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A theoretical study of core excitation spectra of NO molecule

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Abstract. The N 1s and O 1s cores to antibonding $2\pi^*$ transitions for the NO molecule have been investigated using a multiconfiguration self-consistent field approach. The core excitation spectra have been simulated using a Lorentzian band shape function with the full width at half maximum obtained from a time-dependent formulation. The calculations confirm the different split schemes for the N 1s and O 1s dipole-allowed core-excited states. Spectral characteristics related to nitrogen and oxygen excitation have been discussed in detail.

1. Introduction

Recent developments in inner-shell excitation spectroscopy have yielded detailed studies of the electronic structure of open-shell molecules such as NO. Inner-shell excitation spectroscopy is also a prerequisite to the understanding of other molecular processes such as photodissociation, photofragmentation, electronic or radiative de-excitation processes [1]. Due to the localized nature of the highly excited core hole states, spectroscopy of the inner shells presents unique regimes of various interactions and couplings. Sophisticated theoretical calculations are required for the interpretation.

Core excited states of open-shell molecules can have complex multiplet structures with nearly degenerate energies. High-resolution spectroscopy is needed to study the electronic structures. The first high-resolution N K-shell excitation spectrum of NO was given by Tronc *et al* [2] using inner-shell electron-energy-loss spectroscopy (EELS). Their study left open some questions of the NO K-shell excitation spectrum, such as the energy ordering of the N 1s core excited states.

In recent years with the development of high-resolution experimental techniques, excitation to the partially filled π^* orbital of NO has received a great deal of experimental attention [3]. For example, the N K- and O K-edge spectra of NO were studied by several groups. Kosugi *et al* [4] used symmetry-resolved ion-yield spectroscopy and high-resolution electron-yield spectroscopy; Ma *et al* [1, N 1s spectrum] and Remmers *et al* [5] employed photon-absorption spectroscopy with synchrotron radiation sources; Carroll *et al* [3] used de-excitation electron spectroscopy and most recently Erman *et al* [6] employed high-resolution mass selective ion-yield measurement. However, due to the relatively poor signal-to-noise ratio at higher energy losses [4], some experiments reported only the N K-shell spectrum [2, 6] of NO or only the strong (but incomplete series) transitions [1, 4]. Furthermore, in the analysis of vibrationally resolved spectrum, a fitting procedure such as least-squares fit is used to analyse experimental data under certain assumptions such as the energy ordering of the states involved. While researchers have now reached an agreement with the energy

ordering for N 1s and O 1s excited states of NO, the spectral intensity patterns yielded from various experimental analyses are very different for the same spectrum, especially for the O 1s case.

Theoretical studies to aid the quantitative interpretation of the core excitation spectra of NO are limited. Tronc *et al* [2] used an equivalent-core model in the analysis while Kosugi *et al* [4] undertook a valence configuration interaction (CI) study within a frozen orbital framework. A more complete *ab initio* multiconfiguration self-consistent field (MCSCF) treatment of the problem is reported in this paper, in order to aid the understanding of both the energy and intensity characteristics of the states manifest in the spectral profile.

2. Computational details

The present calculations were carried out employing the following basis functions. The primitive basis functions from Huzinaga *et al* [7] were contracted to [4111111/31111] as suggested by Kosugi *et al* [4]. The innermost 2s exponents of N and O were changed to 1.485 88 and 2.003 92, respectively, in order to accommodate the calculations for core excited states. The basis set was augmented with two d polarization functions: $\zeta_d = 2.704$ and 0.535 for oxygen and $\zeta_d = 1.986$ and 0.412 for nitrogen [4]. Hence, the basis set was constructed to give {10s7p2d}/[7s5p2d] for both the nitrogen and oxygen atoms. The 86 primitive basis functions were contracted to 64 basis functions. The calculated Hartree–Fock (HF) energy of the ground state of NO with this basis set was $-128.969\,292\,90E_h$.

