

ON THE PHOTOIONIZATION CROSS SECTION AND RYDBERG SERIES OF $O_2(X^3\Sigma_g^-)$

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Abstract — The cross section for photoionization of the $\pi_g 2p$ electron of O_2 is calculated from threshold to about 60 Å wavelength of the incident radiation, thus complementing some previous results. The transition strengths of various continua for initial $\pi_g 2p$, $\pi_u 2p$, $\sigma_g 2p$ and $\sigma_u 2s$ M.O.'s are also given and used to interpret Rydberg series of $O_2(X^3\Sigma_g^-)$. A preliminary result for the threshold cross section of $NO(X^2\Pi)$ is found to be in good agreement with the experimental value.

INTRODUCTION

IN A previous article⁽¹⁾ we calculated the photoionization cross section for the $\pi_u 2p$, $\sigma_g 2p$, and $\sigma_u 2s$ electrons of N_2 using S.C.F.–L.C.A.O.–M.O.'s for the initial states and both ordinary Coulomb and Q.D.M. (Quantum Defect Method) spheroidal waves for the final electronic states. Q.D.M. calculations have also been performed for N_2 by SCHNEIDER and BERRY⁽²⁾ using a pseudopotential method.⁽³⁾ Quantum defects, which are used to estimate the phase shifts of the various continua, are obtained from Rydberg series of terms. Unfortunately, no confirmed data exists on any series converging to the ground state of $O_2^+(4)$ so that we are not able to determine the cross section for the removal of the $\pi_g 2p$ electrons of $O_2(X^3\Sigma_g^-)$, and hence the total cross section by Q.D.M. techniques. We therefore give results for the $\pi_g 2p$ electron using the two-centre Coulomb approximation for the final states, which completes the set of such calculations. The results obtained with this model are expected to yield useful information concerning the following.

- (1) The magnitudes of the cross sections for higher angular momentum states and whether these continua should be included in future calculations. Further, the phase shifts for waves with $l \geq 3$ are expected to be small so that the matrix elements involving them can be quite accurately estimated with ordinary 2-centre Coulomb waves.
- (2) The strongest continua at and near thresholds. On the basis of a nearly continuous oscillator strength at series limits we can tentatively interpret or predict Rydberg series of terms which converge to these limits.

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CALCULATIONS AND RESULTS

The general formula for the cross section has been given previously.^(1,5) In this work only the gross features of the variation of the matrix elements with energy are of interest, so we ignore the vibrational and rotational contributions. Without a large expected error we can reduce the transition integrals involving many-electron wave functions to ones involving the one-electron molecular orbital vacated and one-electron continuum functions. If the initial state molecular orbital has quantum numbers (n, l, m) in the united atom designation, then the cross section at energy k^2 of the ejected electron is given by the formula

$$\sigma(k^2) = \frac{4\pi^2\alpha a_0^2}{3}(I+k^2) \sum_{l'} \sum_{m'} |\mathbf{M}(k^2, l', m'|n, l, m)|^2 \quad (1)$$

$$\mathbf{M}(k^2, l', m'|n, l, m) = \int \bar{\Psi}_i(n, l, m, |\mathbf{r}|) \mathbf{r} \Psi_f(k^2, l', m', |\mathbf{r}|) d\mathbf{r} \quad (2)$$

and the quantum numbers l' and m' are obtained from the relations

$$\left. \begin{aligned} \Delta m &= 0, \pm 1, \\ \Delta l &= 1, 3, 5, \dots, \\ |m'| &\leq l'. \end{aligned} \right\} \quad (3)$$

In Table 1 are listed the various states of O_2^+ which are produced by photoionization in the wavelength range 1026 Å to 450 Å. The data for $X^2\Pi_g$, $a^4\Pi_u$, $A^2\Pi_u$ and $b^4\Sigma_g^-$ were obtained from COOK and METZGER.⁽⁶⁾ More recent studies of Rydberg series of excited states of $\text{O}_2(X^3\Sigma_g^-)$ by CODLING and MADDEN⁽⁷⁾ and YOSHINO and TANAKA⁽⁴⁾ have yielded appearance thresholds for the ion states $B^2\Sigma_g^-$ and $c^4\Sigma_u^-$.

