

PHOTOIONIZATION OF INNER VALENCE ELECTRONS IN GASEOUS NO: A SYNCHROTRON RADIATION STUDY

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We report photoelectron spectra of the outer and, in particular, the inner valence electron region of gaseous NO for several photon energies between 45 and 110 eV. The spectra are measured at the quasi magic angle, so that the electron distribution curves represent the variation of the cross section independent of the β parameter. We find 16 bands in the inner valence region which can be tentatively correlated to various shake-up excitations. On the basis of published theoretical work, a comparison is made with spectra taken with soft X-ray excitation.

1. Introduction

The breakdown of the one-particle picture of ionization is a well known theoretical, and by now, also, experimentally verified phenomenon [1,2]. Detailed analyses of the complete valence region have been presented mainly for closed-shell molecules [1-3]. Nitric oxide (NO) is one of the simpler examples of a molecule with a degenerate, open-shell ground state, and there have been a few experimental [4-11], and theoretical [12-20] studies on this system. In contrast to CO [21] and N₂ [22,23], where the inner valence region has been studied in some detail [24], similar detailed studies for NO have been rather scarce.

Siegbahn et al. [4] presented the full photoelectron spectrum of NO covering the valence and the core electron regions using MgK excitation. Subsequently, Lindholm and co-workers [5,6] reported high-resolution photoelectron spectra up to a binding energy of approximately 22 eV using HeI and HeII excitation. In the latter work it was possible to assign definitely nine out of the eleven final ion states which are expected for ionization of the four outer

valence shell electrons 2π , 1π , 5σ and 4σ , respectively (see table 1).

Assignments so far have been based on the results of several calculations [12-20]. Above 21 eV binding energy some assignments appear to be slightly controversial, namely the peak around 23 eV binding energy which is assigned to either $^1\Sigma^+$ originating from 1π ionization [6,25], or to $^1\Pi$ originating from 4σ ionization [4]. Even though the vibrational structure resolved in the spectra published by Edqvist et al. [6] and also (e, 2e) momentum distributions [25] support the assignment as a $^1\Sigma^+$ state, the issue cannot be considered as settled since calculations [14,15] cannot straightforwardly verify the experimental observations.

For binding energies above 23 eV the lack of well-resolved experimental data has prevented a more detailed discussion: Brion and Tan [8] report quasi-photoionization (e,2e) data, barely resolving two broad bands at around 32 and 40 eV, and Siegbahn et al. [4] have observed one broad structure at 40.6 eV; a weak feature at 31 eV has been attributed to excitation processes with MgK α LFe_{3,2} satellites. In analogy with CO and N₂ multi-electron excitations are considered [4,8,15] as the origin for these bands:

Table 1

Electron configurations and resulting possible final ion state symmetries. Classifications of the electron configurations are given in the two columns on the left

	Symmetry	Configuration	Possible final states
single-hole states	σ	$4\sigma^2 1\pi^4 5\sigma^1 2\pi^1$ $4\sigma^1 1\pi^4 5\sigma^2 2\pi^1$	$^1\Pi, ^3\Pi$
	π	$4\sigma^2 1\pi^4 5\sigma^2$ $4\sigma^2 1\pi^3 5\sigma^2 2\pi^1$	$^1\Sigma^+$ $^1\Sigma^+, ^3\Sigma^+, ^1\Sigma^-, ^3\Sigma^+, ^1\Delta, ^3\Delta$
2hp states $\sigma + \sigma \rightarrow \sigma^*$	σ	$4\sigma^2 1\pi^4 2\pi^1 6\sigma^1$ $4\sigma^1 1\pi^4 5\sigma^1 2\pi^1 6\sigma^1$	$^1\Pi, ^3\Pi$ $^1\Pi(2), ^3\Pi(3)$
	σ	$4\sigma^2 1\pi^3 5\sigma^1 2\pi^2$ $4\sigma^1 1\pi^3 5\sigma^2 2\pi^2$	$^1\Pi(3), ^3\Pi(4), ^1\Phi, ^3\Phi, ^5\Pi$
2hp states $\sigma + \pi \rightarrow \pi^*$	σ		
	π	$4\sigma^2 1\pi^2 5\sigma^2 2\pi^2$	$^1\Sigma^+(3), ^3\Sigma^+(2), ^1\Sigma^-, ^3\Sigma^-(2)$ $^1\Delta(2), ^3\Delta(2), ^1\Gamma, ^5\Sigma^+$