The active CI space was constructed from configurations which distribute electrons in the five occupied σ and the first two occupied π plus the virtual 6σ and 3π orbitals. The core excited states were calculated using the restriction of configurations with singly occupied core orbitals. The calculations have been performed at the level of multiconfiguration self-consistent field (SCF) [9, 8]. The initial guesses of the direct MCSCF calculations for the core excited states of NO were determined from appropriate preceding SCF calculations.

Calculations of vertical transition energies were performed at the experimental bond length [10] of the ground state NO at $R_0^{\text{expt}} = 2.175 a_0$ and the optimized N–O bond length at $R_0^{\text{opt}} = 2.205 a_0$, respectively. Adiabatic studies were performed using the individual N–O bond lengths of the core excited states given by Remmers *et al* [5]. Spectral profiles were simulated using a Lorentzian band shape function. The individual spectral band widths, full width at half maximum (FWHM), were calculated using the time-dependent formulation suggested by Cederbaum and Tarantelli [11]. Electronic structure calculations were carried out using the MOLPRO96 [12] suite of programs [8] and CLUSTER suite of programs [13] on an IBM AIX RISC/6000 work station and a Cray J916 supercomputer.

3. Results and discussion

3.1. Ground electronic state of NO

The ground-state ($X^2\Pi$) configuration of the open-shell NO molecule is dominated by $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^4 5\sigma^2 2\pi^1$ (93% CI coefficient). An optimization yields the ground-state N–O bond length R_0^{opt} at $2.205 a_0$, with $-0.000\,42E_h$ (-0.01 eV) improvement in energy, compared with the energy at the experimental geometry (R_0^{expt}) of $2.175 a_0$. The energy derivatives $\partial E/\partial R$ calculated at R_0^{expt} and R_0^{opt} are given by -1.628 and -1.633×10^{-3} eV a_0^{-1} , respectively. The values indicate that the potential energy surface of the NO ground state is quite flat at the bottom of the potential well. As a result, vertical

Table 1. Calculated vertical (most probable) and adiabatic ($\Delta v = 0$) transitions for nitrogen and oxygen core excitation spectra. The experimental N–O bond lengths of the individual core excited states are given by [5]. The N 1s and O 1s FWHM are reported experimentally to be 0.71 and 0.95 eV, respectively [3].

State	Vertical						Adiabatic			
	Spectrum I			Spectrum II			Spectrum III			
	ν	FWHM	rate	ν	FWHM	rate	R_i^{exp}	ν	rate	
	(eV)	(eV)	ratio	(eV)	(eV)	ratio	(a_0)	(eV)	ratio	
		$R_0^{\text{opt}} = 2.205 a_0$			$R_0^{\text{exp}} = 2.175 a_0$					
N 1s	$^2\Delta$	400.06	0.33	0.77	400.16	0.46	0.76	2.294	399.99	0.79
N 1s	$^2\Sigma^-$	400.41	0.28	1.00	400.50	0.40	1.00	2.294	400.36	1.00
N 1s	$^2\Sigma^+$	400.58	0.40	0.41	400.70	0.53	0.41	2.338	400.45	0.42
O 1s	$^2\Sigma^-$	532.15	0.93	1.00	532.37	1.07	1.00	2.470	531.37	1.00
O 1s	$^2\Delta$	533.33	0.75	0.75	533.52	0.89	0.75	2.425	532.79	0.74
O 1s	$^2\Sigma^+$	534.09	0.74	0.40	534.27	0.88	0.40	2.394	533.59	0.39

transitions of the core excitation spectra using R_0^{exp} and R_0^{opt} did not yield significant differences as shown in table 1.

3.2. Energy ordering of core excited states

Core resonant excitation processes selectively excite one of the 1σ (O 1s) or 2σ (N 1s) electrons into the partially occupied $2\pi^*$ orbital. Due to interactions among electrons in $2\pi^*$ and core σ orbitals, each of the bound-state resonances $\text{N } 1s^{-1}-2\pi^*$ and $\text{O } 1s^{-1}-2\pi^*$ results in four final states, $^2\Sigma^-$, $^2\Delta$, $^2\Sigma^+$ and $^4\Sigma^-$, with the three doublet states being dipole allowed. The localized nature of the processes results in the core excited states being dominated by their corresponding HF configurations. The CI coefficients for such HF configurations in the representation of $^2\Sigma^-$, $^2\Delta$ and $^2\Sigma^+$ states are given by 94%, 97% and 94% for O 1s and 91%, 91% and 89% for N 1s core excited states, respectively.