TABLE 1. APPEARANCE THRESHOLDS FOR VARIOUS STATES OF O_2^+ AND THE MOLECULAR ORBITALS VACATED IN THEIR PRODUCTION BY IONIZATION OF $\text{O}_2(X^3\Sigma_g^-)$

Electronic state	Threshold (eV)	M.O. Vacated
$X^2\Pi_g$	12.08	$\pi_g 2p(3d\pi_g)$
$a^4\Pi_u$	16.1	$\pi_u 2p(2p\pi_u)$
$A^2\Pi_u$	16.8	$\pi_u 2p(2p\pi_u)$
$b^4\Sigma_g^-$	18.2	$\sigma_g 2p(3s\sigma_g)$
$B^2\Sigma_g^-$	20.3	$\sigma_g 2p(3s\sigma_g)$
$c^4\Sigma_u^-$	24.75	$\sigma_u 2s(3p\sigma_u)$

We computed the cross sections, using methods described previously,⁽¹⁾ for all transitions which produce the ion states given in Table 1, in the 2-centre Coulomb approximation. As expected, the results for the $\pi_u 2p$, $\sigma_g 2p$ and $\sigma_u 2s$ electrons do not differ significantly from those for the corresponding M.O.'s of $N_2(X^1\Sigma_g^+)$. The cross section for the photoionization of a $\pi_g 2p$ electron of $\text{O}_2(X^3\Sigma_g^-)$ as a function of the wavelength of the incident radiation is shown in Fig. 1. The curve has, in common with that of the $\sigma_g 2p$ electron, a peak at higher energies, due to the dominance of $l = 3$ continua.

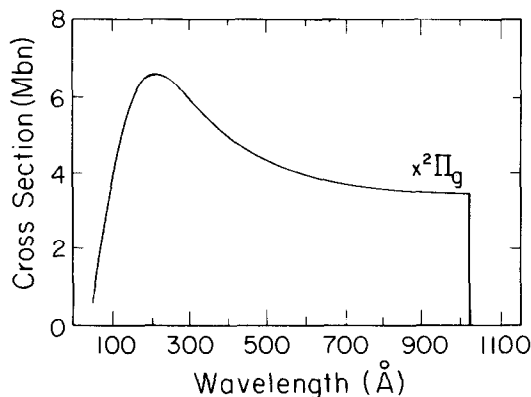


FIG. 1. Cross section for photoionization of a π_g^*2p electron of $O_2(X^3\Sigma_g^-)$ computed from equation (1) by the method described in the text.

In order to understand the differences in behaviour of the cross sections of the four M.O.'s so far considered, it is useful to consider the corresponding variations in the transition strengths for the various continua, as measured by the quantities $|\mathbf{M}(k^2, l', m' | n, l, m)|^2$. In Figs. 2-5 are shown these quantities, in atomic units and including degeneracy factors,

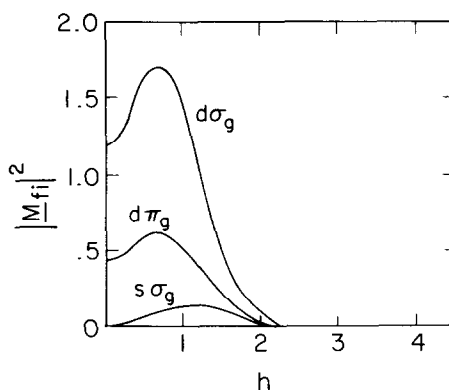


FIG. 2. Contributions to the photoionization cross section for a σ_u^*2s electron of $N_2(X^1\Sigma_g^+)$. (2-centre Coulomb approximation for final states in this and all subsequent figures. The results for the corresponding orbitals of O_2 are very similar. See text for interpretations in the case of O_2 .)

plotted against h , which is related to the kinetic energy k^2 and the internuclear separation by the equation $k^2 = 4h^2/R^2$ Rydbergs. For the σ_u^*2s and π_u^*2p initial states the same continua dominate throughout a great range of energies. In contrast, for the σ_g^*2p and π_g^*2p M.O.'s, transitions to those final states that are strongest at threshold cease to dominate at higher energies, where the matrix elements for $l = 3$ continua become large, though states with $l \geq 5$ are very weak.

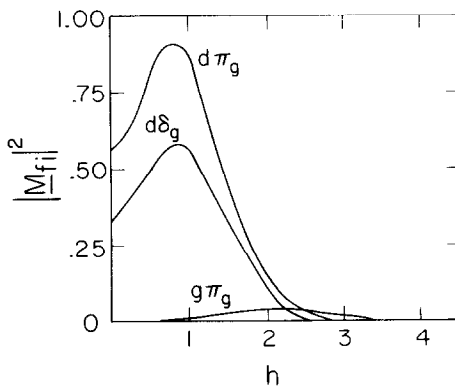


FIG. 3. Contributions to the photoionization cross section for a $\pi_u 2p$ electron of $N_2(X^1\Sigma_g^+)$.