The broad peak around 40 eV binding energy is assigned to ionization of the inner valence 3σ level, and strong interaction with configurations created from outer valence shell ionization and simultaneous electron-hole pair excitation processes.

It is the aim of the present paper to provide a more detailed examination of the binding energy region between 22 and 45 eV employing synchrotron radiation. Synchrotron studies have so far only been reported for the outer valence region of NO [7,9–11]. We resolve 16 peaks in the inner valence electron region, and discuss possible assignments on the basis of a calculation by Honjou et al. [15] which is the only ab initio calculation available covering this energy region.

2. Experimental details

The experiments were performed at the BESSY storage ring in Berlin using a toroidal grating monochromator (TGM4) [26] for monochromatization of the radiation. Photoelectrons were detected after passing a double sector cylindrical mirror analyser (CMA) which is placed, and can be rotated, in the plane perpendicular to the photon beam direction to allow angular distribution measurements [27]. The spectra for the present study have been taken at the quasi-magic angle. The experimental details were the same as in a previous study on CO_2 [28] and will not be repeated here. NO (98% Linde) was intro-

duced into the photon interaction volume via a multicapillary array. A typical pressure in the interaction volume was 8×10^{-4} mbar with a pressure of 8×10^{-4} mbar in the recipient. The resolution of the CMA was about 0.5% and the bandpass of the monochromator at 55 eV in the spectra of fig. 1 was 150 meV and in fig. 2 90 meV.

3. Results and discussion

Fig. 1 shows a set of four spectra taken at different photon energies between 45 and 110 eV. As is often the case, the outer valence region can be clearly differentiated from the inner valence region. While the outer valence region is characterized by a series of sharp peaks which have been discussed in detail by Lindholm and co-workers [5,6], the inner valence region shows broad and overlapping bands. The primary reason for this basic difference is the so-called breakdown of the quasi-particle picture in the inner valence region as pointed out by Cederbaum and co-workers [1,2]: Within the inner valence region many two-hole-particle (2hp) states are situated energetically such that any hole state of appropriate symmetry can couple to a manifold of these 2hp states. Therefore the hole state loses intensity via interactions with these 2hp states. On the other hand, in the outer valence region the hole states are energetically isolated. This gives rise to a number of sharp peaks as observed. As fig. 1 clearly indicates, the

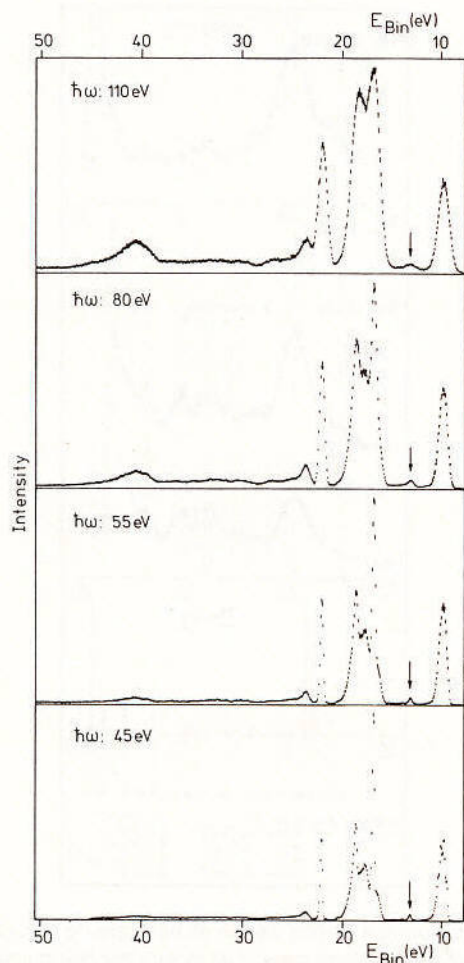


Fig. 1. Complete photoelectron spectra of the valence electron region of NO for 45, 55, 80 and 110 eV photon energy taken at the quasi-magic angle. Note that the small peak around 14 eV, marked with an arrow is due to N_2 contaminant.