A population analysis of the ground-state NO indicates that the 5σ and $2\pi^*$ orbitals are dominated by contributions from the nitrogen atom (69% and 70%, respectively). Therefore, interactions between the nitrogen dominant orbitals, e.g. $2\sigma^{-1}2\pi^2$, and between the orbitals dominated by both oxygen and nitrogen, such as $1\sigma^{-1}2\pi^2$, may result in different multiplet splitting schemes in the energy. Table 1 provides details of the simulated core excitation spectra of the NO molecule calculated vertically, at the optimized and experimental N–O bond lengths, and adiabatically. The energy ordering in this table is $E(^2\Delta) < E(^2\Sigma^-) < E(^2\Sigma^+)$ for the core excited nitrogen spectrum, whereas oxygen core excitation leads to an energy ordering of $E(^2\Sigma^-) < E(^2\Delta) < E(^2\Sigma^+)$. As stated previously, the difference in energy ordering could stem from interactions between configurations dominated by nitrogen alone and by both nitrogen and oxygen. Apparently, the equivalent-core model, which simply predicts the ordering as $E(^2\Sigma^-) < E(^2\Delta) < E(^2\Sigma^+)$ for N 1s excited states [2], is not valid for the N 1s excitation spectrum.

3.3. Potential energy surfaces and spectral band shape

Excitation is a fast process so that the changes in internuclear distances of the final core excited states are very small. Lifetimes of the core hole states are short so that the effective

Franck–Condon regions are intermediate between the values for the NO ground state and the N 1s and O 1s core hole states. A description of the excitation processes in terms of vertical transitions is therefore a good approximation.

Spectral band shape (FWHM) of the vertical spectra has been calculated using the time-dependent formulation suggested by Cederbaum and Tarantelli [11]. That is, for an excitation process the spectral FWHM is given by $[\kappa_c^2 8 \ln 2 + \Gamma^2]^{\frac{1}{2}}$ (where κ_c is the energy derivative of the core hole states at the geometry of the initial (ground) state and Γ the resolution parameter). Obviously, no dynamical contributions of the wavepacket's motion to the width are present. The width of the spectrum results from the initial wavepacket itself possessing a width. The projection of the initial wavepacket on the potential curve of the final (core) state leads to the observed width of the band [11].

Energy derivatives of the core excited states, i.e. κ_c , which are obtained from parallel calculations at R_0^{opt} and its vicinity $R_0^{\text{opt}} \pm 0.015 a_0$ are given by -2.587 , -2.128 and $-1.796 \text{ eV } a_0^{-1}$ for $^2\Sigma^+$, $^2\Delta$ and $^2\Sigma^-$ states of N 1s core excitation; and -4.846 , -4.887 and $-6.076 \text{ eV } a_0^{-1}$ for corresponding O 1s excited states. The fact that these energy derivatives are negative in value implies that the core excited states have longer N–O bond lengths than the ground state. Moreover, such a prediction made from the energy derivatives has been supported by pointwise optimizations of these states in this work, which yield the bond lengths of about $2.30 a_0$ and $2.50 a_0$ for the N 1s and O 1s core excited states, respectively. As a consequence, the predicted bond lengths of $R_{\text{O } 1s} > R_{\text{N } 1s} > R_0$ agree well with the experimental findings of Remmers *et al* [5].