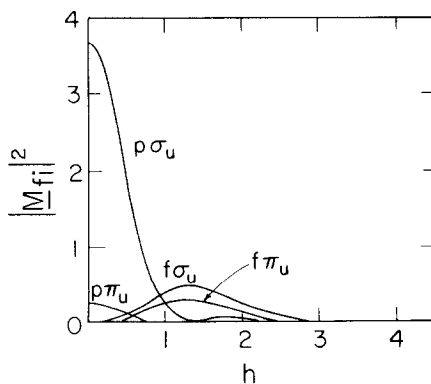


FIG. 4. Contributions to the photoionization cross section for a $\sigma_g 2p$ electron of $N_2(X^1\Sigma_g^+)$.

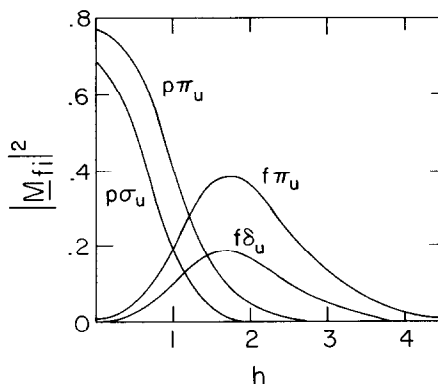


FIG. 5. Contributions to the photoionization cross section for a $\pi_g 2p$ electron of $O_2(X^3\Sigma_g^-)$.

These differences can be explained in terms of the relation between the first nodes of the various continuum waves and the distribution of the initial state, a factor which had been found important in determining the behaviour of many atomic cross sections.^(8,9) As shown in Figs. 4 and 5 the chief contributions to the cross sections for $\sigma_g 2p$ and $\pi_g 2p$ initial states are from transitions to p -states, whose first nodes for $h = 0$ are just inside the region where the bound state radial functions are appreciable. Thus cancellation occurs in the corresponding transition integrals as the energy increases. Further, at $h = 0$, the f -waves have their first nodes beyond the region of appreciable bound state density so that with increasing energy the corresponding transition integrals initially increase until $h \simeq 2$ whereupon cancellation causes them to decrease. In the case of $\pi_u 2p$ and $\sigma_u 2s$ initial M.O.'s, however, d -waves dominate at threshold and their first nodes are well beyond the high density regions of the initial states. As h increases, therefore, the transition integrals increase until $h \simeq 1$. Further, of the higher angular momentum continua only the $g\pi_g$ states contribute appreciably to the cross section for the $\pi_u 2p$ initial state. The low energy g -waves ($l = 4$) have first nodes at extremely large distances from the molecule and small amplitudes so that their transition integrals never attain such values which would cause a high energy peak in the cross section curve.

We also performed a preliminary calculation of the photoionization cross section of the 2π electron of $NO(X^2\Pi)$. Utilizing the small difference between the orbital exponents of the $2p$ electrons of N and O atoms in the L.C.A.O.-M.O. formulation of the 2π electron wave function^(10,11) we used an average value of 2.1125 for the Slater exponent. This gave the result 0.486 Mbn for the transition to the ground vibrational and electronic state of NO^+ when the Franck-Condon factor of WACKS⁽¹²⁾ was employed. This is close to the average experimental value of 0.47 Mbn for the wavelength range 1300–1340 Å.^(13,14)

RYDBERG SERIES IN THE $O_2(X^3\Sigma_g^-)$ ABSORPTION SPECTRUM

There have been many studies of the absorption spectrum of $O_2(X^2\Sigma_g^-)$. PRICE and COLLINS⁽¹⁵⁾ found some of the lower members of series which converge to the ion states $a^4\Pi_u$, $A^2\Pi_u$ and $b^4\Sigma_g^-$. The series converging to the third state was extended by TANAKA and TAKAMINE⁽¹⁶⁾ and higher members have since been reported by YOSHINO and TANAKA.⁽⁴⁾ Both of these sets of authors also studied series converging to the $B^2\Sigma_g^-$ state, the latter finding an additional weak series in both cases. Rydberg series have also been observed converging to the $c^4\Sigma_u^-$ state.⁽⁷⁾

From our preliminary calculations of the transition strengths for various initial M.O.'s and various continua, as shown in Figs. 2–5, we are led to suggest the Rydberg series of terms, with $O_2(X^3\Sigma_g^-)$ as lower state, given in Table 2. There are two reasons why our designations are not conclusive. One is that the potential energy curves of the states of the series are not known so that the effect of the Franck-Condon principle may be to make some of these band progressions weaker and to enhance the oscillator strengths of others whose corresponding continua are weak in the approximation we have used. Potential energy curves of many excited states of $O_2(X^3\Sigma_g^-)$ have been calculated by SCHAEFFER and HARRIS,⁽¹⁷⁾ but explicit electronic configurations were not given. Secondly, the effect of introducing the correct phase shifts into the continuum functions may drastically affect the relative transition strengths, though this is considered unlikely in the cases studied here.

