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**Journal**

Physical Review A. Atomic, Molecular, and Optical Physics, 59(5)

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**Publication Date**

1998-06-23

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June 1998

Submitted to  
*Journal of*  
*Chemical Physics*



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To be published in Journal of Chemical Physics

Light Source Note:	
Author(s) Initials	AS 4/23/98
Group Leader's initials	Z.H. 4/24/98
Date	
Date	

# Vibrationally resolved O 1s core-excitation spectra of CO and NO

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(June 9, 1998)

## Abstract

High-resolution photoabsorption spectra of CO and NO below the O 1s ionization threshold are presented. For both molecules, the vibrational fine-structure of the O 1s  $\rightarrow \pi^*$  and O 1s<sup>-1</sup>Ryd (Rydberg) excitations could be resolved, allowing a derivation of the vibrational energies and intramolecular distances of the core-excitation states in CO and NO from Franck-Condon analyses. The spectral features of the O 1s<sup>-1</sup>Ryd region in CO are reassigned on the basis of the new experimental results. The results obtained for the O 1s<sup>-1</sup>3s Rydberg state in NO support the idea of a weakening of the molecular bond upon an O 1s<sup>-1</sup> ionization process.

PACS numbers: 33.20.Rm, 33.20.Tp, 33.15.Dj, 33.15.Ry

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## I. INTRODUCTION

Measurements of medium-resolution photoemission spectra of core-ionized molecules in the 1970's revealed an asymmetric lineshape indicating the presence of a vibrational fine-structure [1]. These experimental findings stimulated a large number of theoretical investigations on the potential-energy surfaces of C, N, and O  $1s^{-1}$  core-ionized states of small molecules [2-5] and resulted in the conclusion that the C  $1s$ /N  $1s$  (O  $1s$ ) core-ionization leads to a strengthening (weakening) of the molecular bond [6]. These effects on the molecular bond are also expected for core-to-Rydberg excitations according to their similar valence-electron distribution.

Recent improvements in synchrotron light sources and beamlines have made it possible to resolve the vibrational fine-structure of numerous core-excited molecules using photon energies up to  $h\nu \cong 400$  eV. Extensive studies have been performed using photoabsorption and photoemission spectroscopy to obtain information about the potential-energy surfaces of core-excited molecules, see e.g. Si  $2p^{-1}$  in  $SiX_4$  ( $X=H,D,F,CH_3,Cl,Br$ ) [7], C  $1s^{-1}$  in CO [8,9] and  $CH_4$  [10,11], as well as N  $1s^{-1}$  in NO [12] and references therein. These measurements confirmed the predicted strengthening of the molecular bond, i.e., an increase of the vibrational energy and a decrease of the equilibrium distance upon ionization/excitation for C  $1s^{-1}$  and N  $1s^{-1}$  core-ionized states as well as the corresponding Rydberg excitations. However, at even higher energies, the instrumental resolution achieved with photon (photoabsorption and photoemission spectroscopy) and electron (electron-energy-loss-spectroscopy) excitation was not sufficient until recently to obtain complete information on the vibrational fine structure. Therefore, a number of earlier measurements below the O  $1s$  ionization threshold were not able to resolve the vibrational fine structure of CO [13,14] and NO [15,16]. Only recent experiments were able to obtain partial information about the vibrational fine-structure of O  $1s^{-1}$  core-excited and core-ionized states of NO [12] and CO [8,17]. These recent photoabsorption [8] and photoemission [17] spectra of CO exhibited an increase of the equilibrium distance and a decrease of the vibrational energy, i.e., a weakening of the bond and,

therefore, gave a first support of the theoretical predictions.

We report here on new photoabsorption measurements of CO and NO below the O 1s ionization threshold with substantially improved resolution ( $\Delta E \cong 65$  meV), compared to recent measurements performed at the SX700/II monochromator at BESSY/Berlin with a resolution of  $\Delta E \cong 120$  meV [8,12]. This improved resolution results in completely resolved vibrational fine structures and allows Franck-Condon analysis of the spectra, providing information on the potential-energy surfaces of the core-excited states. The vibrational fine-structure of the lowest Rydberg state in NO reveals a lower vibrational energy and a larger equilibrium distance as compared to the ground state, supporting the general conclusion of Ref. [6] of a weakening of the molecular bond upon O 1s core-ionization.

## II. EXPERIMENTAL AND DATA ANALYSIS

The measurements were performed at the 7.0.1 undulator beamline of the Advanced Light Source (ALS) in Berkeley/California, which is equipped with a spherical-grating monochromator. The built-in photoionization cell consisting of two parallel plates with an active length of 20 cm for collecting the charged particles was used. The photoionization cell was separated from the UHV of the monochromator by an 1000-Å thick Al (1% Si) window; it was filled with 10 to 50  $\mu$ bar of CO and NO. The spectra were measured with the 925 l/mm grating using 8- $\mu$ m entrance and exit slits, resulting in a spectral resolution of  $\Delta E \cong 65$  meV.

For an exact calibration of a spherical-grating monochromator, two calibration points are necessary. For the energy range of the grating used no high-accuracy energy values for calibration are available. Therefore, the present spectra were calibrated in a linear way to the value of the O  $1s^{-1} 3s\sigma$  Rydberg state for NO given by Remmers et al. [12]. The energy of the largest photoionization yield of the O  $1s^{-1}\pi^*$  excitation in CO obtained in this way agrees within the error bars with the EELS-values of 534.21(8) eV achieved by Sodhi and Brion [18]. On the basis of the described calibration the absolute error bars in energy are

estimated to be  $\pm 50$  meV; the relative error bars are distinctly smaller (about  $\pm 10$  meV) and given in the tables.

The spectral features were described with Voigt profiles in the least-squares fit analyses, i.e., with Lorentzians convoluted by a Gaussian, to simulate the spectrometer function. The linewidth of the Gaussian was used as a free parameter in the fit procedure of all spectra, yielding a spectral resolution of  $\Delta E = 65 \pm 10$  meV.