3.4. Excitation spectra of NO

Table 1 gives the N 1s and O 1s core excitation spectra of NO simulated in this study. The adiabatic (spectrum III) band positions calculated using the experimental N–O bond distances [5] of the related initial (ground) and final (core-excited) states correspond to the band head ($\Delta v = 0$) positions of the experimental measurements. The vertical band centre positions, however, are calculated at the optimized (spectrum I) and at the experimental (spectrum II) N–O internuclear distances of the ground electronic state of NO and are related to the band centres ($\Delta v \neq 0$, the most probable transition) of the vibrational envelope, between which there is a difference of a few hundreds of meV or more, depending on the FWHM of each band. It can be seen from this table that the adiabatic transition energies of the N 1s and O 1s spectra have smaller values than the vertical counterparts, whereas the relative intensity rate pattern of the spectra does not yield great variations in the vertical and adiabatic spectra. Therefore, table 2 provides the comparison of the adiabatic spectral transition energies calculated in this work with the energies from analysing experimental data, whereas table 3 compares the vertical spectra (band centre positions and band shape parameters) with the estimated experimental band centres and FWHM.

In two sets of the vertical spectra (spectrum I and spectrum II), the pure theoretical spectra (spectrum I) yield slightly smaller band centre positions and FWHM parameters than spectrum II at the experimental N–O bond length. The differences reflect characteristics of the ground-state potential energy surface of NO molecule at the optimized and experimental internuclear distances. The relative intensity rate pattern of the vertical spectra, however, has little changes. As a result, spectrum I will be used to carry out further discussion and comparisons with experiments.

Figures 1 and 2 give the simulated N 1s and O 1s core-excitation spectra of NO. A Lorentzian band shape function with the spectral parameters reported in table 1 is used in the simulations. The resolution parameter is fixed at 0.1 eV [14] which accounts for

Table 2. Comparison of the adiabatic transition energies of the N 1s and O 1s excitation spectra calculated in this work with available experiments ($\Delta v = 0$).

State		This work ν (eV)	Experimental [4] ν (eV)	Experimental [5] ν (eV)	Experimental [3] ν (eV)
N 1s	$^2\Delta$	399.99	399.43	399.38	—
N 1s	$^2\Sigma^-$	400.36	399.70	399.67	—
N 1s	$^2\Sigma^+$	400.45	—	400.00	—
O 1s	$^2\Sigma^-$	531.37	532.11	531.46	531.7
O 1s	$^2\Delta$	532.79	532.70	532.36	532.7
O 1s	$^2\Sigma^+$	533.59	533.64	533.13	533.7

Table 3. Comparison of vertical O and N core excitation spectra simulated in this work with theoretical and estimated experimental data.

State		This work ^a			Theory [4]		Experimental [5]			Experimental [3]		
		ν (eV)	rate ratio	FWHM (eV)	ν (eV)	rate ratio	ν^c (eV)	rate ratio	FWHM ^c (eV)	ν^c (eV)	rate ratio	FWHM (eV)
N 1s	$^2\Delta$	400.06	1.88	0.33	399.83	2.05	399.38 ^d	1.9	0.42	399.45	1.4	0.71
N 1s	$^2\Sigma^-$	400.41	2.44	0.28	399.98	3.01	399.67 ^d	2.9	0.53	399.70	2.0	0.71
N 1s	$^2\Sigma^+$	400.58	1.00	0.40	400.93	1.00	400.00 ^d	1.0	0.47	400.12	1.0	0.71
O 1s	$^2\Sigma^-$	532.15	2.50	0.93	532.61	3.30	532.05	1.04	0.85	532.20	4.29	0.95
O 1s	$^2\Delta$	533.33	1.88	0.75	533.63	2.10	532.80	1.14	0.62	533.20	2.86	0.95
O 1s	$^2\Sigma^+$	534.09	1.00	0.74	535.21	1.00	533.70	1.00	1.30	534.30	1.00	0.95

^a Spectrum I of NO.

^b From the experimental high-resolution spectra (see [4]).

^c Estimated at the least-squares fitted experimental spectra.

