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Evidence derived from angle-resolved electron spectroscopy for a new spectral series in the photoionization continuum of molecular oxygen

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Abstract. Angle-resolved photoelectron spectroscopy measurements on the O_2 molecule are reported, from which β-parameters and vibrational branching ratios have been calculated. The measurements were made with good optical resolution in the wavelength region 670–740Å, where several series converge to the b $^4\Sigma_g^-$ state of O_2^+. The application of the measurements to identifying resonant structure is discussed, and evidence presented for a new series converging to the b state.

1. Introduction

In view of its importance as an atmospheric molecule, there have been many experimental studies of the photoionization spectrum of molecular oxygen. Following the earlier studies by Price and Collins (1935), major spectroscopic investigations were carried out by Takamine and Tanaka (1941), Yoshino and Tanaka (1968), and more recently by Dehmer and Chupka (1975), with the result that the assignments for the most prominent series have been established. There is also a substantial body of theoretical data for neutral and ionic states (Beebe *et al* 1976, Marian *et al* 1982); methods for determining Franck–Condon (FC) factors in regions of autoionizing structure (Smith 1970, Eland 1980), and for determining the influence of underlying perturbing states (Nishitani *et al* 1984), have been published. Despite all this, much of the weaker autoionizing structure in the photon energy region between 16 and 18 eV, which is the primary interest of this work, remains unidentified. The electron configuration of the ground state of O_2^+ is

$$\mathrm{KK}(2\mathrm{s}\sigma_\mathrm{g})^2(2\mathrm{s}\sigma_\mathrm{u})^2(2\mathrm{p}\sigma_\mathrm{g})^2(2\mathrm{p}\pi_\mathrm{u})^4(2\mathrm{p}\pi_\mathrm{g})^2\ \mathrm{X}\ {}^3\Sigma_\mathrm{g}^-.$$

Removal of an electron from the outer orbital leaves the O_2^+ ion in its ground state X $^2\Pi_\mathrm{g}$ and removal of an electron from any of the inner orbitals, all of which are filled, yields doublet and quartet states. In particular we are concerned with the $2\mathrm{p}\sigma_\mathrm{g}$ electrons, which are responsible for the Rydberg series converging to the B $^2\Sigma_\mathrm{g}^-$ and b $^4\Sigma_\mathrm{g}^-$ states of the ion, and it is the series converging to the vibrational levels of the b state which dominate our region of interest. The so-called strong series (Takamine and Tanaka 1941) is thought to be associated with excitation of the $2\mathrm{p}\sigma_\mathrm{g}$ electron to an $n\mathrm{p}\sigma$ orbital (Namioka *et al* 1962), and the weak series with excitation to an $n\mathrm{p}\pi_\mathrm{u}$ orbital, although it has also been suggested that

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the weak series could be associated with excitation to $n\mathrm{s}\sigma$ or $n\mathrm{d}\sigma$ orbitals (Yoshino and Tanaka 1968). The weak series is very difficult to identify from a photoionization spectrum in which the yield of O_2^+ ions is measured (Dehmer and Chupka 1975), but can be identified in a photographic absorption spectrum.

It is now well established that the technique of photoelectron spectroscopy can be used with advantage in determining the origin of resonant structure, particularly when it is weak. Since it is a differential technique, it provides information on the intensity going into alternative decay channels as a resonance decays. When combined with an intense and continuous source of incident photons, such as synchrotron radiation, detailed information on a scale commensurate with the natural width of autoionizing lines can be obtained. Furthermore, the flexibility of tuning the incident photon energy to a resonance allows access to excited configurations of the neutral molecule, with the result that the vibrational branching ratios to the final ion state can be very different from those for the direct transition. This was shown some while ago for the oxygen molecule by Price (1968), who used radiation from a neon resonance lamp and found long vibrational progressions excited in the ion's ground state, as a result of the accidental coincidence between the neon resonance line and an autoionizing transition in the neutral molecule. The ability to exploit this feature using a continuum source can therefore be helpful in identifying weak structure.

Measurements of the photoelectron angular distribution parameter can also reveal the presence of weak structure, because of the sensitivity of this parameter to phase information in the outgoing waves. Great use of this has been made in recent years to highlight weak effects in the molecular photoionization continuum—see, for example, the review by Dehmer *et al* (1987). Later work on continuum–continuum coupling in the photoionization of CO_2 (Siggel *et al* 1993) made the further point that it is often necessary to measure both the dynamical variables, which are in this case the vibrationally resolved branching ratios and angular distribution parameters, to establish the presence of resonant behaviour. Bearing this in mind, this paper presents such data for oxygen, at a higher level of precision and detail than has previously been obtained for this molecule. In particular, we have focused our attention on some previously unidentified features in the absorption spectrum.

2. Experimental procedure

This work was carried out on a beamline at the Daresbury Synchrotron Radiation Source, using a 5 m normal incidence monochromator and an angle-resolving photoelectron spectrometer system. This system contained two hemispherical electron spectrometers equipped with multichannel detection at their exit planes. The analysers made measurements at 0° and 90° with respect to the principal E-vector of the incident radiation, and a three-mirror-type polarization analyser was used to measure the polarization of the incident radiation. Typically, the electron spectrometer resolution was 40 meV for the measurements presented here, and the optical monochromator resolution was 2 meV; measurements were taken in photon energy steps of 2 meV. The calibration procedure and further details of the electron spectrometer system are to be found in the papers by West *et al* (1996) and Parr *et al* (1982) respectively; the monochromator has been fully described by Holland *et al* (1989). The analysis of the data was carried out in a similar way to that used for our earlier work on CO_2 (West *et al* 1996); it was simplified here by the fact that there is only one vibrational mode. As in our earlier work, the spin–orbit splitting was not resolved and an allowance was made for it in the fitting procedure.