The potential-energy surfaces of a non-dissociative molecular state can be described with a Morse potential, which is characterized by the equilibrium distance  $r$ , the vibrational energy  $\hbar\omega$ , and the anharmonicity  $x\hbar\omega$ . In this paper double prime and single prime denotes the values of  $r$ ,  $\hbar\omega$ , and  $x\hbar\omega$  for the ground and core-excited state, respectively. To obtain information about the values  $r'$ ,  $\hbar\omega'$ , and  $x\hbar\omega'$  of the core-excited states, Franck-Condon analyses were performed. In these analyses the intensity distribution of the vibrational substates of the core-excited states are calculated by using the overlap of the vibrational wavefunction of the ground and core-excited states. For this purpose, the vibrational wavefunctions of the ground state are calculated on the basis of  $r''$ ,  $\hbar\omega''$ , and  $x\hbar\omega''$ ; these values are taken from literature [19]. The vibrational wavefunctions of the core-excited states are calculated by varying of the fit parameters  $r'$ ,  $\hbar\omega'$ , and  $x\hbar\omega'$ .

Two different algorithms were used to calculate the vibrational wavefunctions and the intensity distributions of the vibrational substates of the core-excited state: The Franck-Condon analyses of the Rydberg states in CO and NO are performed with the simple and fast algorithm of Hutchisson [20,21]; however, it considers only the terms  $(R-r)^2$  and  $(R-r)^3$  in the development of the potential energy surface  $V(R)$ , with  $R$  being the internuclear distance; it underestimates the intensity of the higher vibrational substates [22]. It turned out that this approximation was not sufficient to describe the O  $1s \rightarrow \pi^*$  excitations, which reveal a large number of vibrational substates. The latter states were fitted with an algorithm that is based on the publications of Halman and Laulich [23] and Ory et al. [24]; it uses the complete Morse potential to calculate the vibrational substates and leads to highly improved fit results.



### III. CO O 1s EXCITATIONS

#### A. Valence Region

The photoionization spectrum of the O  $1s^{-1}\pi^*$  excitation in CO, with completely resolved vibrational fine structure, is shown in Fig. 1. This improved spectrum allowed, for the first time, a Franck-Condon analysis of this excitation, resulting in an increase of the equilibrium distance from  $r''=1.1283$  Å in the electronic ground state to  $r'=1.291(3)$  Å in the core-excited state. In addition, a decrease of the vibrational energy from  $\hbar\omega''=269.025$  meV in the ground state to  $\hbar\omega'=166(1)$  meV in the core-excited state as well as a slight increase of the anharmonicity from  $x\hbar\omega''=1.647$  meV to  $x\hbar\omega'=1.8(1)$  meV were derived. We obtain a decrease of the dissociation energy from  $D_e''=11.0$  eV in the ground state to  $D_e'=3.9$  eV in the core-excited state according to  $D_e=(\hbar\omega)^2/4x\hbar\omega$ . The resulting parameters of the core-excited state agree fairly well with calculations of Correia et al. [25], with  $\hbar\omega'=176.8$  meV,  $x\hbar\omega'=2.3$  meV, and  $r'=1.280$  Å. The parameters agree also very well with the values of the Z+1 molecule CF, with  $\hbar\omega'=162$  meV,  $x\hbar\omega'=1.4$  meV, and  $r'=1.2718$  Å [19]. The increase of the equilibrium distance as well as the decrease of the vibrational energy and the dissociation energy upon excitation can readily be understood on the basis of an excitation into an antibonding  $\pi^*$  orbital. In addition to the above results, the lifetime width of the O  $1s^{-1}\pi^*$  excitation was determined to be  $143(5)$  meV.

#### B. Rydberg Region

The Rydberg region of the O 1s core-excitation spectrum of CO is shown in Fig. 2 together with the assignment. For the two lowest Rydberg states at  $h\nu\cong 539$  (O  $1s^{-1}3s\sigma$ ) and 540 eV (O  $1s^{-1}3p\pi$ ), Franck-Condon analyses has been performed, resulting in different values for the equilibrium distance (see below). The equilibrium distance of the O  $1s^{-1}3p\pi$  state was transferred to the higher Rydberg states to describe their lineshapes in the fit analysis of the complete spectrum. The result of this fit analysis is presented by the solid line

through the data points of Fig. 2. The derived energy positions of the resonances, together with the quantum defects  $\delta$  and the assignment, are given in Table I. For comparison, the energy positions and quantum defects calculated by Yi Zhang et al. [26] are also given. By presupposing the  $n\pi$  states to be more intense than the  $n\sigma$  states, which is in agreement with calculations by Yi Zhang et al. [26] and Padial et al. [27], there remains only one small uncertainty in the assignment. The assumption of constant quantum defects for the Rydberg series leads to the assignment  $O\ 1s^{-1}4s\sigma$  for the resonance at 540.980 eV with a quantum defect  $\delta=1.05$  ( $\delta=1.06$  for  $O\ 1s^{-1}3s\sigma$ ). As a consequence, the resonance at 540.777 eV has to be assigned to  $O\ 1s^{-1}3d\sigma$ . However, calculations of Yi Zhang et al. [26] predict an increase of the quantum defect for the s-series from  $\delta=1.07$  for  $O\ 1s^{-1}3s\sigma$  to  $\delta=1.18$  for  $O\ 1s^{-1}4s\sigma$  state (see also Table I). A similar increase of the quantum defect was calculated for NO by Kosugi et al. [16] in agreement with the experimental findings of Remmers et al. [12] and the results of the present work (see below). On the basis of the given arguments, the inverted assignment, i.e.  $O\ 1s^{-1}4s\sigma$  for the resonance at 540.777 eV and  $O\ 1s^{-1}3d\sigma$  for the resonance at 540.880 eV, is preferred. This does not influence the assignment of the higher Rydberg states since the splitting of the  $nd\sigma$  and  $(n-1)s\sigma$  states cannot be resolved for  $n\geq 5$ .

The assignment presented leads to good agreement with the energies and intensities of theoretical results given in Ref. [26]. The main difference between experiment and theory is an inversion of the orbital order of the  $nd$  states due to the small  $nd\sigma$ – $nd\pi$  splitting:  $3d\sigma-3d\pi(\text{exp}) = 69\ \text{meV}$  and  $3d\sigma-3d\pi(\text{th}) = -27\ \text{meV}$ .

However, the assignment obtained in this work differs from the results given by Domke et al. [8]. In the latter work, it was assumed that the  $n\pi$  series was the most intense one. This is in contradiction to the latest theoretical results [26] and leads to the doubtful intensity ratio of the  $O\ 1s^{-1}3p\pi$  and  $O\ 1s^{-1}4p\pi$  states; therefore, their assignment has to be rejected.

