

Anomalous multiplet-splitting intensity ratios in K -level x-ray photoemission spectra of NO and O_2

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The intensity ratios of the multiplet-split $N1s$ peak of NO and $O1s$ peak of O_2 in the x-ray photoemission spectra of these paramagnetic molecules were found to exceed the simple multiplet ratios $(S+1)/S$. Hartree-Fock calculations were performed on the ground state and the $1s$ -hole states in each case, and total overlap probabilities for the passive orbitals were computed. Positive deviations from the multiplet ratios were obtained, but they were smaller than the experimental deviations. The NO($N1\bar{s}$, ${}^3\Pi/{}^1\Pi$) ratios were 3.43(8) (expt.), 3.09 (calc.), and 3 (multiplet), while for $O_2(O1\bar{s}$, ${}^4\Sigma/{}^2\Sigma$) the ratios were 2.47(3) (expt.), 2.28 (calc.), and 2 (multiplet). Thus incomplete overlap accounts for some, but not all, of the observed deviation. Another consequence of incomplete overlap is multiple excitation during photoemission. The total probabilities for multiple excitation were computed as 0.25(NO, $N1\bar{s}$), 0.28(NO, $O1\bar{s}$), and 0.42(O_2 , $O1\bar{s}$), in agreement with the observation by Carlson *et al.* of large multiple-excitation probabilities.

I. INTRODUCTION

When photoelectrons are ejected from atomic core levels of paramagnetic molecules¹ or salts,² multiplet splitting may be observed in the characteristic photoelectron peaks. This splitting arises from final-state multiplet structure established by coupling of the open core shell with the valence shells. The simplest case is one in which a valence level of character ${}^{2S+1}L$ (or ${}^{2S+1}\Lambda$ for molecules) couples to a core s electron. Two peaks are observed: a lower-binding-energy, higher-multiplicity peak corresponding to the final state ${}^{2S+2}L$, and a second peak associated with the final state ${}^{2S}L$. The intensity ratio of these two peaks is nominally the multiplicity ratio $(S+1)/S$.

Positive deviations from the $(S+1)/S$ intensity ratio have been observed in a number of cases, and this may be a rather general phenomenon. In the $3s$ photoemission spectrum of $Mn^{2+}(3d^5; {}^6S)$, the very large positive deviation [a ratio of 2.0 rather than $(S+1)/S = 7/5$]² has been explained³ as arising from electron-correlation effects. New structure predicted by a configuration-interaction calculation³ has in fact been observed.⁴ This calculation suggests, however, that the correlation effects, which affect both the multiplet-splitting energy and the intensity ratio, are largest when the photoelectron is ejected from a core state having the same principal quantum number as the unpaired valence orbital, and much less important otherwise. For transition-metal^{4,5} and rare-

earth⁶ ions, this is consistent with experiment.

Inspection of the published spectra¹ for O_2 and NO confirms that the multiplet ratios ${}^4\Sigma/{}^2\Sigma = 2$ and ${}^3\Pi/{}^1\Pi = 3$ are approximately satisfied, but especially in the O_2 case there is apparent evidence for a positive deviation. In particular, the peak heights in the partially resolved spectra stand in a ratio of 2:1, implying that this ratio would increase on resolution of the peaks. This result is surprising, because it seems very unlikely that the correlation effect mentioned above could be large enough to account for sizable deviations in these $1s$ spectra. It is also disquieting. Multiplet structure in photoemission spectra has potential as a diagnostic tool for studying spin-density distributions. To apply it in this way, one should first assess and understand deviations from the multiplet intensity ratios. To this end, we present below both experimental and theoretical results which show that the intensity ratios of the $1s$ photoelectron multiplet peaks do indeed depart significantly from the final-state multiplicity ratios in NO and O_2 . The measured and calculated (in parentheses) ratios are, for NO($N1s$), $R({}^3\Pi/{}^1\Pi) = 3.43(8):1$ (3.09:1) and for $O_2(O1s)$, $R({}^4\Sigma/{}^2\Sigma) = 2.47(3):1$ (2.28:1). These values are in every case larger than the multiplicity ratios.

