~ 179 ns in the measurement with the sample gas (Fig. 5) shows an exponential tail on the shorter times, as would be expected for radiative decay that is characterized by a lifetime of the order of a couple of ns. The tail is on the left side of the peak because VUV photons start the time measurement. The time structure of the peak at 179 ns was analyzed after the subtraction of the two spectra of Fig. 5. The subtracted spectrum is shown in Fig. 6. The temporal profile in the measurement without gas is given by the incident SR pulse, whose width is about 60 ps, and by any possible broadening effects due to the detector, electronics, etc. Let us call it as an instrumental profile. We assume that the same instrumental profile is maintained in the measurement with the NO gas, in which case the peak shape is further modified by the decay of the emitting states. Accordingly, the observed line shape in the measurement with NO was taken to be the convolution of the peak observed around 179 ns in the measurement without gas (Fig. 5) and an exponential decay function that described the lifetime dependence of the emitting state. The largest contribution to VUV emission could come from the O and N emission lines at 130.4 and 120.0 nm, respectively, as they are the most intense ones in the published fluorescence spectra [24,25]. The lifetimes of the emitting states have been determined to be $1.82 (\pm 0.05)$ ns for the O I line at 130.4 nm [14] and ~ 2.4 ns for the N I lines at 120.0 nm [15], the latter value being the average of several experiments. The results of convolution with these lifetimes are shown in Fig. 6. The convoluted curve follows the experimental data points better when the lifetime of the emitting state is 2.4 ns. This could imply a significant contribution from the N emission line at 120.0 nm, which is due to the $2p^2(^3P)3s(^4P) \rightarrow 2p^3(^4S)$ transitions. However, this result is not conclusive, as an equally good correspondence could

be achieved, for instance, by a sum of two decay curves, one with a slightly shorter and the other with a slightly longer lifetime. The variation in the detection efficiency of the MCP may also have an influence: perhaps photons at 130.4 nm (9.51 eV), corresponding to possibly intense emission from the excited O atom, are detected with much less efficiency than those from N at 120.0 nm (10.33 eV). There are several other atomic emission lines in the VUV range of interest; the calculated lifetimes of their upper states were tabulated in [16]. Note that the emission system $A^1\Pi \rightarrow X^1\Sigma^+$ of the NO^+ ion as the origin of the decay profile is excluded because the lifetimes of the vibrationally “resolved” upper states are about 50 ns or longer [25,28]. Nevertheless, this molecular emission probably creates considerable background in the spectra of Figs. 5 and 6.

5. Discussion

We first exclude the possibility that the observed electron–VUV photon coincidences originate from photoionization of the $\text{NO}^+ A^1\Pi$ state, followed by the $A^1\Pi \rightarrow X^1\Sigma^+$ emission. The ionization energy of the $A^1\Pi$ state is 18.3 eV [26]. Therefore the photoelectrons created have relatively high kinetic energies (~ 20 eV) in the excitation energy of interest and they are not collected efficiently. In fact, we do not see any coincidences at 25 and 30 eV photon energies (Fig. 4), where the $\text{NO}^+ A^1\Pi$ photoionization channel is open. No other molecular emission in NO^+ was observed in the wavelength region below 150 nm [24,25].

The VUV photons observed in coincidence with slow electrons could, in principle, originate either from decay of doubly excited (superexcited) states or from dissociative photoionization with excitation. We consider first double excitations, taking into account only those decay channels that lead to VUV emission. A doubly excited state could autoionize to a state of NO^+ which further fluoresces in the VUV region. The $A^1\Pi \rightarrow X^1\Sigma^+$ transition in NO^+ emits VUV light that can be detected by our MCP. Some doubly excited states could obviously decay to the $A^1\Pi$ state. If such a doubly excited state were, for instance, at 38-eV excitation energy, the electron emitted would have a kinetic energy of about 20 eV. However, such a fast electron would not create a sharp peak in the electron–VUV photon coincidence spectrum. Possible decay channels involving other molecular emission of NO^+ in the VUV region should be much weaker, if they exist at all, and can also be neglected for the same reason that electrons emitted would have too high kinetic energies.

Other possible VUV emitters are produced when a doubly excited state dissociates into two excited neutral fragments. If both fragments fluoresce, as it was actually observed for NO by Odagiri et al. [16], no electron is coming out. Therefore this channel cannot explain the electron–VUV photon coincidences. However, if one of the fragments autoionizes, it provides an electron for coincidence events. Hikosaka et al. [29] have observed autoionization in the N atom after excitation of NO to superexcited states at photon energies between 21.5 and 27 eV. Autoionization peaks lie in the electron spectrum at low kinetic energies between 0 and 2 eV, so such electrons would be efficiently collected by the e-TOF spectrometer. Superexcited states of NO have also been observed at ~ 33 -eV excitation energy [30,31] and recently at even higher energies up to 47 eV [16]. However, we can give some arguments suggesting that this channel is not responsible for the detected electron–VUV photon coincidences. Superexcited states are of resonant nature and do not give rise to a smooth intensity distribution at all excitation energies above a given threshold, as it is observed in the VUV yield of Fig. 3. The existence of “suitable” superexcited states across the whole inner-valence region is highly unlikely. Additionally, following superexcitation of NO, autoionization was observed only in the N fragments [29], which implies that VUV emission should take place in the O atom. Our decay time analy-

sis rather points out that most VUV emission comes from N atoms. Finally, autoionization of a fragment is typically characterized by constant electron kinetic energies as a function of the excitation energy. In contrast, the coincidence peak shape in our measurements varies with the photon energy (Fig. 4), which suggests that an electron is produced by photoionization rather than by autoionization. We therefore conclude that superexcited states are extremely unlikely to be the origin of the observed coincidences between slow electrons and VUV photons.