The results of the Franck-Condon analysis of the  $O\ 1s^{-1}3s\sigma$  and  $O\ 1s^{-1}3p\pi$  states are summarized in Table II. For comparison, the results of Domke et al. [8] and the values of the  $Z+1$  molecule CF are also given, showing good agreement. From the different intensity distribution for the vibrational substates of these states, as seen in Fig. 2, we estimate from

Franck-Condon analysis that the change of the equilibrium distances is larger by approximately 25% for the  $O 1s^{-1}3s\sigma$  state. We conclude that the lowest Rydberg state is a mixed state, i.e., a Rydberg state with some valence character. Valence contributions for the lowest Rydberg state were observed previously in  $SiF_4$  [28] and  $SiH_4/SiD_4$  [29].

Although the equilibrium distances in the  $O 1s^{-1}3s\sigma$  and  $O 1s^{-1}3p\pi$  states clearly differ, differences in the vibrational energy were not observed. This is in contradiction to the expectation that a larger change in the equilibrium distance upon excitation results in a larger change of the vibrational energy. The deviation from the expected results can be explained with the calculations of Yi Zhang et al. [26]; they predict a small contribution of the  $O 1s^{-1}3p\sigma$  state to the spectrum, which may influence the energy region between the  $v' = 0$  and  $v' = 1$  vibrational substates of the  $O 1s^{-1}3p\pi$  state. In accordance with its small predicted intensity, the  $O 1s^{-1}3p\sigma$  state is not resolved; however, its possible presence in the spectrum may cause a slightly incorrect value for the vibrational energy of the  $O 1s^{-1}3p\pi$  state.

An increase of the equilibrium distance and a decrease of the vibrational energy is found, in agreement with Domke et al. [8] and Kempgens et al. [17] for the  $O 1s^{-1}$  Rydberg states in CO. A lifetime width for the Rydberg states of 135(8) meV was observed.

#### IV. NO $O 1s$ EXCITATIONS

##### A. Open-Shell Molecules

NO has one additional electron compared to CO, which is located in the antibonding  $\pi^*$  orbital. Due to the single occupancy of the  $\pi^*$  orbital in its electronic ground state, NO is an open-shell molecule. Upon core excitation, the single  $\pi^*$  electron can interact with the core hole and the excited electron, leading to new effects as compared to CO. The final-state symmetries resulting from the interaction of the electrons in the partially filled orbitals are summarized in Table III. Note that a pure molecular assignment of the orbitals

is used in Table III, i.e., the O 1s ( $\pi^*$ ) orbital is described with  $1\sigma$  ( $2\pi$ ). Certain states can be observed on the basis of spin-selection rules: the doublet states for photoabsorption ( $\Delta S=0$ ), and the singlet and triplet states for photoemission ( $\Delta S=\pm 1/2$ ). Thus, e.g., three out of the four O  $1s^2\pi^* \rightarrow O 1s^1(\pi^*)^2$  excitations and two O  $1s^{-1}$  ionization thresholds are allowed and expected to contribute to the spectrum. A more detailed discussion of the interaction between the electrons in the partially filled orbitals and its influence on the spectral features is given by Wight and Brion [15].

### B. Valence Region

Figure 3 shows the O  $1s^2\pi^* \rightarrow O 1s(\pi^*)^2$  excitations in NO, including the three different electronic states due to the interaction between the core hole and the two  $\pi^*$  electrons. The assignment of the states is adopted from the calculations performed by Kosugi et al. [16], Wight and Brion [15], and Fink [30]; all authors agree with the sequence  $^2\Sigma^-$ ,  $^2\Delta$ ,  $^2\Sigma^+$ . Contrary to previous high-resolution photoabsorption measurements [12], the vibrational fine-structures of the states are completely resolved and allow a more reliable Franck-Condon analysis. The results of this analysis are represented by the solid line through the data points and the three subspectra. The results obtained for the equilibrium distances  $r'$ , the vibrational energies  $\hbar\omega'$ , the energies E, the intensity ratios (normalized to the  $^2\Sigma^+$  state), and the lifetime width  $\Gamma$  for the core-excited states are summarized in Table IV. For comparison, the results of the Franck-Condon analysis performed by Remmers et al. [12], the values of the Z+1 molecule NF, and the theoretical results obtained by Fink [30] are also given. It can be seen that for all three states, the vibrational energies decrease from  $\hbar\omega''=235.9$  meV to  $\hbar\omega' \cong 150$  meV and the equilibrium distances increase from  $r''=1.151$  Å to  $r' \cong 1.32$  Å. Again, this can be understood by excitation into an antibonding orbital. A more detailed consideration of the O 1s  $\rightarrow \pi^*$  excitations shows that the equilibrium distance of the  $^2\Sigma^-$  state is larger by  $\cong 30$  mÅ and the vibrational energy smaller by  $\cong 20$  meV than for the  $^2\Delta$  and  $^2\Sigma^+$  states.

The results obtained from the Franck-Condon analysis differ considerably from the values given by Remmers et al. [12]. This is especially valid for the vibrational energy of the  ${}^2\Sigma^+$  state. The differences can be explained by the fact that a distinct vibrational fine structure is missing in the spectrum of Remmers et al., and that they used the algorithm of Hutchisson [20,21], which is not appropriate to describe transitions with a large number of vibrational substates. Good agreement of the results of the present work with the values for the Z+1 molecule is found. This is especially valid for the  ${}^2\Delta$  and  ${}^2\Sigma^+$  states; however, the differences for the  ${}^2\Sigma^-$  state are larger.

The experimental results are also compared with the theoretical calculation of Fink [30]. The experimental vibrational energies were found to be  $\cong 5$  meV smaller and the equilibrium distances to be slightly larger than the calculated values; however, Fink expected this tendency due to his calculation. By performing the Franck-Condon analysis, the values of the anharmonicity  $x\hbar\omega'$  were kept constant to the values calculated by Fink, with  $x\hbar\omega'({}^2\Sigma^-)=1.2$  meV,  $x\hbar\omega'({}^2\Delta)=1.1$  meV, and  $x\hbar\omega'({}^2\Sigma^+)=1.2$  meV; the good fit result of the spectrum with these values indicates that the experimental values should be very similar to the theoretical values. The experimental energies are  $\cong 200$  meV larger than the calculated values, and the experimental and theoretical intensity distribution (normalized to the  ${}^2\Sigma^+$  state) of the three substates are similar. The experimental and theoretical lifetime widths agree within the errors. Altogether, an excellent agreement between the experimental results and the recent calculations by Fink [30] was found.