We also present theoretical results for the probability of multiple excitation ($1s$ ionization plus valence-shell excitation or ionization) relative to the probability of formation of "normal" single $1s$ -hole final states. For NO, the probabilities

of multiple excitation, P_M , are $P_M(\text{N } 1s\text{-hole}) = 0.25$ and $P_M(\text{O } 1s\text{-hole}) = 0.28$; for O_2 , $P_M(\text{O } 1s\text{-hole}) = 0.42$ or more than 50% larger than for NO. For both molecules the values of P_M are sufficiently large to indicate that "shake-up" satellite peaks should be observed.

Experimental results for R are given in Sec. II. The theoretical discussion is given in Sec. III, and conclusions are summarized in Sec. IV.

II. EXPERIMENTAL

Gaseous O_2 and NO were subjected to irradiation by $\text{MgK}\alpha_{1,2}$ x rays in the Berkeley Iron-Free Spectrometer. Photoelectrons were analyzed at an energy resolution of 0.06%. The experiments were carried out at room temperature with sample pressures in the $(1-5) \times 10^{-2}$ Torr range. The spectrometer current was stepped in 0.1-mA (~ 0.1 eV) intervals. Counting was continued in each case until $\sim 5 \times 10^3$ counts were obtained in the peak channels. Peak/background ratios were typically (8-10):1. The N 1s line in NO and the O 1s line in O_2 showed easily resolved splitting, but the O 1s line in NO did not. Accordingly, detailed studies were carried out only for the first two cases. Four experiments were done on O_2 and two on NO. Selected spectra are shown in Figs. 1 and 2, respectively.

The spectra were analyzed to yield intensity ratios by least-squares fitting with Lorentzian peaks. The exact peak shape that should be used is not known. Lorentzians usually give good fits for core-level x-ray photoemission spectra (XPS) of gases, however. Two of the three main sources of line broadening—the x-ray profile and the hole lifetime—should in fact have Lorentzian profiles. The third—spectrometer resolution—is approxi-

mately triangular, but not accurately known. Thus it is not surprising that the convolution of these three is essentially Lorentzian. To test the sensitivity of derived parameters to the form of the peaks used in the fitting procedure, we also tried to fit the spectra with Gaussian line shapes. In most cases convergence was obtained and the peak separation ΔE was comparable to that found in the Lorentzian fits. The Gaussian fits were visually very poor, however, and the weighted variances were absurdly large. The derived intensity ratios, which varied widely, were interpreted as meaningless. Thus Gaussian peak shapes, which were grossly incorrect, could be used to derive peak positions but not relative intensities.

One further refinement was made in the peak shape beyond simply using Lorentzians. The incident $\text{MgK}\alpha_{1,2}$ characteristic x ray is of course a doublet, consisting of a lower-energy lower-intensity component from the $(2p_{1/2} - 1s)$ transition in addition to the stronger $(2p_{3/2} - 1s)$ component. The relative intensities of these components should be about 1:2 and their energy separation about 0.3 eV, as judged by x-ray data on neighboring elements. Thus, in addition to using a single Lorentzian line (version L1), we also fitted the spectra with a line shape that was a composite of two Lorentzians, of relative intensity 1:2. Two versions of this approach were used. In the first, denoted as L2, these two components (α_1 and α_2) were separated by 0.40 eV. In the other case, L2', they were separated by 0.32 eV, a figure obtained from relativistic Hartree-Fock-Slater results.⁷ In Table I the intensity ratios and weighted variances from all six data sets are listed. It is very encouraging that the derived intensity ratios are quite insensitive to whether fitting procedure L1, L2, or L2' was used. It is especially pleasing that the two-Lorent-

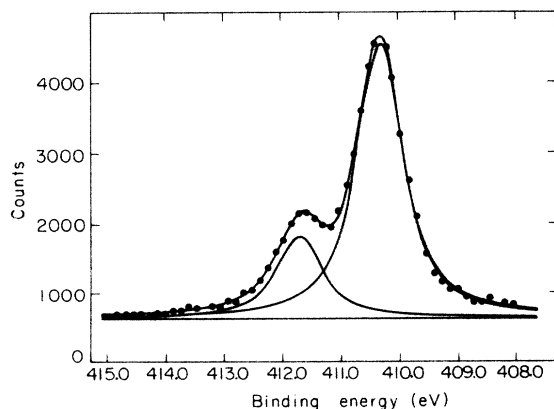


FIG. 1. Photoelectron spectra of the NO N1s doublet. Points denote experimental spectrum. Fitted full and component curves are shown.