3. Results

Following the analysis procedures to which we refer above, we have obtained branching ratios and angular distribution parameters for the $v^+ = 0$–16 members of the O_2^+ X $^2\Pi_g$ ground state in the region from 670–740 Å; as in our previous work, the branching ratio is defined as the intensity of a particular vibrational member divided by the sum of all the measured intensities of the vibrational members of the electronic state. This is in effect a relative partial cross section, within a particular electronic state. Although it would be desirable to give partial cross sections, these would have to be normalized to a total cross section obtained from a separate experiment, preferably one with similar resolution to that being used here. In addition, we would need to be certain that the gas pressure in our sample region remained constant throughout the duration of the experiment.

In this paper we do not present all our data, preferring instead to show examples where particular features are readily identifiable. Since all the Rydberg series we shall be discussing converge to the vibrational levels of the b $^4\Sigma_g^-$ state of the O_2^+ ion, we shall adopt an abbreviated notation for them: for example, 5_0 means the Rydberg member whose principal quantum number is 5, converging to the $v^+ = 0$ level of the b $^4\Sigma_g^-$ ion state.

3.1. The Rydberg series

Our data show clearly the strong and also the weak series converging to the b $^4\Sigma_g^-$ state of the O_2^+ ion. These lines can autoionize into the X $^2\Pi_g$ and a $^4\Pi_u$ continua, and, for lines whose wavelengths are less than 723 Å, into the A $^2\Pi_u$ continuum. Our experiment selects out the fraction of autoionization into the X $^2\Pi_g$ continuum. In figures 1 and 2, the branching ratios for $v^+ = 1$, 4, 7, 8 and 9 are shown, together with the positions of the Rydberg series assigned by Yoshino and Tanaka (1968). It can be seen that there are features, either peaks or shoulders, which correspond to members of both strong and weak series, though not all members appear in both branching ratios. This is generally true for all the branching ratio measurements: a particular series member will appear strongly in one branching ratio, but not necessarily in others, as a consequence of channel interaction. Rather than present all the spectra here, we show in figure 3 branching ratios plotted as a function of the final vibrational level of the ion, for five prominent autoionizing lines in the absorption spectrum, the $5_{0,1,2}$ and $6_{0,1}$ members, chosen because they are prominent in the absorption spectrum and relatively free of overlapping structure. In this and the following discussion these symbols will refer to the so-called strong series, identified as (S) in the figures.

From figure 3 it can be seen that there are two regions of peak intensity, centred around $v^+ = 1$ and $v^+ \sim 7$, which influenced our choice of data for figures 1 and 2. Also, we have calculated the associated FC factors, assuming that the molecular constants for the autoionizing level are the same as those for the ion state to which it converges, in this case the b $^4\Sigma_g^-$ state. The results are shown in figure 4; without an accurate knowledge of the Fano q parameter it is difficult to separate the resonant and direct contributions to the cross section in the experimental data, so we do not show the calculated FC factors for direct ionization to the ion ground state. We make the following observations from the data contained in figures 1–4.

(1) The bimodal structure predicted for (0–1, 1–v^+) transitions appears for all the lines except 6_1, which follows the prediction for a (0–0, 0–v^+) transition.

(2) The prediction for (0–2, 2–v^+) transitions is scarcely reflected in the 5_2 line.

(3) The peak predicted for $v^+ = 4$ appears only for the 6_1 line; for the others, the data