contribution of the outer valence regime to the total intensity dominates, in particular at low photon energies. However, towards higher photon energies, i.e. above 100 eV, the inner valence region picks up more and more intensity and its contribution to the total intensity increases considerably. In the limit of the soft X rays [4] the inner and outer valence region have almost equivalent intensities.

Due to the "natural" subdivision of the spectra into inner and outer valence region we shall divide the discussion accordingly: Firstly, we shall briefly review the assignment of the outer valence bands, and then,

Table 2

NO binding energies (this work)

X $^1\Sigma^+$	($2\pi^{-1}$)	9.7 eV	
a $^3\Sigma^+$	(1 π^{-1})	15.7–20.0 eV	16.1 eV ^{a)}
$^3\Delta$			17.2 eV ^{a)}
$^3\Sigma^-$			17.9 eV ^{a)}
$^1\Sigma^-$			18.4 eV ^{a)}
$^1\Delta$			18.9 eV ^{a)}
b $^3\Pi$	(5 σ^{-1})	16.6 eV	
A $^1\Pi$			18.3 eV
C $^3\Pi$	(4 σ^{-1})	21.7 eV	
Π		23.3 eV	
A		24.8 eV	
B		26.6 eV	
C		29.2 eV	
D		29.8 eV	
E		30.3 eV	
F		31.1 eV	
G		32.0 eV	
H		32.6 eV	
I		33.9 eV	
K		34.6 eV	
L		35.3 eV	
M		36.0 eV	
N		37.8 eV	
O	(3 σ^{-1})	39.2 eV	
P			40.4 eV
Q			45.1 eV ^{b)}

^{a)} From ref. [6]. ^{b)} From ref. [4]

secondly, turn to the details of the inner valence region.

The ground state electronic configuration of neutral NO is $(2\pi)^1(1\pi)^4(5\sigma)^2(4\sigma)^2(3\sigma)^2$ leading to a $^2\Pi$ ground state. Detachment of the 2π electron leads to the closed-shell ground state ($^1\Sigma^+$) of NO^+ . The corresponding peak is observed in the spectra at 9.6 eV (see table 2 and fig. 1). If we ionize a 1π electron we are left with a configuration equivalent to two unpaired π electrons, which yields six ion states as given in table 1 fourth row. The $^3\Sigma^+$ state is expected at lowest, the $^1\Sigma^+$ state at highest binding energy. For the diatomics this is generally observed [29]. The whole manifold of ion states can be populated via ionization since the spin selection rule $\Delta S=1$ applies. Except for the $^1\Sigma^+$ state the five remaining ion states have been definitively assigned by Edqvist et al. [6] as given in table 2. They all cluster between 15.5 and 19 eV binding energy. In the