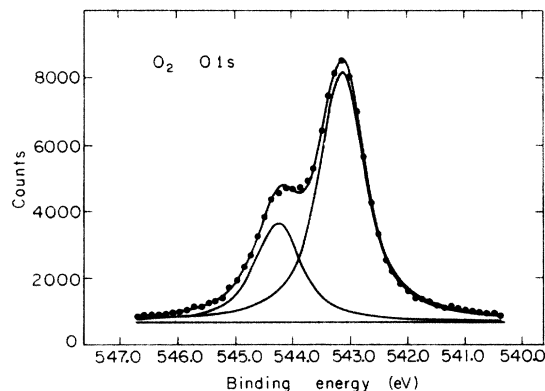


FIG. 2. Photoelectron spectra of the O_2 O1s doublet. Points denote experimental spectrum. Fitted full and component curves are shown.

zian fits give significantly improved variances. We emphasize that use of two rather than one Lorentzian in this way does not constitute the addition of a new parameter, but rather a change in the line shape to recognize the known structure of the exciting radiation. We suggest that all XPS spectra obtained with characteristic x rays should be analyzed in this way. The better variances obtained with the $L2$ spacing rather than with $L2'$ probably arise because of an asymmetry in the spectrometer response function, which would have the effect of exaggerating the apparent $\alpha_1 - \alpha_2$ spacing.

The fitting results given in Table I give quantitative support to our intuitive observation, and establish unambiguously that the intensity ratios in both cases substantially exceed the multiplicity values. Thus it is worthwhile to seek a theoretical explanation for this phenomenon. Because extensive configuration interaction, which sufficed to explain a similar observation in the 3s XPS spectrum of Mn^{2+} , seems unlikely here, the possibility that incomplete overlap of the passive orbitals of the initial and final 1s-hole ionic states was responsible was studied theoretically, as described below.

III. THEORETICAL

The theoretical determination of relative intensities and intensity ratios that we present follows from the use of the sudden approximation (SA) as described by Åberg.⁸ The SA is applied using Hartree-Fock (HF) wave functions computed for the initial ground states and final 1s-hole states of NO and O_2 .^{9,10} We review below the application of the SA to the molecules and HF wave functions under consideration.

Let us denote the ground-state molecular wave function as $\Psi_0(1, 2, \dots, N)$. In general, for an open-shell system, the HF Ψ_0 is a linear combination of determinants, chosen to make Ψ_0 an eigenfunction of space and spin symmetry operations.^{11,12}

When a core electron N in spin orbital ψ_i (belonging to the ground-state wave function) is suddenly removed from the system, the normalized wave function of the remaining fragment may be denoted by $\Psi_0^{(-i)}(1, 2, \dots, N-1)$; it has the form

$$\Psi_0^{(-i)}(1, 2, \dots, N-1) = N^{1/2} \int \psi_i^*(N) \times \Psi_0(1, 2, \dots, N) dx_N. \quad (1)$$

For a HF wave function Ψ_0 , $\Psi_0^{(-i)}$ may also be written as a linear combination of determinants. Now, $\Psi_0^{(-i)}$ can be expanded in the eigenstates Φ_n of the $N-1$ electron system:

$$\Psi_0^{(-i)} = \sum C_n^{(-i)} \Phi_n(1, 2, \dots, N-1), \quad (2)$$

where the Φ_n are the so-called "relaxed" eigenstates of the fragment.¹³ We assume that the first few Φ_n are wave functions for "normal" single-core-hole final states (of different multiplicity); the remaining Φ_n are for multiple-excitation final states in which a core electron is removed and a valence-shell electron is excited as well. (The Φ_n may be exact or HF eigenstates of the $N-1$ electron system. Here, of course, we consider only HF eigenstates.)