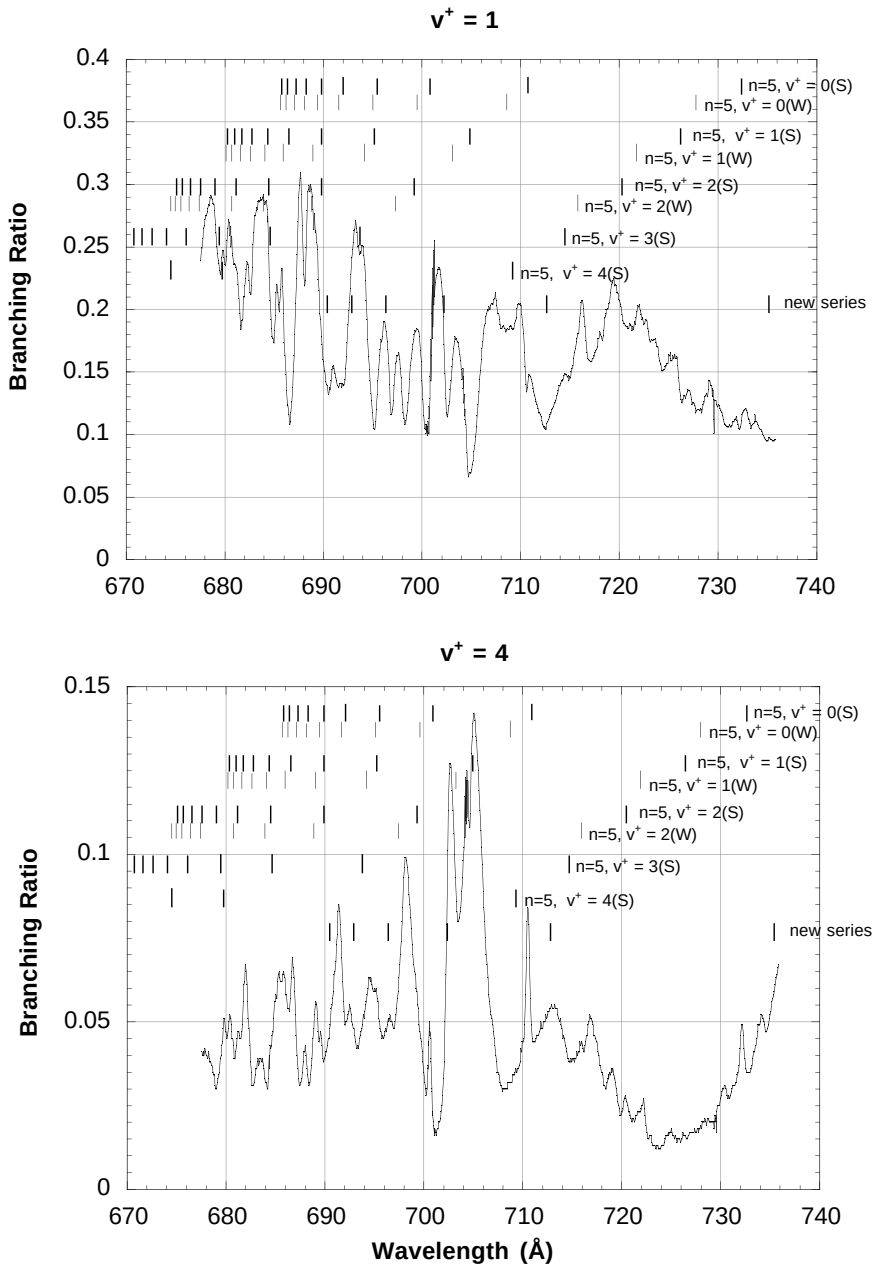

Figure 1. Branching ratios for $v^+ = 1$ and $v^+ = 4$.

peak around $v^+ = 1$.

(4) The experimental data are less 'peaked' than the FC calculations predict, with intensity still appearing in regions where the calculations predict $\sim$0, particularly for $v^+ > 13$.

The fact that the data show strong population of the $v^+ = 1$ ion level indicates that there is a substantial non-resonant contribution, which agrees with both FC calculations and a