^d Vertical transitions from the ground state within the NO potential curve were assumed (see [5]).

the finite lifetime of the core hole state and for the experimental resolution. It has been found that a reasonably wide variation of this parameter (0.1–0.5 eV) does not appreciably alter the resultant spectrum [14]. The full curves in these figures are spectral profiles related to the electronic states given in tables 1 (spectrum I) and 3. The two sets of the N 1s and O 1s split core excited states have a different ordering in their band centre positions: $\nu_{2\Delta} < \nu_{2\Sigma^-} < \nu_{2\Sigma^+}$ and $\nu_{2\Sigma^-} < \nu_{2\Delta} < \nu_{2\Sigma^+}$ for N 1s and O 1s spectra, respectively. However, the ordering of relative intensities remains unchanged in the two spectra: $I(^2\Sigma^-) > I(^2\Delta) > I(^2\Sigma^+)$. Moreover, the widths (FWHM) of N 1s and O 1s spectra with moderate resolution (broken curves in the figures) that are superpositions of each of the three profiles are given by 0.70 eV and 2.50 eV, respectively, which are in good agreement with the measurements of NO at moderate energy resolution given by 0.8 and 2.3 eV [4], and estimated to be 1.0 eV and 2.3 eV for the N 1s and O 1s spectra [3], respectively.

3.4.1. N 1s excitation spectrum. The simulated vertical N 1s core excitation spectrum of NO is presented in figure 1, which is calculated at the optimized geometry of $R_0^{\text{opt}} = 2.205 a_0$ (spectrum I). In this work, the band centre positions of transitions to the N 1s core excited states ($^2\Delta$, $^2\Sigma^-$ and $^2\Sigma^+$) are given by 400.06, 400.41 and 400.58 eV, respectively, and the relative intensity ratio of the above transitions is 1.88:2.44:1.00 with corresponding FWHMs of 0.33, 0.28 and 0.40 eV. The theoretical band centres differ by 0.61, 0.71 and 0.46 eV,

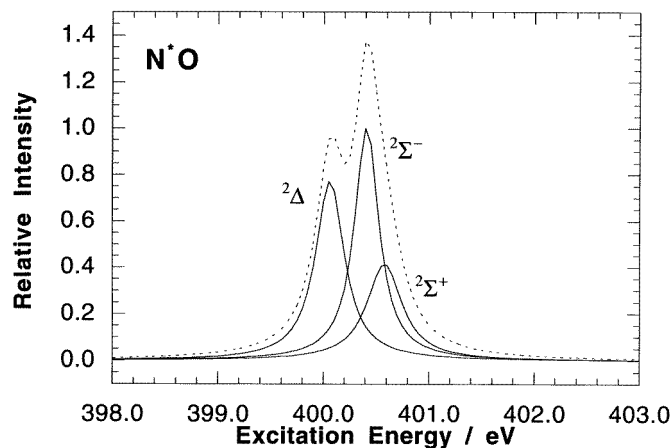


Figure 1. Simulated excitation spectrum for core excitation at the nitrogen π resonance in NO using the optimized N–O bond length of the ground state. A Lorentzian band shape function was used with the individual band widths given by table 1. The resolution parameter Γ is 0.1 eV [14].

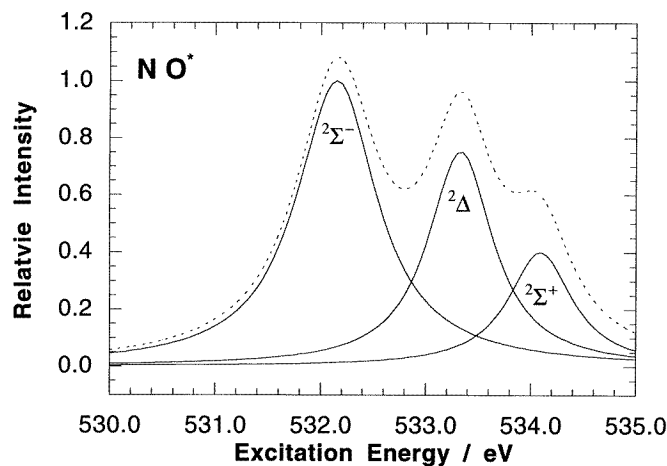


Figure 2. Simulated excitation spectrum for core excitation at the oxygen π resonance in NO using the optimized N–O bond length of the ground state. Lorentzian band shape function was used with the individual band widths given by table 1. The resolution parameter Γ is 0.1 eV [14].