### C. Rydberg Region

The Rydberg region of NO below the O 1s ionization threshold is shown in Fig. 4. The vertical-bar diagrams above the spectrum represent the assignments of the Rydberg states converging towards the O 1s ionization thresholds  ${}^3\Pi$  and  ${}^1\Pi$ . This splitting of the thresholds is due to an interaction between the O 1s core hole and the  $\pi^*$  electron. Three Rydberg series with quantum defects of  $\delta=1.10$  (ns Rydberg series),  $\delta=0.75$  (np), and  $\delta=0.00$  (nd) are

identified. The energies and quantum defects obtained from the fit analysis are summarized in Table V. The assignment given in this work is similar to the results of Remmers et al. [12], however, some previously unobserved resonances were resolved. The improved spectrum allowed a determination of the  $^3\Pi - ^1\Pi$  splitting of the O 1s ionization threshold to  $\Delta I_p = I_p(^3\Pi) - I_p(^1\Pi) = 456(15)$  meV. This value is more precise and significantly smaller than previous results of 510 meV [12] and 550 meV [31].

The vertical bars diagram in Fig. 4 represent the intensity of the weakly overlapping Rydberg states. The thin (bold) bars represent the intensity of the states converging towards the  $^3\Pi$  ( $^1\Pi$ ) ionization threshold. For the triplet and singlet core-ionized states, an intensity ratio of 3:1 is expected; this also holds for the higher Rydberg states. Contrary to this, the intensity ratio of the two components of the O  $1s^{-1}3s\sigma$  state exhibit an intensity ratio of  $\cong 15.5:1$ .

For the well-resolved and intense Rydberg states a lifetime width of  $\Gamma=150(10)$  meV was obtained. This value was transferred to the overlapping O  $1s^{-1}3p$  states and made it necessary to describe this part of the spectrum with 7 different resonances. This large number of 3p states is due to the interaction of the  $nL\pi$  Rydberg states with the  $\pi^*$  electron and the O 1s core hole and will be discussed in more detail.

By considering the 3p states in a simple way, a symmetry splitting into  $3p\sigma$  and  $3p\pi$  as well as the splitting of the ionization threshold lead to four different final states; that is not appropriate to describe the measured spectrum and demonstrates the presence of a more complicated coupling scheme in a convincing way. The coupling scheme given in Table III results in nine different final states for the O  $1s^{-1}3p\pi$  excitations. The six final states with  $^2\Sigma^-$ ,  $^2\Delta$ , and  $^2\Sigma^+$  symmetry are allowed on the basis of selection rules. Therefore, the seven observed structures can only be explained with a symmetry splitting of the 3p states into a  $p\sigma$  and a  $p\pi$  component as well as with a coupling of the  $3p\pi$  electron with the electrons in the  $\pi^*$  and O 1s orbitals. An exact assignment of the 3p region on the basis of the present data is not possible. We, therefore, want to give some arguments and a preliminary assignment.

The observed splitting of  $\cong 100$  meV between the different O  $1s^{-1}3p$  states is smaller than the  ${}^3\Pi-{}^1\Pi$  splitting of the ionization thresholds of 456(15) meV. It can be, therefore, concluded that the interaction between the core-hole and the  $\pi^*$  electron is stronger than the interaction between the 3p electron and the core hole or the  $\pi^*$  electron. This fact is considered in the assignment of the O  $1s^{-1}3p$  excitations and, in the first step, the O 1s core hole and the  $\pi^*$  electron are coupled to the O  $1s^{-1}\pi^*({}^3,{}^1\Pi)$  core-ionized states. In a second step, the Rydberg electron is coupled with the O  $1s^{-1}\pi^*({}^3,{}^1\Pi)$  ionic states, i.e., we consider the influence of the 3p electrons as a small perturbation. This leads to the O  $1s^{-1}\pi^*({}^3,{}^1\Pi)3p\sigma({}^2\Pi)$  and O  $1s^{-1}\pi^*({}^3,{}^1\Pi)3p\pi({}^2\Sigma^-, {}^2\Delta, {}^2\Sigma^+)$  final states that are allowed on the basis of the selection rules for the spin component of the wavefunction. In this way the first (last) three observed resonances can be assigned as states converging towards the  ${}^3\Pi$  ( ${}^1\Pi$ ) ionization threshold. The peak in the middle ( $h\nu = 540.933$  eV) cannot clearly be assigned to belong to one specific ionization threshold.

Assuming the interaction of the  $3p\pi$  electron with the O  $1s^{-1}\pi^*({}^3,{}^1\Pi)$  configuration to be small is in full agreement with calculations by Kosugi et al. [16]. These authors calculated the splitting between the lowest and highest O  $1s^{-1}\pi^*({}^3\Pi)3p\pi$  and O  $1s^{-1}\pi^*({}^1\Pi)3p\pi$  state to be 220 meV and 100 meV, respectively. Due to the distinctly smaller splitting of the O  $1s^{-1}\pi^*({}^1\Pi)3p\pi$  states, it can be expected that the three components are not completely resolved. The symmetry-resolved photoabsorption spectra of Kosugi et al. [16] allow the  $n\pi$  and  $n\pi^*$  states to be distinguished and show that the  $3p\pi$  contributions to the spectrum are more intense than the  $3p\sigma$  contributions in agreement with their calculations.

We suggest the following preliminary sequence for the 3p states: The first three states are assigned to O  $1s^{-1}\pi^*({}^3\Pi)3p\pi$ , the fourth state to O  $1s^{-1}\pi^*({}^3\Pi)3p\sigma$ , the fifth and sixth state to O  $1s^{-1}\pi^*({}^1\Pi)3p\pi$ , and the seventh state to O  $1s^{-1}\pi^*({}^1\Pi)3p\sigma$ . This assignment results in an intensity ratio for the O  $1s^{-1}\pi^*({}^3\Pi)3p\pi$  states to the O  $1s^{-1}\pi^*({}^1\Pi)3p\pi$  states of 5.5:1, which differs distinctly from the expected value of 3:1. The mean energy of the  $3p\pi$  states is  $\cong 200$  meV lower than of the  $3p\sigma$  states; this splitting is twice the calculated splitting of the  $3p\sigma/\pi$  splitting in CO below the O  $1s^{-1}$  ionization threshold [26].