In the SA, the probability that the ionization of spin orbital ψ_i will leave the $N-1$ electron system in state n is simply

$$P_n^{(-i)} = |C_n^{(-i)}|^2 = |\langle \Phi_n | \Psi_0^{(-i)} \rangle|^2. \quad (3)$$

The probability that the target will be left in some other final state is $1 - P_n^{(-i)}$. The $N-1$ electron overlap matrix element of Eq. (3) is evaluated by forming determinants of the overlap integrals between the nonorthogonal sets of orbitals ψ_k determined for Ψ_0 and ϕ_k^n determined for Φ_n .¹⁴ That is, although the HF orbitals for the initial and final hole states are orthogonal among themselves,

$$\langle \psi_k | \psi_l \rangle = \delta_{kl}, \quad \langle \phi_k^n | \phi_l^n \rangle = \delta_{kl}, \quad (4)$$

TABLE I. Experimental final-state intensity ratios R of the N 1s ($^3\Pi/{}^1\Pi$) peaks in NO and the O 1s (${}^4\Sigma/{}^2\Sigma$) peaks in O_2 following x-ray photoemission. Results of three fitting procedures ($L1$, $L2$, and $L2'$, explained in text) are given.

Spectrum	Fit $L1$		Fit $L2$		Fit $L2'$	
	R	Variance	R	Variance	R	Variance
NO(N 1s) run 1	3.64(23)	3.2	3.52(16)	1.6	3.57(17)	1.9
NO(N 1s) run 2	3.48(14)	2.8	3.34(9)	1.5	3.38(10)	1.6
O_2 (O 1s) run 1	2.52(8)	3.1	2.47(8)	2.2	2.48(7)	1.7
O_2 (O 1s) run 2	2.53(9)	6.1	2.51(6)	2.4	2.49(6)	2.7
O_2 (O 1s) run 3	2.55(10)	10.0	2.53(5)	2.8	2.52(6)	4.5
O_2 (O 1s) run 4	2.41(10)	4.2	2.41(7)	2.1	2.39(7)	2.3

Final adopted values: R (NO, N 1s) = 3.43(8); R (O_2 , O 1s) = 2.47(3).

they do not form mutually orthogonal sets,

$$\langle \psi_k | \phi_l^* \rangle \neq \delta_{kl}. \quad (5)$$

The relative intensities of observed multiplet peaks in open-shell molecules are obtained by (i) summing over the probabilities of Eq. (3) for the removal of appropriate spin-orbitals i ; (ii) averaging over the spin (and symmetry) of the electron removed; and (iii) averaging over the degenerate initial states of the N -electron system.

We consider specifically first the case of NO, then that of O₂. For NO, the molecular orbital (MO) configuration of the ground state is

$$\Psi_0(X^2\Pi) = 1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 1\pi^4 2\pi^1(^2\Pi), \quad (6a)$$

where 1σ is an O $1s$ orbital and 2σ a N $1s$ orbital. The final "normal" hole-state configurations upon ionization of the O $1s$ or N $1s$ electron are

$$\Phi(\text{O } 1s\text{-hole}) = 1\sigma^1(^2\Sigma^+) 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 1\pi^4 2\pi^1(^2\Pi), \quad (6b)$$

$$\Phi(\text{N } 1s\text{-hole}) = 1\sigma^2 2\sigma^1(^2\Sigma^+) 3\sigma^2 4\sigma^2 5\sigma^2 1\pi^4 2\pi^1(^2\Pi), \quad (6c)$$

where the open core shell and the 2π shell may couple to either $^3\Pi$ or $^1\Pi$. In terms of determinants of $\langle \psi_k | \phi_l \rangle$, the intensities of the $1s$ -hole singlet or triplet final-state peaks are proportional to

$$\begin{aligned} P(\text{O } 1s\text{-hole}, ^2S'^{+1}\pi) &= \frac{1}{4}(2S' + 1)[D^\sigma D_{11}^\sigma D^\pi (D_{22}^\pi)^3]^2, \\ P(\text{N } 1s\text{-hole}, ^2S'^{+1}\pi) &= \frac{1}{4}(2S' + 1)[D^\sigma D_{22}^\sigma D^\pi (D_{22}^\pi)^3]^2, \end{aligned} \quad (7)$$

where $S' = 0$ or 1 . Here D^σ is the 5×5 determinant with elements $(D^\sigma)_{ij}$ given by