respectively from the estimated experimental band centre positions of 399.45, 399.70 and 400.12 eV (intensity ratio 1.4:2.0:1.0) given by Carroll *et al* [3]. The differences become 0.68, 0.74 and 0.58 eV, respectively from the vertical transitions at 399.38, 399.67 and 400.00 eV (intensity ratio of 1.9:2.9:1.0) given by Remmers *et al* [5] from a least-squares fit of their high-resolution photoionization spectral data. Nevertheless, the theoretical intensity rate ratio agrees with the above experiments. The present band centres are in reasonably good agreement with the band centres calculated at 399.83, 399.98 and 400.93 eV (intensity ratio 2.05:3.01:1.00) obtained from a less accurate frozen orbital approximation [4].

The experimental analyses are subject to some uncertainties because of the overlapping

bands requiring judgment regarding *inter alia* the quality of the least-squares fitting procedures. To agree with the theoretical prediction of the intensity ratio of 2:3:1 obtained from a frozen orbital approximation [4], the analysis in [5] was confined to the intensity ratio of 1.9:2.9:1.0 which in fact could be varied up to 1.6:3.8:1.0 with a similar quality fit.

From the calculated slopes, the three N 1s excited states exhibit different characteristics in the vicinity of the ground-state bond length. The $^2\Sigma^-$ and $^2\Delta$ states do not exhibit any particular similarities in their potential energy curves as claimed in [5]. Nevertheless, that the most intense feature of the N 1s $\rightarrow \pi^*$ transitions was observed at $h\nu \approx 400$ eV [5] agrees well with the present calculations (see table 3). Furthermore, Remmers *et al* [5] claimed that the measured resonance energies of $^2\Delta$ and $^2\Sigma^-$ states differed by about 300 meV. This experimental finding has been supported in the present theoretical prediction at 350 meV.

Least-squares fit of the ion-yield experimental data [3] was performed assuming that the Gaussian widths of the three profiles were constant at 0.71 eV as given by Tronc *et al* [2]. In fact, the widths of different bands are unlikely to be the same, due to the differences in potential energy curves of the excited states and nuclear motions. As such a fit was restricted to the knowledge of energy ordering and spectral structure from previous investigations [2,4], it would not necessarily give the best fit amongst the possible ones. In the present calculations the predicted FWHM are considerably smaller in the range 0.28–0.40 eV (table 3) depending on the state being considered.

3.4.2. O 1s excitation spectrum. Experimental measurement for the O 1s transitions is a rather difficult task due to the poor signal-to-noise ratio at high energy losses [4]. As a result, relatively fewer data are available for the O 1s excitation spectrum. The intensity ratio for the O 1s excitation spectrum ($^2\Sigma^-:^2\Delta:^2\Sigma^+$) from experiments has been given significantly different results. For example, the ratio of 1.04:1.14:1.00 was given by Remmers *et al* [5] from high-resolution photoionization spectrum. The three profiles have competitive intensities with the $^2\Delta$ the most intense transition. However, the ratio of the same series of states was given as 3.0:2.0:0.7 from the ion-yield spectroscopy of Carroll *et al* [3]. Using a frozen orbital approximation, Kosugi *et al* [4] predicted the ratio to be 3.3:2.1:1.0, whereas their high-resolution electron-yield O 1s spectrum [4, figure 4] seemed to yield the most intense transition as $^2\Delta$ rather than the $^2\Sigma^-$ state. The relative populations for the core excited states are predicted to be 2.50:1.88:1.00 in this work. The result is close to the previous prediction [4], and to the experiment given by [3], but does not support the conclusion in [5].

In table 2, the predicted adiabatic O 1s transition energies at $\Delta v = 0$ are in better agreement with the experimental results than are the N 1s energies due to the more localized feature of the O 1s core excited states. In table 3, the vertical band centre positions of the O 1s spectrum are calculated at 532.15, 533.33 and 534.09 eV with respect to the three O 1s states of $^2\Sigma^-$, $^2\Delta$ and $^2\Sigma^+$. The values are close to the estimated experimental band centres at 532.20, 533.20 and 534.30, respectively [3], but have small shifts when compared with the estimated experimental band centres at 532.05, 532.80 and 533.70 eV, respectively [5]. Compared with N 1s excited NO, the more extensive vibrational fine structure of the O 1s spectrum is due to the much larger difference in equilibrium internuclear distances between ground and excited states [5]. This is supported by larger band widths (FWHM) of the O 1s spectrum evaluated using time-dependent formulation [11]. The FWHM of the N 1s spectrum is in the range 0.28–0.40 eV, whereas the FWHM of the O 1s spectrum is in the range 0.74–0.93 eV.