For a more reliable assignment of the  $O 1s^{-1}3p$  region of the spectrum further measurements are necessary; e.g., by using high-resolution symmetry-resolved photoionization spectroscopy, which can clearly distinguish between the  $O 1s^{-1}3p\sigma$  and  $O 1s^{-1}3p\pi$  states. In principle, this splitting of the  $O 1s^{-1}nl\pi$  excitations into different states is also present for the higher Rydberg states. However, according to the increase of the distance between the  $O 1s^{-1}\pi^*(^3,^1\Pi)$  configuration and the  $nl\pi$  electron with increasing  $n$ , this splitting becomes smaller and cannot be resolved for the higher Rydberg states.

The vibrational fine structure of the  $O 1s^{-1}(^3\Pi)3s$  Rydberg state is clearly resolved for the first time, and a Franck-Condon analysis is performed, resulting in a decrease of the vibrational energy from  $\hbar\omega''=235.9$  meV to  $\hbar\omega'=218(2)$  meV, and an increase of the equilibrium distances from  $r''=1.151$  Å to  $r'=1.190(2)$  Å. The values obtained agree with those of the  $Z+1$  molecule  $NF^+$  with  $\hbar\omega=195(5)$  meV and  $r=1.180(6)$  Å [32]. This experimental result on the  $O 1s^{-1}(^3\Pi)3s$  state in NO is similar to the results in CO at the  $O 1s$  ionization threshold. It is in agreement with the conclusion of Müller and Ågren [6] and supports the idea of a weakening of the molecular bond upon  $O 1s^{-1}$  core-excitations into Rydberg states or core-ionization. This effect can be understood for CO and NO in a simple way using the  $Z+1$  approximation and it will be explained on the basis of the  $C 1s^{-1}$  and  $O 1s^{-1}$  core-ionization process in CO: After a  $C 1s^{-1}$  ionization, CO can be compared with the  $Z+1$  molecule  $NO^+$ . In  $NO^+$ , the difference of the electronegativity of the atoms is smaller than in CO. However, an  $O 1s^{-1}$  ionization of CO leads to the  $Z+1$  molecule  $CF^+$  and a larger difference of the electronegativity of the atoms. This results in a stronger polarization of the valence shell towards the  $O 1s^{-1}$  or F atom and a weakening of the multiple bond structure.

For the higher Rydberg states, no vibrational substates were found. This is probably due to the strong overlap of the higher Rydberg states and may be reinforced by the possibility that vibrational substates for the higher Rydberg states are smaller than for the  $O 1s^{-1}(^3\Pi)3s$  Rydberg state. This possible effect can be understood by assuming the  $O 1s^{-1}(^3\Pi)3s$  Rydberg excitation to be a mixed state; it was observed for the  $O 1s^{-1}3s\sigma$  and  $O 1s^{-1}3s\pi$  Rydberg states in CO (see above).



## V. CONCLUSIONS

The significantly improved energy resolution of the present work allows experimental observation of the complete vibrational fine-structure, and thus Franck-Condon analyses, resulting in detailed information on the potential-energy surfaces, i.e., on the vibrational energies and equilibrium distances of molecules after O 1s core excitations. The vibrational fine-structure of the O 1s  $\rightarrow \pi^*$  excitations in CO and NO are completely resolved, allowing Franck-Condon analyses. The values obtained by these analyses are compared with calculations and reveal good agreement between experiment and theory. For the O 1s<sup>-1</sup>Ryd excitations a new assignment is given. The O 1s<sup>-1</sup>(<sup>3</sup>II)3s Rydberg state in NO is shown to have a lower vibrational energy and a larger equilibrium distance than the electronic ground state; this supports the idea of a weakening of the molecular bond upon O 1s<sup>-1</sup> excitations.

### Acknowledgement:

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Science, Materials Science Division, of the Department of Energy under Contract No. DE-AC03-76SF00098. The work in Berlin was supported by the Bundesminister für Bildung, Wissenschaft, Forschung und Technologie, project No. 05-SR8KE1-1, and the Deutsche Forschungsgemeinschaft, project Do-561/1-3. The authors thank T. X. Carroll and T. D. Thomas for providing the computer code that was used to perform Franck-Condon analyses of the O 1s  $\rightarrow \pi^*$  excitations in CO and NO.

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## FIGURES

FIG. 1.  $O\ 1s^{-1}\pi^*$  excitation in CO. The solid line through the data points represents the results of a Franck-Condon analysis.

FIG. 2. Rydberg region of CO below the O 1s ionization threshold. The solid line through the data points represents the results of a fit analysis. The subspectra below the spectrum represent the results of a Franck-Condon analysis of the Rydberg states  $O\ 1s^{-1}3s\sigma$  and  $O\ 1s^{-1}3p\pi$ . The assignment is given by the vertical bar diagrams above the spectrum. The first bar for each resonance represents the  $v''=0 \rightarrow v'=0$  excitation, while the other bars represent higher vibrational substates.

FIG. 3. The  $O\ 1s^{-1}\pi^*$  excitation in NO. The solid line through the data points represents the result of a Franck-Condon analysis. The three subspectra describe the three different electronic states.

FIG. 4. The Rydberg region of NO below the O 1s ionization threshold. The solid line through the data points represents the result of a fit analysis. The subspectrum below the spectrum describes the result of a Franck-Condon analysis of the  $O\ 1s^{-1}3s\sigma$  Rydberg state. The assignments are given by the vertical bar diagrams above the spectrum. The first bar for the 3s resonance represents the  $v''=0 \rightarrow v'=0$  excitation, while the other bars describe higher vibrational substates. The thin (bold) vertical bars below the spectrum represent the intensities of the weakly overlapping Rydberg states converging toward the  ${}^3\Pi$  ( ${}^1\Pi$ ) ionization threshold.