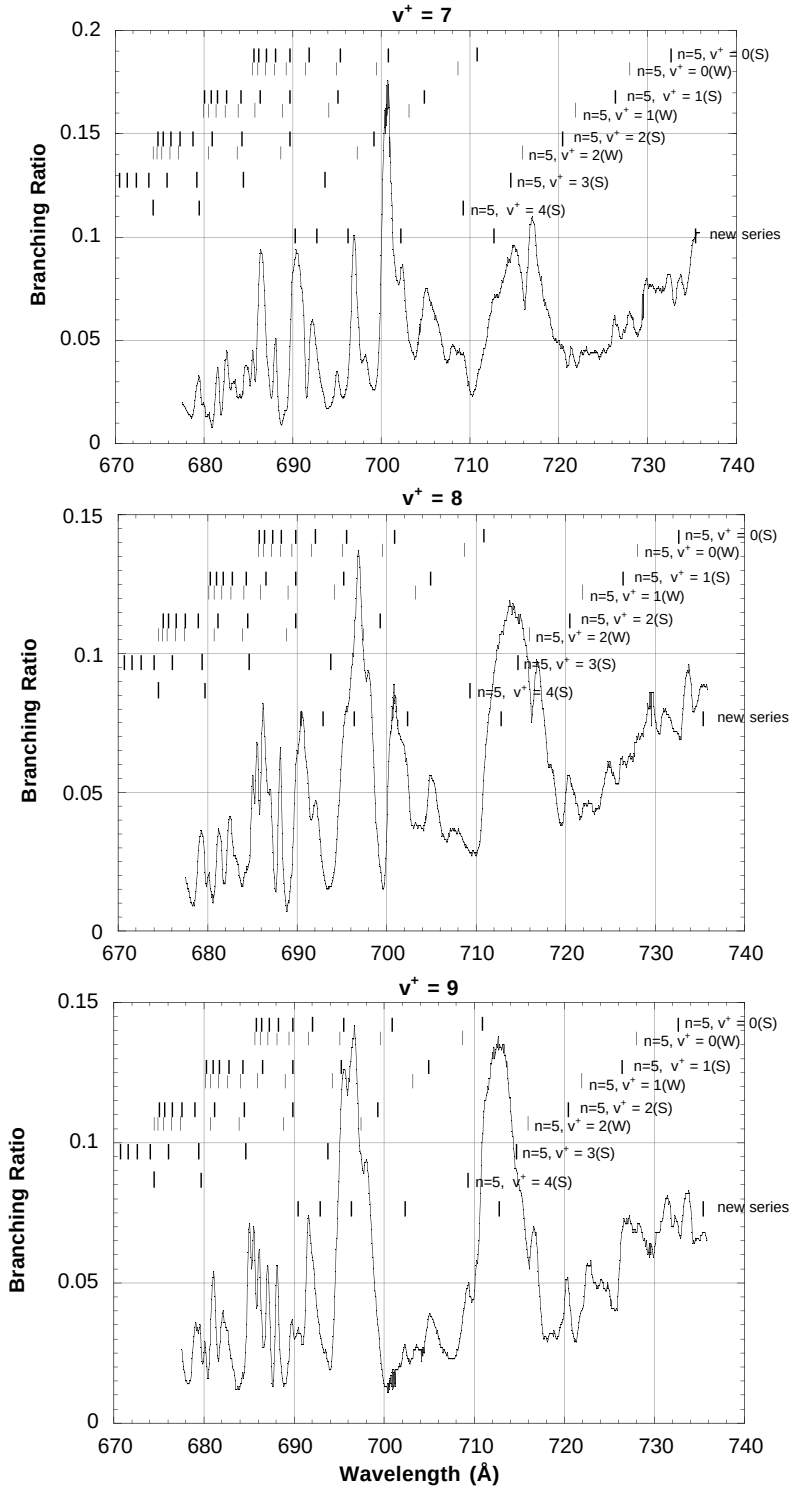

Figure 2. Branching ratios for $v^+ = 7$, 8 and 9.

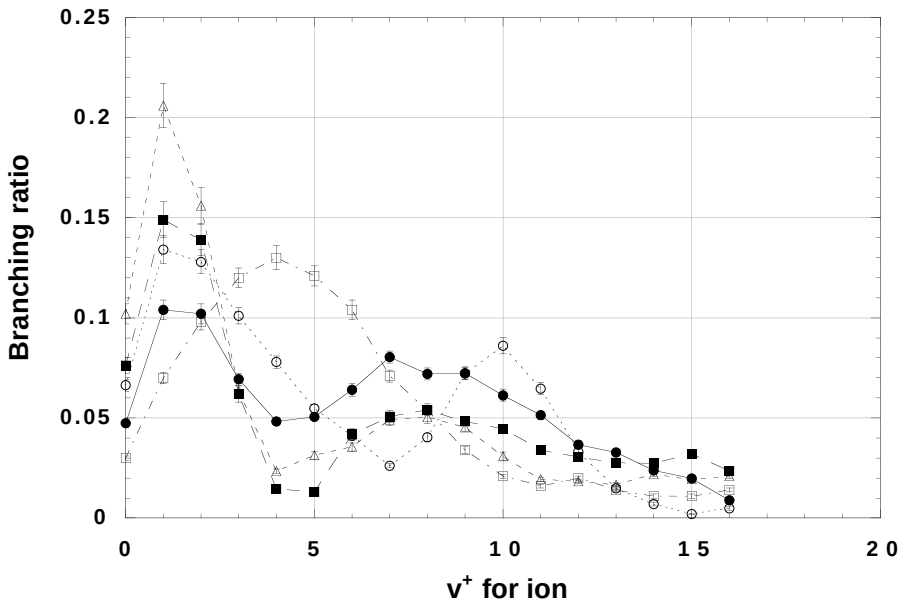

Figure 3. Branching ratios as a function of final ion vibrational level for some prominent autoionizing lines. 5_0 ——●—— ; 5_1 – – –■– – – ; 5_2 - - - -△- - - - ; 6_0 ·····○····· ; 6_1 — · —□— · —.

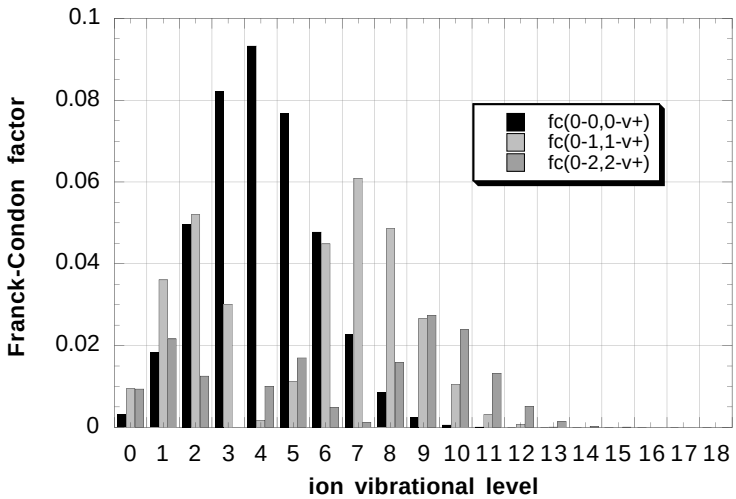

Figure 4. FC factors to the O_2^+ ground state.

non-resonant photoelectron spectrum. The spectral lines we have chosen for the comparison with calculation were selected because of their relative freedom from overlapping structure. The fact that there is a lack of detailed agreement with our FC calculations reflects the non-FC dynamics of the process and, possibly, the effects of unresolved, underlying states. We can conclude, therefore, that transitions to levels between $v^+ = 4$ and 7 are broadly to be expected on the basis of the FC calculations, with transitions to $v^+ = 1$ arising from