$$(D^\sigma)_{ij} = \langle \psi_{i\sigma}(\text{ground state}) | \phi_{j\sigma}(\text{hole state}) \rangle, \quad (8)$$

and D^π is the analogous 2×2 determinant for the π orbitals. The minor D_{11}^σ is formed by deleting the first row ($\psi_{1\sigma}$) and column ($\phi_{1\sigma}$) of D^σ . That Eq. (7) follows from Eqs. (6) is readily shown by writing out the expressions for Ψ_0 and Φ and evaluating their overlap. (The determinants D^σ and D^π for O₂ are given in the Appendix.) The probability of multiple excitation (excitation or ionization of a valence-shell electron accompanying the $1s$ ionization), P_M , for, e.g., O $1s$ ionization is given by

$$\begin{aligned} P_M(\text{O } 1s\text{-hole}) &= 1 - P(\text{O } 1s\text{-hole}, ^3\Pi) \\ &\quad - P(\text{O } 1s\text{-hole}, ^1\Pi). \end{aligned} \quad (9)$$

The multiple excited state may also be coupled to either $^3\Pi$ or $^1\Pi$.

The discussion for O₂ is changed somewhat be-

cause, for HF wave functions, it is appropriate to use a localized description of the orbitals of the $1s$ -hole states. The MO configuration of the O₂ ground state is

$$\Psi_0(X^3\Sigma_g^-) = 1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^4 2\pi_g^2(^3\Sigma_g^-), \quad (10a)$$

where $1\sigma_g = 1s_A + 1s_B$ and $1\sigma_u = 1s'_A - 1s'_B$. One might expect that the MO configuration for the $1s$ -hole states would be formed by removing a $1\sigma_g$ or $1\sigma_u$ electron. However, it has been found¹⁰ that the energies (and ionization potentials) of the $1s$ -hole states are substantially improved if localized orbitals are used. Hence, the MO configuration is

$$\Phi_L(\text{O } 1s\text{-hole}) = 1s_A(^2\Sigma^+) 1s_B^2 3\sigma^2 4\sigma^2 5\sigma^2 1\pi^4 2\pi^2(^3\Sigma^-), \quad (10b)$$

where the two open shells may couple to $^4\Sigma^-$ or $^2\Sigma^-$. As the notation suggests, $1s_A$ is a $1s$ orbital localized on oxygen A and $1s_B$ on oxygen B . The orbitals $1s_A$ and $1s_B$ are orthogonal

$$\langle 1s_A | 1s_B \rangle = 0;$$

however they have different spatial dependence to account for the fact that $1s_A$ is singly and $1s_B$ doubly occupied. We emphasize that in an HF calculation¹⁰ the localized orbitals of Eq. (10b) are determined in the usual variational fashion. The calculation is simply performed in $C_{\infty v}$ symmetry rather than $D_{\infty h}$. In other words, localized orbitals are determined by removing a constraint ($D_{\infty h}$ symmetry) rather than by imposing one. Clearly, Φ_L of Eq. (10b) does not have g or u symmetry under inversion I about the center of O₂:

$$I\Phi_L \neq \pm \Phi_L.$$

Symmetric total wave functions may be formed from combinations of Φ_L and $I\Phi_L$ (which is exactly degenerate with Φ_L):

$$\Phi_g = \Phi_L + I\Phi_L, \quad \Phi_u = \Phi_L - I\Phi_L. \quad (11)$$

The splitting of the $1s$ -hole g and u states is too small to be observed. The splitting may be estimated from HF results using $D_{\infty h}$ symmetry for the hole states, which give¹⁰

$$\Delta E(^4\Sigma_g^- - ^4\Sigma_u^-) = 0.045 \text{ eV}$$

$$\Delta E(^2\Sigma_g^- - ^2\Sigma_u^-) = 0.008 \text{ eV}.$$

Since this splitting cannot be observed, the determination of the relative intensities of the quartet and doublet peaks must include a summation and average over the Φ_g and Φ_u final states of Eq. (11) or equivalently over Φ_L and $I\Phi_L$. In terms of determinants of $\langle \psi_k | \phi_l \rangle$, the intensities of the

1s-hole quartet and doublet multiplet peaks are proportional to

$$P(\text{O } 1s\text{-hole, } ^{2S'+1}\Sigma^-) = \frac{1}{8}(2S'+1)\{[D^\sigma D_{11}^\sigma (D^\pi)^2 (D_{22}^\pi)^2]^2 + [D^\sigma D_{21}^\sigma (D^\pi)^2 (D_{22}^\pi)^2]^2\}, \quad (12)$$

where $S' = \frac{1}{2}$ or $\frac{3}{2}$. The determinants D^λ and minors D_{ij}^λ are defined in the same way as those for Eq. (7).