## TABLES

TABLE I. The energies  $E$  and quantum defects  $\delta$  of the Rydberg states in CO below the O 1s ionization threshold as obtained from the fit analysis. The relative errors for the energies are estimated to  $\pm 10$  meV. For comparison, the theoretical results of Ref. [26] are also given. For the values in brackets see text.

	this work		Ref. [26]	
	E (eV)	$\delta$	E (eV)	$\delta$
3s $\sigma$	538.912	1.06	538.910	1.07
4s $\sigma$ (3d $\sigma$ )	540.777	1.22 (0.22)	541.101	-0.07
5s $\sigma$	541.547	1.30		
6s $\sigma$	541.961	1.34		
3p $\sigma$			540.175	0.61
3p $\pi$	539.906	0.73	540.012	0.68
4p $\pi$	541.279	0.72	541.318	0.67
5p $\pi$	541.819	0.67		
6p $\pi$	542.009	0.95		
3d $\sigma$ (4s $\sigma$ )	540.980	0.05 (1.05)	540.829	1.18
4d $\sigma$	541.547	0.30	541.727	-0.09
5d $\sigma$	541.961	0.34		
3d $\pi$	541.049	-0.02	541.074	-0.04
4d $\pi$	541.694	0.00	541.714	-0.05
5d $\pi$	541.976	0.10		
6d $\pi$	542.170	-0.04		
7d $\pi$	542.266	-0.01		
8d $\pi$	542.329	0.02		
I <sub>p</sub>	542.543			

TABLE II. The results of the Franck-Condon analyses for the  $O 1s^{-1}3s\sigma$  and  $O 1s^{-1}3p\pi$  states in CO. For comparison, the results of Domke et al. [8] and the values for the  $Z+1$  molecule CF [19] are also given. The vibrational energies of the molecule CF are multiplied with  $\sqrt{1.0725}$  according to the different reduced masses.

ground state		this work		Domke et al.		CF	
$r''$	$\hbar\omega''$	$r'$	$\hbar\omega'$	$r'$	$\hbar\omega'$	$r'$	$\hbar\omega'$
(Å)	(meV)	(Å)	(meV)	(Å)	(meV)	(Å)	(meV)
1.12832	269.025						
$3s\sigma$		1.169(2)	223(3)	1.167(9)	227(8)	1.154	229
$3p\pi$		1.158(2)	223(3)	1.159(9)	224(9)	1.151	232

TABLE III. Electronic configurations and molecular states of NO in the electronic ground state, in  $O 1s^{-1} \equiv 1\sigma^{-1}$  core-excited states, and  $O 1s^{-1}$  core ionized states (adapted from Ref. [15]). The numbers in brackets refer to the numbers of states of this symmetry.  $n\sigma$  and  $n\pi$  denote Rydberg orbitals with  $\sigma$  and  $\pi$  symmetry, respectively.

	Electronic configuration								Molecular state	
	$1\sigma$	$2\sigma$	$3\sigma$	$4\sigma$	$1\pi$	$5\sigma$	$2\pi$	$n\sigma$		$n\pi$
NO	2	2	2	2	4	2	1			$X^2\Pi$
$NO^{K*}$	1	2	2	2	4	2	2			$^4\Sigma^-, ^2\Sigma^-, ^2\Delta, ^2\Sigma^+$
$NO^{K*}$	1	2	2	2	4	2	1	1		$^4\Pi, ^2\Pi, ^2\Pi$
$NO^{K*}$	1	2	2	2	4	2	1		1	$^4\Sigma^-, ^4\Delta, ^4\Sigma^+, ^2\Sigma^-(2), ^2\Delta(2), ^2\Sigma^+(2)$
$NO^{K+}$	1	2	2	2	4	2	1			$^3\Pi, ^1\Pi$

TABLE IV. Results of the Franck-Condon analysis of the  $O 1s^{-1}\pi^{*2}$  excitations in NO: Given are the vibrational energies  $\hbar\omega$ , the equilibrium distances  $r$ , the energies  $E$ , the normalized intensities with respect to the  ${}^2\Sigma^+$  state  $f/f({}^2\Sigma^+)$ , and the lifetime widths  $\Gamma$  for the electronic ground state (g.s.) and the core-excited states  ${}^2\Sigma^-$ ,  ${}^2\Delta$ , and  ${}^2\Sigma^+$ . For comparison, the results of Remmers et al. [12], the values for the Z+1 molecule NF, and the theoretical calculation of Fink [30] are also given. The vibrational energies for the states in the Z+1 molecule NF are multiplied with  $\sqrt{1.0795}$  according to the different reduced masses.

		this work	Remmers et al.	NF	Fink
$\hbar\omega$ (meV):	g.s.	235.0			
	${}^2\Sigma^-$	137(3)	157(15)	147	139
	${}^2\Delta$	154(3)	168(15)	152	159
	${}^2\Sigma^+$	157(3)	229(20)	154	162
$r$ (Å):	g.s.	1.151			
	${}^2\Sigma^-$	1.348(3)	1.307(7)	1.317	1.339
	${}^2\Delta$	1.311(3)	1.283(9)	1.308	1.295
	${}^2\Sigma^+$	1.306(3)	1.267(8)	1.300	1.290
$E$ (eV):	${}^2\Sigma^-$	531.48(1)	531.46(3)		531.30
	${}^2\Delta$	532.60(1)	532.36(3)		532.30
	${}^2\Sigma^+$	533.52(1)	533.13(4)		533.38
$f/f({}^2\Sigma^+)$ :	${}^2\Sigma^-$	2.92	1.04		3.52
	${}^2\Delta$	1.95	1.14		2.13
	${}^2\Sigma^+$	1.00	1.00		1.00
$\Gamma$ (meV):	${}^2\Sigma^-$	170(10)	$\cong 200$		174
	${}^2\Delta$	170(10)	$\cong 200$		175
	${}^2\Sigma^+$	170(10)	$\cong 350$		173



TABLE V. The energies  $E$  and quantum defects  $\delta$  of the Rydberg states in NO below the O 1s ionization threshold as obtained from the fit analysis. The relative errors for the energies are estimated to  $\pm 10$  meV.