present spectra these individual peaks cannot be resolved. But even more pronounced, the experimental spectrum shows the two bands arising from the removal of a 5σ electron as being superimposed (see table 2). The removal of a 5σ electron leads to $^3\Pi$ and $^1\Pi$ ion states, which appear in fig. 1 as two sharp peaks at 16.7 and 18.5 eV. The triplet state is more intense as expected. Intuitively, the removal of a 4σ electron should lead to similar spectral features as the detachment of a 5σ electron, and this is why the two peaks at 21.7 and 23.3 eV were originally assigned to the 4σ -derived $^3\Pi$ and $^1\Pi$ states. While there is no doubt about the nature of the more intense $^3\Pi$ state at 21.7 eV, Edqvist et al. [6] assigned the peak at 23.3 eV to the missing $^1\Sigma^+$ state originating from 1π ionization. They argued that the 4σ - $^1\Pi$ state is hidden under the peak at 21.7 eV. A theoretical study of the complete NO photoelectron spectrum published by Honjou et al. [15] reveals, however, why the assignment of spectral features in the energy region above 21 eV becomes difficult: In this energy range 2hp states become very important. The controversial band at 23.3 eV contains only 22% of the 4σ -hole configuration but 69% of 5σ ionization with simultaneous 1π to 2π excitation. Such strong configuration interaction effects will turn out to become even more pronounced at higher binding energies.

Fig. 2 shows magnified views of our best resolved spectra in the binding energy region between 22 and 45 eV together with the ESCA spectrum of Siegbahn et al. [4]. In order to facilitate the subsequent discussion, the lower part of fig. 2 exhibits as a bar diagram the theoretical prediction of Honjou et al. [15]. Our experimental spectra allow the identification of at least 16 ion states between 23 and 45 eV labeled A to Q in fig. 2. This observation compares with the ab initio calculation which predicts 19 bands with appreciable intensity in this energy range. From the calculation it is clear that most of the bands must be due to 2hp states as expected. Although Honjou et al. [15] include in their calculation even more complex processes we restrict the discussion to 2hp states. There are basically three types of electron-hole pairs which have to be considered in a discussion of the nature of the 2hp states;

(i) a 5σ - 6σ excitation in the presence of a 4σ or 5σ hole;

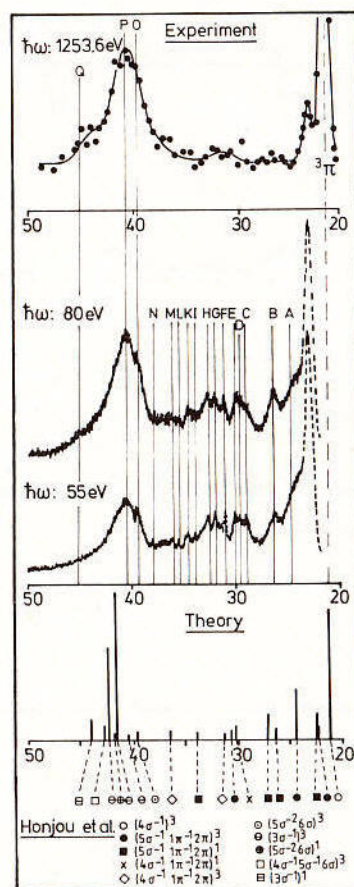


Fig. 2. Comparison of inner valence photoelectron spectra of NO at 55 and 80 eV photon energy (taken with our best resolution, but not at the quasi-magic angle) with a soft X-ray induced spectrum (MgK α : 1253.6 eV) [4], and with results of theoretical calculations [15] as discussed in the text.

(ii) a 1π - 2π excitation in the presence of a 4σ or 5σ hole;

(iii) a 1π - 2π excitation in the presence of a 1π hole.

Table 1 collects the resulting electron configurations together with the possible final states (rows 5 to 8). By angular momentum and spin selection rules the Φ and Γ states, as well as the quintet states can be excluded. Therefore we are left with $^1\Pi$ and $^3\Pi$ states that cause the major part of the intensity of the 2hp states. Of course, the $^1\Sigma$ and $^3\Sigma$ states resulting from the coupling of a 1π - 2π excitation to the 1π hole are also possible (see row 9 of table 1). But the calculation reveals that these 2hp states lead to neg-

ligible satellite intensity for NO. This is in agreement with results for other diatomics [21–24].