Accurate HF wave functions using very extended basis sets have been obtained for the ground and 1s-hole states of NO and O₂^{9,10} at experimental ground-state equilibrium separations (2.1447 Bohrs for NO and 2.282 Bohrs for O₂). These wave functions have been used to evaluate the relative intensities, using Eqs. (7) and (12). The results for the intensities of the multiplet peaks, probabilities of multiple excitation, and intensity ratios of the high-spin and low-spin peaks are given in Table II. Observed values of the intensity ratios for O₂(⁴Σ⁻/²Σ⁻) and the N 1s peaks of NO(³Π/¹Π) from Table I are also given, in parentheses. The values of the orbital overlap integrals and determinants for O₂ are given in the Appendix. We note that the self-consistent convergence for the HF orbitals is sufficiently small that all figures given in Table II and the Appendix are numerically significant. Table II clearly predicts that both the observed and calculated intensity ratios for the different multiplets of the NO(N 1s) and O₂(O 1s) photoelectron peaks deviate significantly from the simple

TABLE II. Calculated relative intensities P for the normal single 1s-hole states of NO and O₂ and intensities for multiple excitation, P_M . Calculated and observed values, in parenthesis, of the intensity ratios R for the multiplet peaks (³Π/¹Π for NO and ⁴Σ⁻/²Σ⁻ for O₂).

Quantity	Calculated value (observed value)	% Deviation from multiplicity ratio
NO		
P (N 1s-hole, ³ Π)	0.568	...
P (N 1s-hole, ¹ Π)	0.184	...
R (N 1s-hole, ³ Π/ ¹ Π)	3.09:1(3.43:1)	3%(14.3%)
P_M (N 1s-hole)	0.248	...
P (O 1s-hole, ³ Π)	0.544	...
P (O 1s-hole, ¹ Π)	0.177	...
R (O 1s-hole, ³ Π/ ¹ Π)	3.08:1	2.7%
P_M (O 1s-hole)	0.280	...
O ₂		
P (1s-hole, ⁴ Σ ⁻)	0.406	...
P (1s-hole, ² Σ ⁻)	0.178	...
R (⁴ Σ ⁻ / ² Σ ⁻)	2.28:1(2.47:1)	14%(23.5%)
P_M	0.417	...

multiplicity ratios. For NO the calculated deviation is ~25% of that observed, while in O₂ it is ~50%. The probability of multiple excitations is quite large; up to 42% for O₂. Multiple-excitation satellites to the O₂ 1s peaks (and for N₂, CO, and CO₂ as well) have, in fact, been reported by Carlson *et al.*¹⁵ They observe satellites starting at kinetic energies 7.5 to 13 eV below the main doublet peaks. The total relative intensity of these peaks is reported as ~10 to 15%. We discuss below the physical basis, in the HF one-electron model, for these features.

The valence-shell charge distribution for the 1s-hole state wave functions is considerably different from that for the ground state. Much of the valence shell rearrangement, which is particularly marked in the π shells, can be described as molecular charge transfer. As noted earlier,¹⁰ the valence shells of the O₂⁺ 1s-hole state resemble those that one would expect for the ground state of the molecule FO⁺. Similarly, for the N 1s-hole states of NO⁺, the valence shells resemble those of O₂⁺. This may be seen from Table III, where Mulliken gross population analyses¹⁶ for the NO ground and N 1s-hole states are compared. The rearrangement leads to values of $\langle \psi_{n\pi} | \phi_{n\pi} \rangle$ significantly smaller than 1; ~0.95 for NO and ~0.90 for O₂. The large powers to which these integrals are raised in the photoemission probability accounts for the "small" probability for direct transitions and the relatively large multiple-excitation probability.