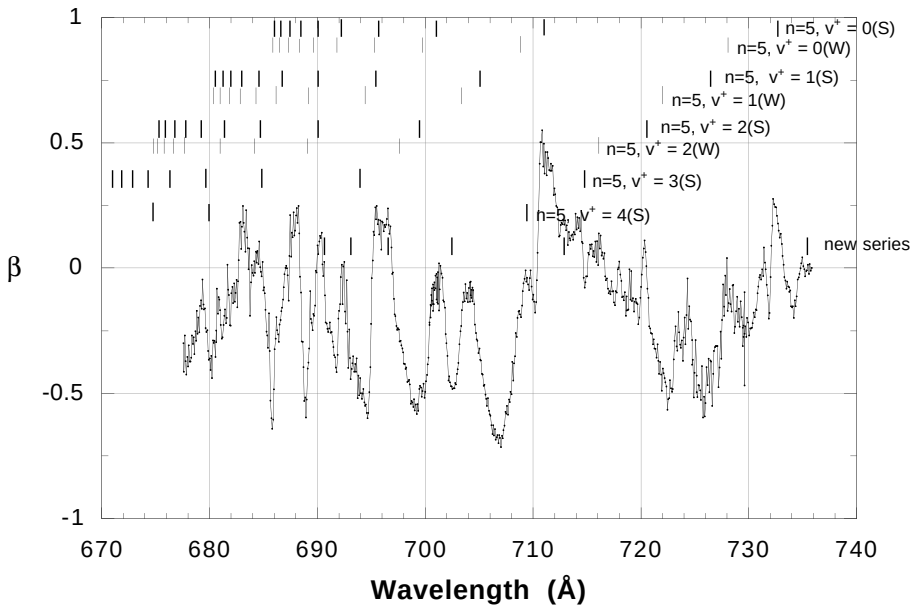

Figure 5. β for $v^+ = 5$.

direct ionization. The 6_1 line is an interesting case; for all the branching ratios shown in figures 1 and 2 this peak is clearly seen as a broad feature, much the same as observed in the photoionization spectrum of Dehmer and Chupka (1975), who suggest that it is partially predissociated; the fact that it appears in their ion pair spectrum supports their conclusion. We note from the $v^+ = 4$ data in figure 1 that the 5_0, 6_0 and 7_0 resonances are not only narrow but also clearly seen, as distinct from the other data in figures 1 and 2 where it is more difficult to identify them despite the fact that the branching ratios for $v^+ = 1$ and 7 in particular are larger. In the case of the $v^+ = 1$ data we conclude that the 5_0 and 6_0 resonances are superimposed on a large direct ionization component, as might be expected; for the $v^+ = 7$, 8 and 9 spectra in figure 2 it would appear that they are overlapped by other structure. The 7_0 resonance seems anomalous; it is located near a minimum in the $v^+ = 1$ and 9 spectra but appears strongly in the $v^+ = 7$ and 8 spectra. The problems with a comparison of this kind, and the application of the Smith model, have been outlined before (Eland 1980). First, the resonances can decay via dissociative channels which do not produce ions; second, our inability to resolve underlying structure will frustrate any attempt to make a detailed analysis based on a straightforward FC model. Nevertheless we have been able to make some general observations.

We have considered so far only the strong series, members of which are readily identifiable in the $v^+ = 4$–7 and $v^+ = 10$–14 branching ratios. Members of the weak series can be identified in most of these spectra, either as peaks or shoulders. The β-parameters also show structures which can be associated with the weak series; in figure 5 the β-parameters for $v^+ = 5$ are shown, where features attributable to the weak resonances are evident, bearing in mind that the profile for β may not be the same as an absorption peak so a peak in the β-value may be displaced from the resonance positions shown. We may use the values of the β-parameters to give a clue to the assignment of the series. The transition we are observing is from the X $^3\Sigma_u^-$ state of O_2 to the X $^2\Pi_g$ state of the O_2^+

ion. To give some idea of what would be expected for the angular distribution parameter, we base the following on angular momentum transfer theory (Dill 1973), of which we give an outline below. The momentum transfer $\boldsymbol{j}_t$ is given by the vector equations

$$\boldsymbol{j}_t = \boldsymbol{J}_{\mathrm{ion}} - \boldsymbol{J}_A \tag{1}$$

which is the difference between the atom momentum $\boldsymbol{J}_A$ and the ion momentum $\boldsymbol{J}_{\mathrm{ion}}$, or alternatively by

$$\boldsymbol{j}_t = \boldsymbol{\ell}_e - \mathbf{1} \tag{2}$$

which gives the difference between the angular momenta of the electron and photon. Since we do not resolve the spin–orbit splitting of the ion in our experiment, equation (1) becomes

$$\boldsymbol{j}_t = \boldsymbol{J}_{\mathrm{ion}} + \boldsymbol{s} - \boldsymbol{J}_A \tag{3}$$

where we combine the unresolved spin of the electron with that of the ion. For the $^2\Pi_{3/2}$ state of the ion, therefore, the allowed values of $\boldsymbol{j}_t$ are **2** and **1**. The parity transfer equations are

$$\pi_t = \pi_A \cdot \pi_{\mathrm{ion}} \tag{4}$$

or

$$\pi_t = -(-1)^{\ell_e}; \tag{5}$$

where ℓ_e is the numerical value of the angular momentum of the electron. When $\boldsymbol{j}_t$ and π_t are both odd or even, the transition is said to be parity favoured; otherwise it is parity unfavoured.

Considering now our case for the oxygen molecule, the direct transition into the continuum is represented by

$$\mathrm{O_2\ X\ ^3\Sigma_g^- + h\nu \rightarrow O_2^+\ X\ ^2\Pi_g + e^-}.$$

This yields $\pi_t = (-1) \cdot (1) = -1$, which means that transitions for which $\boldsymbol{j}_t = \mathbf{2}$ are parity unfavoured, and are parity favoured for $\boldsymbol{j}_t = \mathbf{1}$. In the case of the $^2\Pi_{1/2}$ state of the ion, $\boldsymbol{j}_t = \mathbf{1}$ which is parity favoured. Thus for the direct transitions we expect a mixture of parity favoured and parity unfavoured ($\beta = -1$) transitions, yielding the possibility of β-values over the entire range from -1 to 2, the exact values depending on the partial cross sections for the parity favoured and unfavoured channels. In our case, however, we are interested in ionization via Rydberg levels converging to the b $^4\Sigma_g^-$ state. Taking this as a two-step process, for the strong series the first step is the excitation of a $2\mathrm{p}\sigma_g$ electron to an $n\mathrm{p}\sigma_u$ $^3\Sigma_u^-$ level, followed by autoionization which can be represented by

$$(2\mathrm{p}\sigma_g)(2\mathrm{p}\pi_u)^4)(2\mathrm{p}\pi_g)^2\, n\mathrm{p}\sigma_u \rightarrow (2\mathrm{p}\sigma_g)^2(2\mathrm{p}\pi_u)^4(2\mathrm{p}\pi_g) + \epsilon\sigma_g.$$