The simulated O 1s vertical excitation spectrum (at $R_0^{\text{opt}} = 2.205 a_0$) of π resonance is given in figure 2. The broken spectrum in this figure, that is, the O 1s spectrum under moderate energy resolution, shows features similar to the spectra obtained by high-resolution photoionization spectroscopy [5] except for the intensity of the peak in the middle (i.e. ${}^2\Delta$ state). Intensity pattern of the three profiles in figure 2 given by 2.50:1.88:1.00 has reasonably good agreement with the rate ratio of 3.0:2.0:0.7 from [3]. The present theoretical prediction gives the FWHM of 0.93, 0.75 and 0.74 for the O 1s states of ${}^2\Sigma^-$, ${}^2\Delta$ and ${}^2\Sigma^+$, respectively. The predicted FWHM of the ${}^2\Sigma^-$ state of 0.93 eV is close to the one experimentally determined at 0.95 eV [3].

However, the spectra obtained by [5] were from high-resolution data and were therefore considered to be more accurate. The present calculations agree reasonably well with most of the experiments except the intensity pattern for the O 1s spectrum. A re-analysis of high-resolution experimental data in the context of the present theoretical work could be beneficial.

Note added in proof. A recent theoretical study of the $1s-2\pi$ excitation spectra of NO using multiconfiguration coupled electron pair approximation [15] yields consistent results and supports the conclusions drawn in this work.

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References

- [1] Ma Y, Chen C T, Meigs G, Randall K and Sette F 1991 *Phys. Rev. A* **44** 1848–58
- [2] Tronc M, King G C and Read F H 1980 *J. Phys. B: At. Mol. Phys.* **13** 999–1008
- [3] Carroll T X, Coville M, Morin P and Thomas T D 1994 *J. Chem. Phys.* **101** 998–1005
- [4] Kosugi N, Adachi J, Shigemasa E and Yagishita A 1992 *J. Chem. Phys.* **97** 8842–9
- [5] Remmers G, Domke M, Puschmann A, Mandel T and Kaindl G 1993 *Chem. Phys. Lett.* **214** 241–9
- [6] Erman P, Hatherly P A, Karawajczyk A, Koble U, Rachlew-Kallne E, Stankiewicz M and Yoshiki-Franzen K 1996 *J. Phys. B: At. Mol. Opt. Phys.* **29** 1501–13
- [7] Huzinaga S, Andzelm J, Klobukowski M, Radzio-Andzelm E, Sakai Y and Tatewaki H 1984 *Gaussian Basis Sets for Molecular Calculations* (Amsterdam: Elsevier)
- [8] Werner H-J and Knowles P J 1985 *J. Chem. Phys.* **82** 5053–63
- [9] Knowles P J and Werner H-J 1985 *Chem. Phys. Lett.* **115** 259–67
- [10] Huber K P and Herzberg G 1979 *Molecular Spectra and Molecular Structure, IV Constants of Diatomic Molecules* (Toronto: Van Nostrand Reinhold)
- [11] Cederbaum L S and Tarantelli F 1993 *J. Chem. Phys.* **98** 9691–706
- [12] MOLPRO 1996 is a package of *ab initio* programs written by Werner H-J and Knowles P J, with the contributions from Almlöf J *et al*
- [13] Hermann K 1996 *SCF CLUSTER Suite of Programs* (Berlin: Fritz-Haber-Institut)
- [14] Cederbaum L S, Campos P, Tarantelli F and Sgamellotti A 1991 *J. Chem. Phys.* **95** 6634–44
- [15] Fink R 1997 *J. Chem. Phys.* **106** 4038–52