We note also (cf. Appendix) that the integrals $\langle \psi_{1\pi} | \phi_{1\pi} \rangle$ are consistently smaller for the low-spin coupling (¹Π or ²Σ⁻) than for the high-spin coupling of the hole states. This is true also for $\langle \psi_{2\pi} | \phi_{2\pi} \rangle$ except for the N 1s-hole states of NO,

TABLE III. Mulliken gross atomic populations for the ground-state and N 1s-hole ³Π and ¹Π states of NO. The orbital populations are normalized to the number of electrons in the orbital.

	Orbital	Ground state X ² Π		N 1s-hole states			
		N	O	³ Π	O	¹ Π	O
Core	1σ	-0.00	2.00	-0.00	2.00	-0.00	2.00
	2σ	2.00	-0.00	1.00	-0.00	1.00	-0.00
Valence	3σ	0.77	1.23	0.93	1.07	0.90	1.10
	4σ	0.86	1.14	0.94	1.06	0.86	1.14
	5σ	1.37	0.66	1.20	0.80	1.28	0.72
	1π	1.32	2.68	2.07	1.93	2.22	1.78
	2π	0.70	0.30	0.50	0.50	0.45	0.55
Total							
valence shell		4.99	6.01	5.64	5.36	5.71	5.29

TABLE IV. Overlap integrals $\langle \psi_{n\lambda} | \phi_{n'\lambda} \rangle$ between the HF orbitals of the initial state, $O_2(X^3\Sigma_g^-)$, and the final state, $O_2^+(1s\text{-hole}, ^4\Sigma^-)$. Values of the determinants required for Eq. (12) are also tabulated. See Eq. (10b) for the MO configuration of the $1s\text{-hole}$ state.

Initial state	Final state						
	$1s_A$	$1s_B$	3σ	4σ	5σ		
$1\sigma_g$	0.7065	0.7074	0.003	0.003	0.001		
$1\sigma_u$	0.7070	-0.7068	0.003	0.002	0.001		
$2\sigma_g$	-0.005	0.000	0.9959	0.0626	0.0268		
$2\sigma_u$	-0.005	0.000	0.0601	0.9944 ₅	-0.0165		
$3\sigma_g$	-0.002	0.000	-0.0268	0.0152	0.9935		
						1π	2π
	$D^\sigma = -0.987$		$D^\pi = 0.983$		$1\pi_u$	0.9093	-0.3958
	$D_{11}^\sigma = -0.700$		$D_{22}^\pi = 0.909$		$1\pi_g$	0.3908	0.9106
	$D_{21}^\sigma = -0.699$						

where the integral for $^1\Pi$ coupling is 0.0005 larger than for $^3\Pi$ coupling. The differences between the values of the integrals for the different couplings are small:

$$\frac{\langle \psi_{1\pi}(\text{NO gs}) | \phi_{1\pi}(\text{NO, N } 1s\text{-hole } ^3\Pi) \rangle}{\langle \psi_{1\pi}(\text{NO gs}) | \phi_{1\pi}(\text{NO, N } 1s\text{-hole } ^1\Pi) \rangle} = \frac{0.9747}{0.9670} = 1.008$$

and

$$\frac{\langle \psi_{1\pi}(\text{O}_2 \text{ gs}) | \phi_{1\pi}(\text{O}_2^+, ^4\Sigma^-) \rangle}{\langle \psi_{1\pi}(\text{O}_2 \text{ gs}) | \phi_{1\pi}(\text{O}_2^+, ^2\Sigma^-) \rangle} = \frac{0.9093}{0.8792} = 1.033,$$

where gs stands for ground state. However, the ratios above are effectively taken up to the *eighth* power to determine their contributions to the intensity ratios of the respective peaks. (This is an oversimplified statement: expansion of the determinants yields complicated expressions.) Small differences in the values of orbital overlap

integrals can thus lead to large effects in the intensity ratios.

It is somewhat disturbing that the changes in the overlap integrals between different spin couplings, particularly for NO^+ states, are so small. The HF charge distributions are known to be modified by correlation effects, and we might expect that the small changes in the HF wave functions would be significantly altered by inclusion of correlation. However, all observed and calculated intensity ratios are consistently greater than the multiplet ratio $S/(S+1)$. This consistency gives confidence to the qualitative, if not the quantitative, value of the above interpretation based on Hartree-Fock wave functions. An investigation of the valence shell "internal" and "semi-internal" correlations¹⁷ for both the ground and $1s\text{-hole}$ states should provide a reasonable basis for a quantitative estimate of correlation effects.