TABLE 2. MAIN RYDBERG SERIES OF EXCITED STATES OF $O_2(X^3\Sigma_g^-)$ OBTAINED BY EXTRAPOLATING TRANSITION STRENGTHS OF THE CORRESPONDING LOW ENERGY CONTINUA

Series limit	Progression (upper states)	Terms	Initial n
$X^2\Pi_g$	$(\sigma_u 2s)^2(\sigma_g 2p)^2(\pi_u 2p)^4\pi_g 2p\ n p\sigma_u$	$^3\Pi_u$	4
	$(\sigma_u 2s)^2(\sigma_g 2p)^2(\pi_u 2p)^4\pi_g 2p\ n p\pi_u$	$^3\Sigma_u^-$	3
$a^4\Pi_u$	$(\sigma_u 2s)^2(\sigma_g 2p)^2(\pi_u 2p)^3(\pi_g 2p)^2\ n d\sigma_g$	$^3\Pi_u$	3
$A^2\Pi_u$	$(\sigma_u 2s)^2(\sigma_g 2p)^2(\pi_u 2p)^3(\pi_g 2p)^2\ n d\pi_g$	$^3\Sigma_u^-$	3
$b^4\Sigma_g^-$	$(\sigma_u 2s)^2\sigma_g 2p(\pi_u 2p)^4(\pi_g 2p)^2\ n p\sigma_u$	$^3\Sigma_u^-$	4
$B^2\Sigma_u^-$	$(\sigma_u 2s)^2\sigma_g 2p(\pi_u 2p)^4(\pi_g 2p)^2\ n p\pi_u$	$^3\Pi_u$	3
$c^4\Sigma_u^-$	$\sigma_u 2s(\sigma_g 2p)^2(\pi_u 2p)^4(\pi_g 2p)^2\ n d\sigma_g$	$^3\Sigma_u^-$	3
	$\sigma_u 2s(\sigma_g 2p)^2(\pi_u 2p)^4(\pi_g 2p)^2\ n d\pi_g$	$^3\Pi_u$	3
	$\sigma_u 2s(\sigma_g 2p)^2(\pi_u 2p)^4(\pi_g 2p)^2\ n s\sigma_g$	$^3\Sigma_u^-$	4

As far as is known to the author, no previous attempts have been made to classify the series converging to the states $a^4\Pi_u$ and $A^2\Pi_u$. If one of the $\pi_u 2p$ electrons of $O_2(X^3\Sigma_g^-)$ is promoted to the $n d\pi_g$ sequence we obtain $^3\Sigma_u^-$ terms which converge to $a^4\Pi_u$ or $A^2\Pi_u$ depending on the spin of the excited, and eventually ionized, electron. Using the data of MATZANUGA and WATANABE⁽¹⁸⁾ for the H , I and M , N terms first observed by PRICE and COLLINS,⁽¹⁵⁾ we obtain effective quantum numbers 1.90, 2.95, 1.89 and 2.77 respectively. If we assume for the M , N sequence an earlier member with effective quantum number 0.83, we expect a band around 2250 Å. This is sufficiently close to the possible position of the (0, 0) Schumann–Runge band that we are led to postulate that the well known $B^3\Sigma_u^-$ state of O_2 ⁽¹⁹⁾ is the first member of one of the above, or related, progressions which converge to either $A^2\Pi_u$ or $a^4\Pi_u$, but probably the former. The only reason for suspecting that this is not the case is that the quantum defect is around 2.2 which seems very high. In either case we are fairly confident that the progressions which have been observed belong to one of the two types given in Table 2, though the values of n for the individual terms cannot at present be ascertained.

Our results indicate that the progressions $\sigma_g 2p\ n p\sigma_u \leftarrow (\sigma_g 2p)^2$, which converge to the $b^4\Sigma_g^-$ states, should be quite strong, thus supporting this interpretation of these strong series by YOSHINO and TANAKA.⁽⁴⁾ However it is difficult to accept their interpretations of the weak series as $n s\sigma$ or $n d\sigma$ progressions because such states are not permitted by the selection rules. According to Table 2 the weak series are probably $n p\pi_u$ progressions. For the two main series converging to $c^4\Sigma_u^-$ the progressions $n d\pi_g$ and $n s\sigma_g$ were given by CODLING and MADDEN.⁽⁷⁾ Our results agree with the former classification but we expect the $n d\sigma_g$ progression to be stronger than the $n s\sigma_g$ sequence. However there is at present no other evidence to help decide which classification is correct.

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