For the first step, using equations (2) and (5), $\boldsymbol{j}_t = \mathbf{1}$ and $\pi_t = -1$, so this is parity favoured; in the second step ($^3\Sigma_u^- \rightarrow^2 \Pi_g$), from equations (1) and (5), $\boldsymbol{j}_t = \mathbf{1}$ and $\pi_t = -1$, also parity favoured. For the weak series the $2\mathrm{p}\sigma_g$ electron is being excited to an $n\mathrm{p}\pi_u$ $^3\Pi_u$ level, so $\boldsymbol{j}_t = 0$ and $\pi_t = -1$, which is parity unfavoured, and for the decay $\boldsymbol{j}_t = 0$ and $\pi_t = 1$ which is parity favoured. In summary, autoionization via the state with Σ symmetry has only parity favoured components, whereas autoionization via the Π state should contain a mixture of parity favoured and unfavoured components. We note that in figure 5 the β-parameters for the strong series members do tend, in general, to be larger and around zero or positive in comparison to those for the weak series, which tend to be negative. In table 1 we show the average β-values for the same set of strong series members we have considered above, and the corresponding weak members. The results are somewhat mixed,

Table 1. Average β-values β_{avge} for the prominent strong (S) and weak (W) lines; error in $\beta \pm 0.05$.

Line	5_0 (S)	5_0 (W)	5_1 (S)	5_1 (W)	5_2 (S)	5_2 (W)	6_0 (S)	6_0 (W)	6_1 (S)	6_1 (W)
β_{avge}	−0.2	−0.36	−0.42	−0.35	−0.41	−0.32	−0.082	−0.31	−0.12	−0.35

with the 5_0, 6_0 and 6_1 members following the pattern suggested for figure 5. We cannot therefore confirm that our data are consistent with the assignment of the strong series as $^3\Sigma_u^-$, and the weak series as $^3\Pi_u$, but the data in figure 5 and table 1 show a tendency in this direction. It would follow, therefore, that the alternative suggestion that the weak series could correspond to excitation to $ns\sigma$ or $nd\sigma$ orbitals, which would have Σ symmetry, would be less likely. Our analysis must be regarded as speculative, in view of the presence of overlapping structure in these spectra, much of which remains unassigned. Furthermore, it makes the assumption that the Born–Oppenheimer approximation is valid, i.e. that there is no interaction between vibrational and electronic motion.

3.2. The new series

As we have pointed out above, there are many features in the photoionization spectrum of O_2 which remain unidentified, the main difficulty being that they are strongly overlapped. There are however some features which stand out quite clearly, namely the broad peaks at 735 and 712.5 Å, the second of these being substantially less broad than the first, as would be expected if they are indeed members of a series. These are seen clearly in Dehmer and Chupka's spectrum; they also appear clearly in the photoionization efficiency curves and fluorescent yield spectra of Holland *et al* (1993). The 712.5 Å peak was also noted by Tabché-Fouhaile *et al* (1981), who stated that it decays by fluorescence to both the a- and X-states. By taking these two peaks as the first members of a Rydberg series converging to the $v^+ = 0$ level of the b $^4\Sigma_g^-$ state of the ion, the positions of the next four members have been calculated, and are shown on all the figures. In particular, we note features in the branching ratio for $v^+ = 14$ (figure 6), and the β-parameters for $v^+ = 3$, 4 and 11 (figure 7) that can definitely be associated with the higher members of this series. In some cases a peak in the partial cross section appears at a slightly different position from the resonance position, for example the first member of the series in figure 6; also our experimental peak is much narrower than the rather broad peak seen in the total photoionization spectrum of Dehmer and Chupka. This comes about because the branching ratios respond individually to the resonance, i.e. their partial cross sections vary with the final ion state vibrational quantum number. This is why more structure can be seen in the partial cross section or branching ratio data than in a total cross section spectrum, which is the sum of the partial cross sections. We observed this effect previously in our CO_2 data set (West *et al* 1996). In the case of the β-parameters, peaks or dips will not necessarily coincide with the absorption peak position, depending upon the degree of interaction of the resonance with the continuum and the associated phase changes between the outgoing waves in the region of the resonance. We assume, however, that the wavelength position of the resonance is the one obtained from the total absorption cross section.