Remembering the transmission behavior of the e-TOF spectrometer under the present measuring conditions, the electrons detected in the electron–VUV photon coincidence spectrum at 41-eV photon energy (the one with highest intensity in Fig. 4) should originate predominantly from photoionization channels whose ionization energies are between 40 and 41 eV. The photoelectron spectrum of NO [26,32] shows a wide peak whose maximum is at the binding energy of 40.4 eV. It was originally assigned to primary photoionization from the 3σ orbital [32], but the calculations of Honjou et al. [33] attributed the intensity to the states having mostly $2h-1e$ character and to a lesser extent $3\sigma^{-1}$ character, i.e., to the correlation satellite states. These inner-valence photoionization processes are also visible as a very weak structure between 39 and 42 eV in Fig. 3b and partly also in the threshold PES of Ref. [27], which was measured only up to 40 eV. The latter spectrum proves that there is a continuous supply of slow electrons available also for our coincidence measurements at 35 and 38-eV photon energy. The last satellite state in the PES appears at ~ 45 -eV ionization energy [26]. At the photon energy of 50 eV (Fig. 4), very few electrons may therefore have less than 5-eV kinetic energy, which would explain the spreading of the coincidence peak. According to the calculations presented in [27], inner-valence states are characterized by dissociative potential energy curves that correlate with excited neutral and ionic fragments. Fluorescence emission can therefore be expected to follow inner-valence photoionization in NO. The basic features of our electron–VUV photon coincidence spectra can be accounted for if DIE takes place in the context of photoionization to $2h-1p$ states. This interpretation agrees with the one made for inner-valence ionization of the N_2 molecule [6,7]. The analogous effect has also been suggested to occur in NO with electron impact excitation [25]. The N I emission at 120.0 nm resulting from a DIE process is energetically possible at excitation energies above 30.45 eV [21,34]. This energy limit is well below the photon energies where we observe the electron–VUV photon coincidences.

There is a variation of DIE that produces an excited ion and a neutral atom in the ground or lowly excited state. Ebresmann et al. [35] observed N II emission lines at 91.6 and 108 nm in the N_2 molecule using synchrotron excitation between 37 and 69 eV photon energies. They attributed these lines to DIE. The transitions around 108 nm could also contribute to VUV emission observed in the present study, as the lifetime of their upper states is about 2.7 ns [36]. The dissociation limit in the NO molecule to produce the fragment in question, $\text{N}^+(2s2p^3, ^3D)$, together with the ground-state O atom lies at 32.47 eV [21,34]. Similar DIE processes involving emission in O^+ ions appear less likely, as transitions having a wavelength below 150 nm and the excitation energy of the upper state less than 20 eV are spin-forbidden except for the O II lines around 83 nm [21]. The upper states of these transitions have ~ 14.9 eV excitation energy [21] (which sets the corresponding dissociation limit at about 35.0 eV [34]) and ~ 1.2 ns lifetime [37].

Finally, we consider expected similarities in fluorescence emission of NO following the $(\text{N and O}) 1s \rightarrow 2\pi$ excitations, studied in [24], and after inner-valence photoionization. The core-excited states decay predominantly via spectator transitions to such $2h-1e$ final states where the 2π orbital remains occupied. These final states of spectator decay are similar to the correlation satellites in the inner-valence photoionization. In fact, according to the-

ory [33], the most important $2h-1e$ configurations that mix with the inner-valence state $3\sigma^{-1}$ have the 2π orbital occupied. We expect therefore that dissociation of the $2h-1e$ states yields the same excited fragments after spectator decay of the $(N/O\ 1s)^{-1}2\pi^1$ states and after direct inner-valence photoionization. The decay time analysis performed in Fig. 6 gives partial support to this idea, as it suggests a significant contribution from the N I emission line at 120.0 nm. The same emission line was observed to be the most intense one after core excitation of NO [24].

6. Conclusions

We have performed exploratory electron-VUV photon coincidence experiments using an electron TOF spectrometer for electron detection and an MCP detector for VUV photon detection. The performance of the setup was successfully tested at the Ne 2s edge, where the emission of the 2s photoelectron is followed by VUV emission due to the $2s^{-1} \rightarrow 2p^{-1}$ transitions. Slow electron-VUV photon coincidences were also detected in the inner-valence region of the NO molecule. The highest intensity was related to the photoelectron band around the ionization energy of 40 eV. This band has been previously associated with the correlation satellite states ($2h-1e$ states) that mix with the inner-valence single-hole state $3\sigma^{-1}$ of NO. These highly excited states of NO^+ dissociate mostly into $O^+ + N^*$ and $N^+ + O^*$. Excited neutral O and N atoms have transitions in the VUV range that is detected in the present experiment ($\lambda < 150$ nm). The temporal behavior of VUV emission was also measured. An important part of VUV emission could be explained with a decay time of ~ 2.4 ns, which together with intensity considerations points out to the neutral excited N atom emitting at 120.0 nm as the most important emitter.

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