We consider now the validity of the use of the

TABLE V. Overlap integrals $\langle \psi_{n\lambda} | \phi_{n'\lambda} \rangle$ between the HF orbitals of the initial state, $O_2(X^3\Sigma^-)$, and the final state, $O_2^+(1s\text{-hole}, ^2\Sigma^-)$. Values of the determinants required for Eq. (12) are also tabulated. See Eq. (10b) for the MO configuration of the $1s\text{-hole}$ state.

Initial state	Final state						
	$1s_A$	$1s_B$	3σ	4σ	5σ		
$1\sigma_g$	0.7066	0.7072	0.003	0.003	0.001		
$1\sigma_u$	0.7068	-0.7070	0.004	0.003	0.001		
$2\sigma_g$	-0.006	0.000	0.9968	-0.0506	0.0263 ₅		
$2\sigma_u$	-0.006	0.000	0.0476 ₅	0.9952	0.0115		
$3\sigma_g$	-0.002	0.000	-0.0286	-0.0133	0.9941		
						1π	2π
	$D^\sigma = -0.989$		$D^\pi = 0.983$		$1\pi_u$	0.8792	0.4562
	$D_{11}^\sigma = -0.700$		$D_{22}^\pi = 0.879$		$1\pi_g$	0.4545	0.8818
	$D_{21}^\sigma = -0.699$						

SA for the relative intensities. First we note that if, in Eqs. (7) and (12), we had included terms involving the minors D_{i1}^a ($i=1,2,3,4,5$, not only 1 or 1 and 2), we would have obtained a formulation of the generalized sudden approximation (GSA).⁸ The GSA takes into account the nonzero overlap of the initial-state $1s$ orbital with final-state valence-shell orbitals. From the values of these overlap integrals for NO and O₂, the use of the GSA will alter the relative intensities by less than 10^{-4} , an insignificant change. The SA (or GSA) is valid only for photoionization for sufficiently high-energy incident photons. Åberg⁹ estimated that the SA is valid if the photon energy E_{ph} satisfies

$$E_{ph} \geq 1.5E_{KL} \text{ to } 2.0E_{KL}, \quad (13)$$

where E_{KL} is the energy required for simultaneous ionization of a K and a valence-shell electron. For O, E_{KL} is ≤ 600 eV¹⁰; since the energy of the incident MgK α photons is 1250 eV, the validity criterion of Eq. (13) is satisfied.

IV. CONCLUSIONS

Observations showing a significant departure of the intensity ratios of $1s$ photoelectron multiplet peaks from the ratio of multiplicities have been reported for the paramagnetic molecules NO and O₂. Theoretical values, using the SA and HF wave

functions, also depart from the ratio of multiplicities but the departures are smaller than observed: 25% for NO and 50% for O₂. The departures are ascribed to differences in the valence-shell (particularly the π shell) charge distribution between the high-spin and low-spin final $1s$ -hole state multiplets. Inclusion of correlation effects in the wave functions may change, quantitatively, the theoretical values of the intensity ratios. The large difference between the $1s$ -hole state and ground-state charge distributions leads to the prediction of high probability for multiple excitations. The differences are describable in large part as molecular charge transfer in the valence shells, again particularly the π shells. These predictions are at least qualitatively consistent with observations of multiple excitations in O₂ reported by Carlson *et al.*¹⁵

APPENDIX: VALUES OF ORBITAL OVERLAP INTEGRALS AND MINORS

In this appendix, we give explicitly the elements and values of the determinants and minors used in Eq. (12). We recall that the elements of D^λ are the orbital overlap integrals $\langle \psi_{n\lambda} | \phi_{n'\lambda} \rangle$ where ψ is an HF orbital of the ground state and ϕ a (relaxed) HF orbital of a $1s$ -hole state. The results are presented for the O₂ $^4\Sigma^-$ and $^2\Sigma^-$ states in Tables IV and V, respectively.

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