Let us now compare the experimental spectra with the calculation [15] in more detail. Between 22 and 27 eV the calculation predicts five states which are all derived from 2hp states caused by coupling a $1\pi-2\pi$ excitation to a 5σ hole. All states are Π states. In fact, there is no $^1\Sigma^+$ state of appreciable intensity predicted in this energy range. Theoretically, the most intense peak in this range is calculated to be a $^3\Pi$ state at 24.4 eV which arises from configuration interaction of the 4σ ionization and the configuration resulting from 5σ ionization and simultaneous $1\pi-2\pi$ excitation. Therefore, the rather intense peak at 23.3 eV observed in the experimental spectrum is assigned to this $^3\Pi$ state. A closer look at the theoretical results reveals that the wavefunctions of the states in this energy region [15] contain dominating 2hp and smaller hole (4σ) character. It is known experimentally, and has been pointed out by Cederbaum and Domcke [1,2] that the vibrational progressions associated with 2hp states are rather pronounced in contrast to those associated with non-bonding hole states such as 4σ or 5σ , and are similar to those found for strongly bonding or antibonding hole states such as 2π and 1π . Thus we consider that the assignment ($^3\Pi$) suggested by the calculation is compatible with the experimental findings even though explicit calculations taking vibrational coupling into account have not yet been done. A clear decision as to whether this is a $^3\Pi$ or a $^1\Pi$ state cannot be made at present since the theoretical calculation also predicts close lying $^1\Pi$ states. The two shoulders (A and B in fig. 2) observed at the high binding energy side of the peak at 23.3 eV may then originate from the other $^1,^3\Pi$ states predicted in this region. At higher binding energy we find experimentally two band systems, one centered around 30 eV (lines C to E in fig. 2), the other centered around 33 eV (lines F to I). Even though this correlates well with the two groups found in the calculation, we do not think that this suggests a one-to-one correspondence. This is evident if we look at the observed fine structure of the band systems which is of course not (and cannot be expected to be) reproduced by the calculation. Also, the weak peaks between 35 and 40 eV are not predicted theoretically. However, the structured, intense band around 40 eV is found in

the calculation. It is associated with ionization of the 3σ electrons. Its intensity is distributed over several states as has been observed previously for several other diatomic molecules [1,2,24]. According to the calculation the singlet and triplet components of the 3σ ionization are separated by less than 2 eV [15]. The assignment of the broad band system to the 3σ ionization is also corroborated by the observed intensity variations as a function of photon energies. With increasing photon energies the relative intensity of this band increases (see fig. 1, and the ESCA spectrum in fig. 2) which can be traced back to the rather large $2s$ contribution of the constituent atomic orbitals to the molecular wavefunction. Such a behaviour has been observed for many molecules and has always been interpreted in a similar fashion [30]. We note that about 1 eV below the band maximum there is a characteristic dip in intensity.

4. Summary

We have studied in the present work the photoelectron spectrum of NO in the gas phase at photon energies between 55 and 110 eV. Our outer valence spectra agree with spectra reported in the literature. The particular emphasis of our study, however, lies in the inner valence region where we identify at least 16 peaks, most of which have not been previously observed. We compare our experimental results with results of *ab initio* calculations reported by Honjou et al. [15]. The agreement between experiment and theory is reasonable but far from quantitative.

The peak at 23.3 eV binding energy has been discussed controversially in the literature. We suggest it to be due to a $^3\Pi$ or a $^1\Pi$ state resulting from 5σ ionization with accompanying $1\pi-2\pi$ excitation, and not due to a $^1\Sigma^+$ state connected with ionization of a 1π electron as suggested by Edqvist et al. [6]. The observed strong vibrational progression, which was the basis for the assignment by Edqvist et al. [6], may be caused by the strong admixture of 2hp states in the wavefunction [1,2].

The photon energy dependence of the relative peak intensities allows us to clearly assign those peaks in the inner valence region that result from ionization of NO 3σ electrons. In the energy region of the 3σ

ionizations the breakdown of the one-particle picture is most pronounced.

From our comparison between experiment and theory it is obvious that much more detailed theoretical calculations are necessary to find a definitive, conclusive assignment of the inner valence electron region. We hope, however, that the present results will stimulate further research in this area.

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