In figure 8 we show the β-parameters and branching ratios for the members of this series for each of the ion vibrational levels. The branching ratios show a bimodal structure similar to that seen in figure 3, with a varying contribution from direct ionization to the ion $v^+ = 1$ level, as might be expected since the resonances, judging from the first two

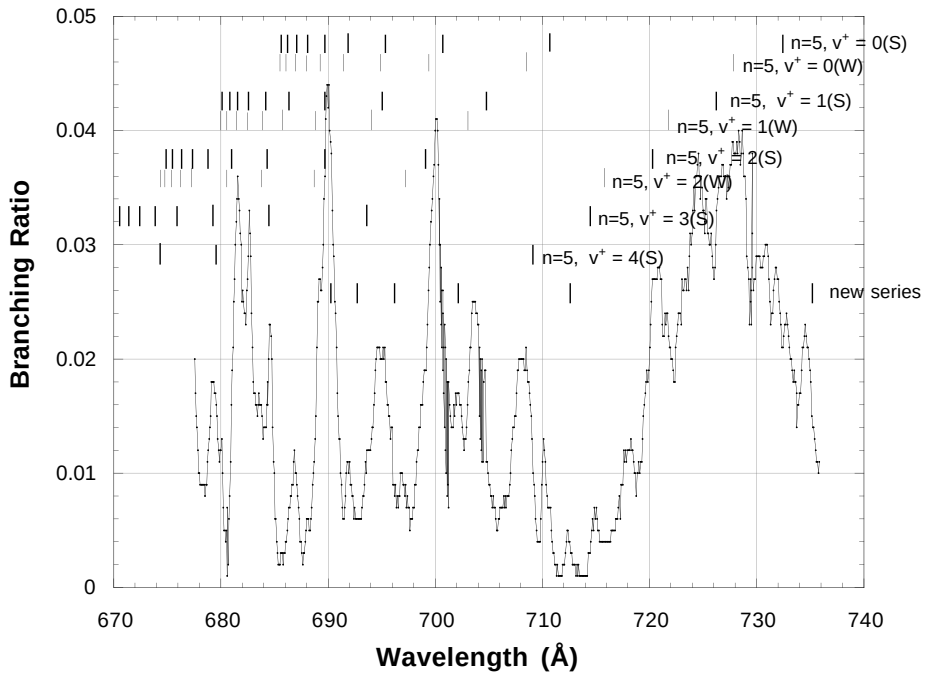

Figure 6. Branching ratio for $v^+ = 14$.

members, are broad and sit on top of a large background. Decay to levels around $v^+ = 8$ appears more prominent for this series in comparison to the Rydberg members we selected above; β-values tend to be negative, and their averages are given in table 2, from which we deduce that there is a significant parity unfavoured contribution to the transitions. The width of the resonances would indicate that interaction with dissociative levels is taking place. A recent calculation by Krauss (1997) shows that interloper states associated with excitation of two electrons exist in the energy region of interest here; in particular a $^3\Pi_u$ state resulting from excitation of both a σ_g and π_u electron have the required symmetry to interact with a number of Rydberg states in the 17 eV region. Rydberg-valence states have already been calculated for the case of series converging to the ground state of the ion (Yoshimine *et al* 1976, Buenker *et al* 1976), and the interlopers of interest in this work would be the doubly excited analogues of those. Krauss points out that they are highly repulsive, with a broad region of FC overlap, gaining oscillator strength from their interaction with the Rydberg states. Because they are embedded in the Rydberg series an accurate calculation is complicated, but they certainly have the right characteristics and binding energies to explain the features we see in our experiment.

4. Conclusions

The high resolution data for O_2 photoionization shown here indicate that the effects of autoionization can be explained by the separation of the transitions into channels which are characterized by the angular momentum transfer components. Accessing parity unfavoured channels through autoionization processes appears to depress the value of the β-parameters in the region of the autoionization and is suggestive of the nature of the intermediate