	$^3\Pi$		$^1\Pi$	
	E (eV)	$\delta$	E (eV)	$\delta$
3s $\sigma$	539.540	1.10	539.930	1.11
4s $\sigma$	541.551	1.21		
3p $\pi$	540.463	0.81		
3p $\pi$	540.624	0.74	540.981	0.78
3p $\pi$	540.711	0.70	541.095	0.74
3p $\sigma$	540.933	0.65	541.220	0.68
4p $\pi$	542.000	0.76	542.455	0.76
5p $\pi$	542.539	0.76	542.994	0.76
6p $\pi$	542.800	0.76	543.255	0.76
5p $\pi$	542.946	0.76	543.501	0.76
6p $\pi$	543.035	0.77	543.490	0.78
3d	541.788	-0.01	542.243	0.00
4d	542.447	0.00	542.902	0.00
5d	542.752	0.00	543.207	0.00
6d	542.918	0.00	543.373	0.00
7d	543.018	0.00	543.473	0.00
$I_p$	543.295		543.751	

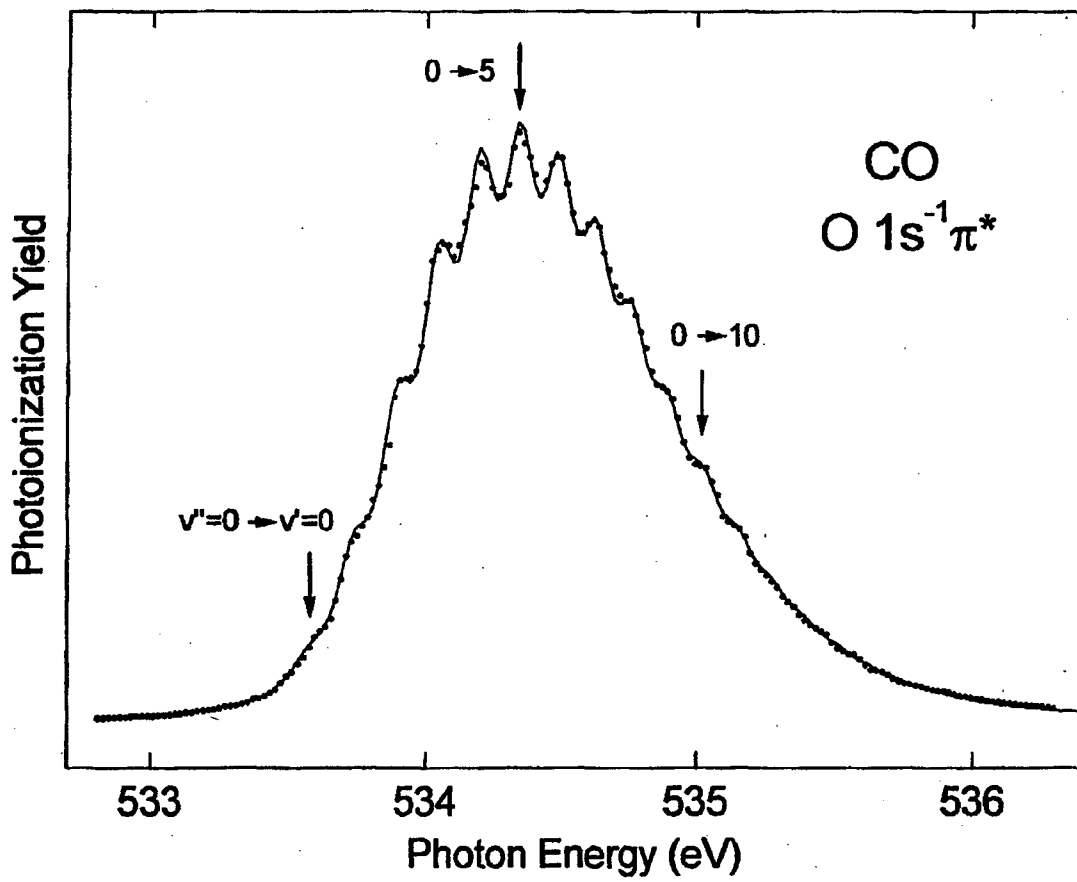


Fig. 1

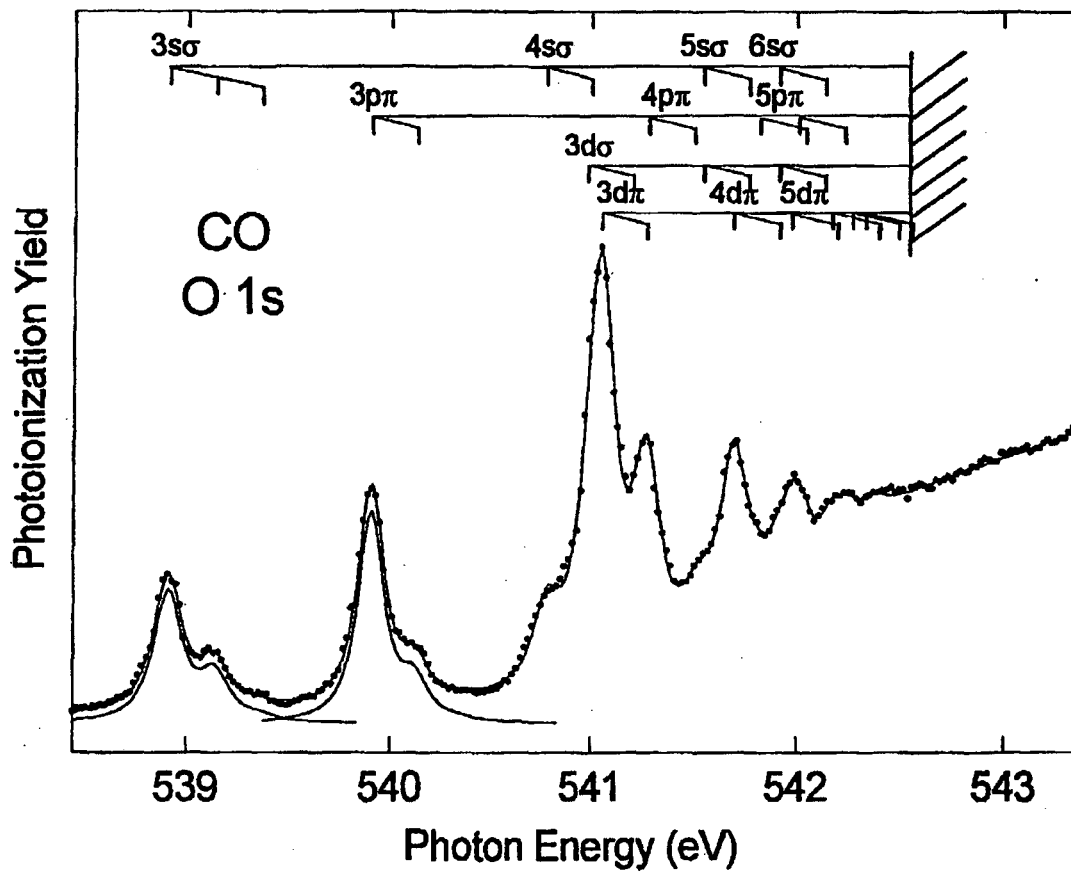


Fig. 2

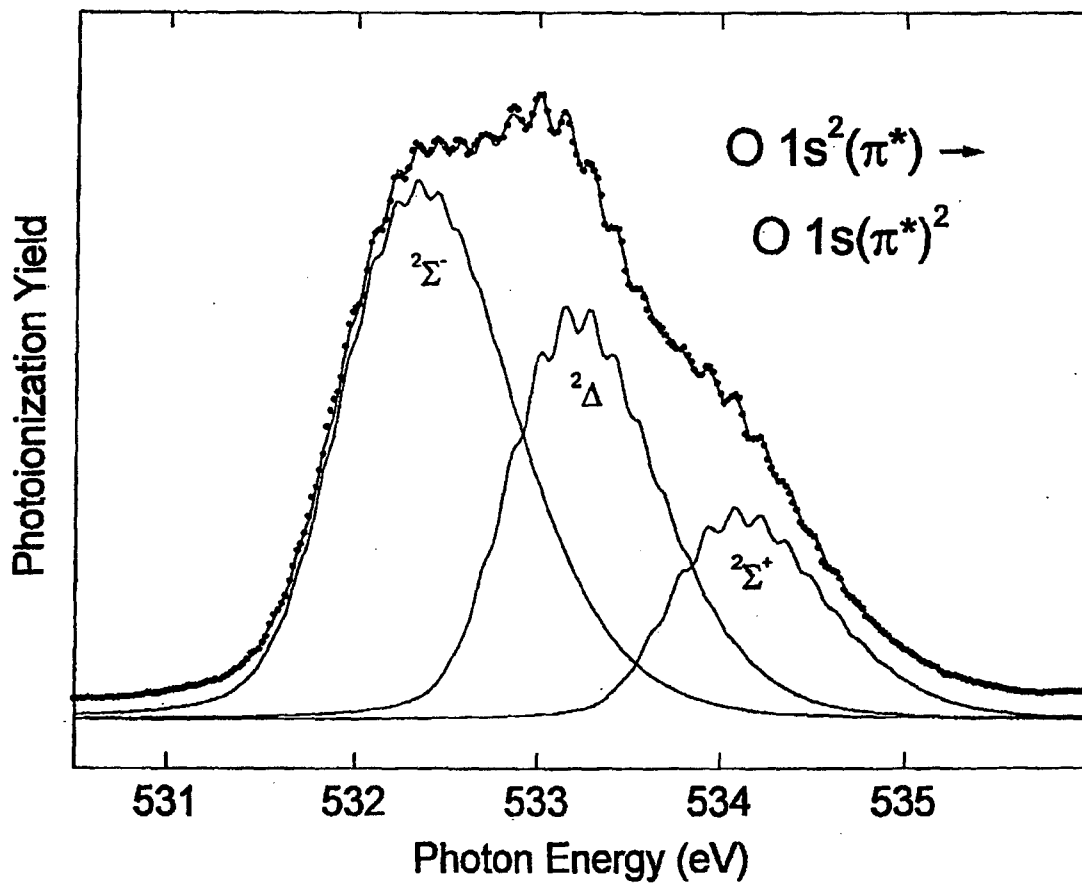


Fig. 3

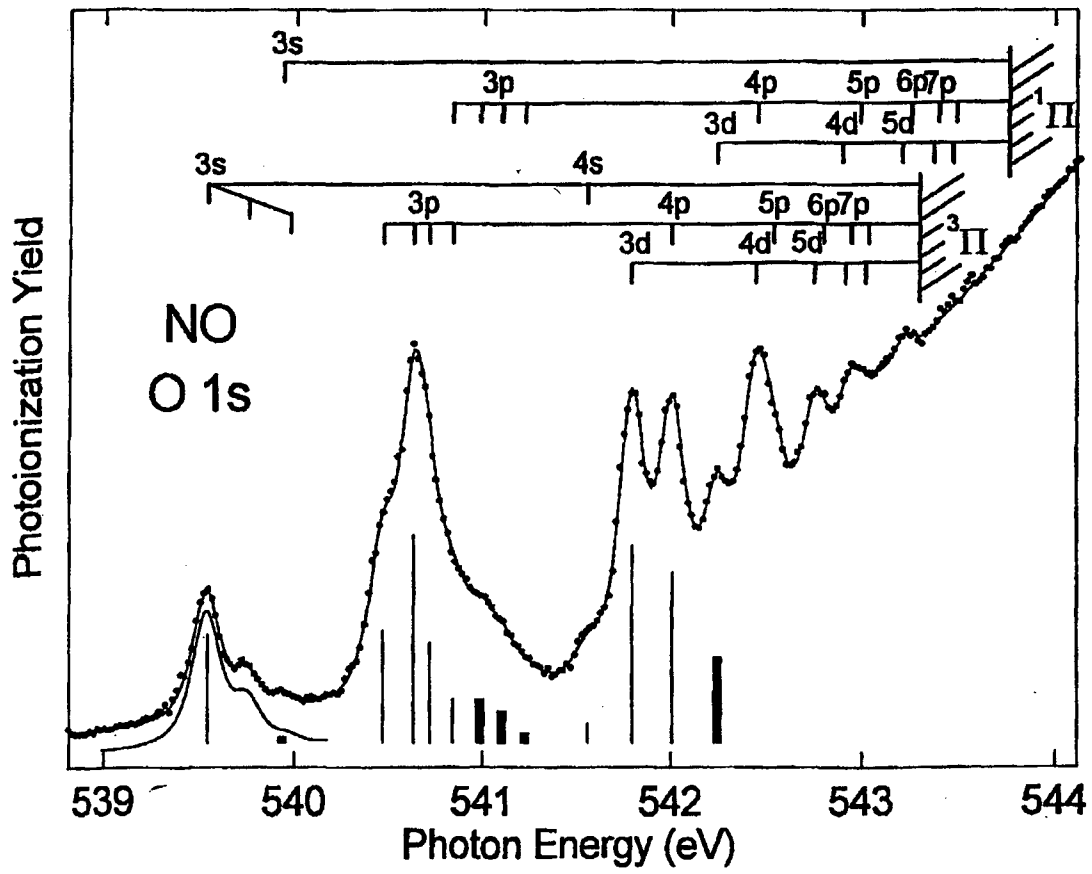


Fig. 4

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