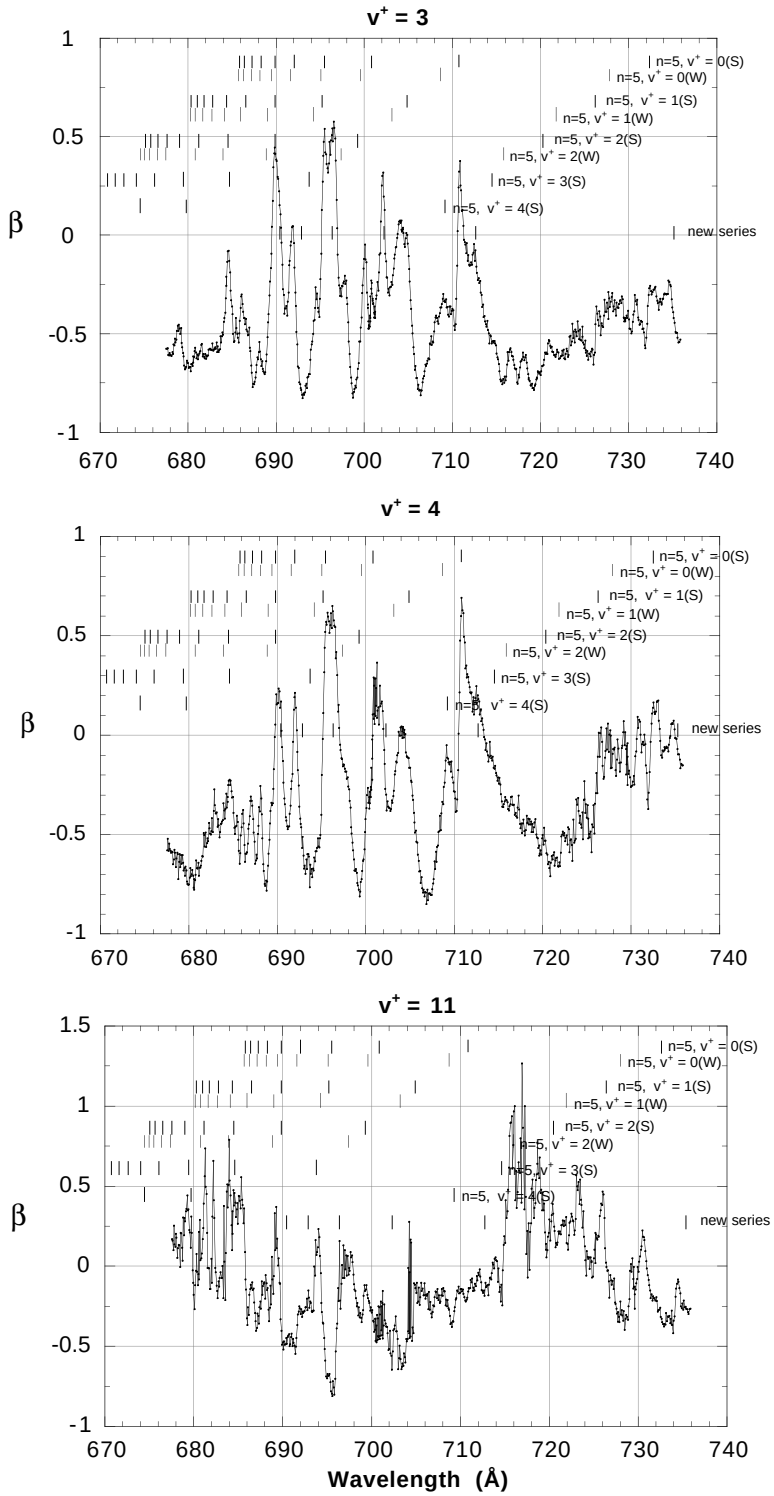

Figure 7. β for $v^+ = 3$, 4 and 11.

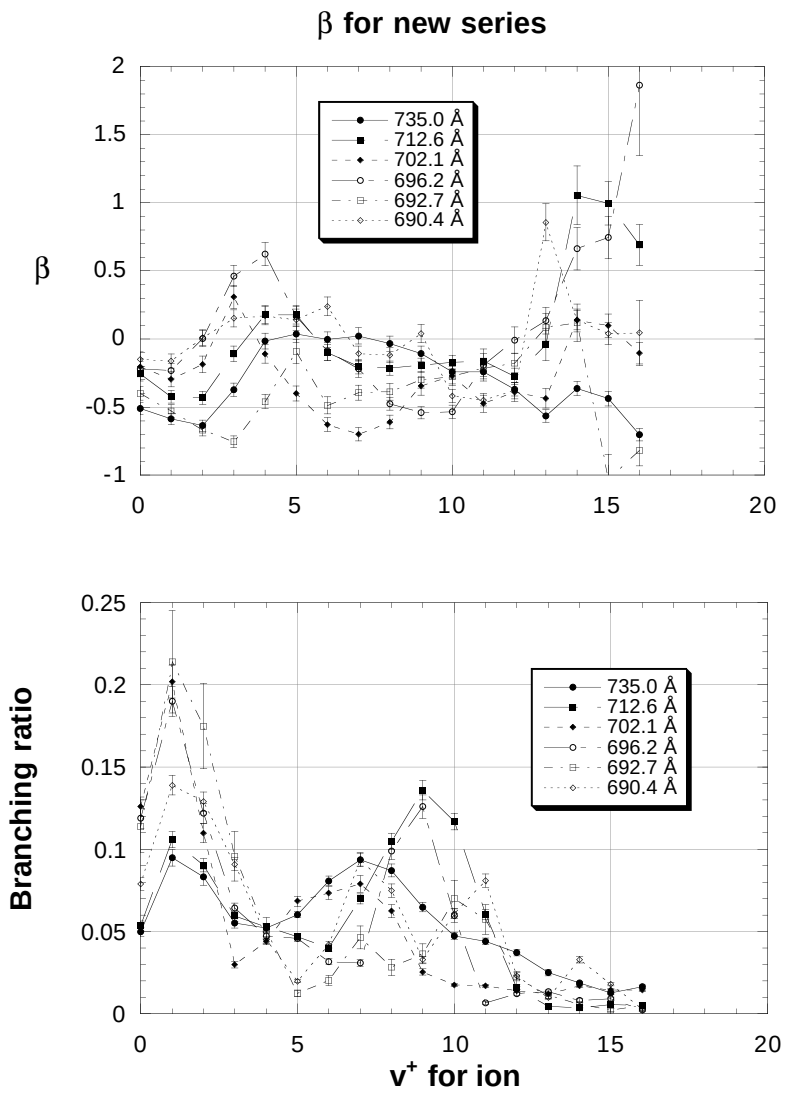

Figure 8. New series β-parameters and branching ratios as a function of the final ion vibrational level.

Table 2. Average β-values β_{avge} for the new series; error in β ± 0.05.

Line (Å)	735.0	712.6	702.1	696.2	692.7	690.4
β_{avge}	−0.26	−0.18	−0.32	−0.14	−0.48	−0.074

state. The study of vibrationally resolved data shows that the effects of autoionization are vibrationally dependent and lead to the production of ions in higher vibrational states. The analysis of the β-parameter data indicates the presence of additional heretofore undesignated transitions in molecular oxygen that are due to double electron excited states that couple to Rydberg states in this energy region. It is established that high resolution angle resolved

photoelectron spectra can be used as an aid in ascertaining the nature of broad features in the photoionization cross section of oxygen.

Acknowledgments

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