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An optical–optical double-resonance study of the Rydberg states of O2. II. The np and nf (ungerade) states excited via single-rotational levels of the b 1Σ0g+ valence state
A. Marica Sjödin, Trevor Ridley, Kenneth P. Lawley, and Robert J. Donovan

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An optical–optical double-resonance study of the Rydberg states of O$_2$. II. The $np$ and $nf$ (ungerade) states excited via single-rotational levels of the $b^1\Sigma^+_0$ valence state

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The $np$ ($n=3–10$) and $nf$ ($n=4–9$) Rydberg states of O$_2$ converging on $O_2^+ + X^2\Pi_{1/2,3/2}$ and $X^2\Sigma_{3/2,5/2}$ have been studied between 75 000 and 99 900 cm$^{-1}$ using optical–optical double resonance with multiphoton ionization. Three-photon excitation from single rotational levels of the initially excited $b^1\Sigma^+_0$ valence state was used to access these states. The $nf$ states show a strong tendency towards $(\Omega,\omega)$ coupling for all values of $n$, whereas the $np$ states appear to be best described by $(\Lambda,S)$ coupling for $n=8$. The intensities of some of the $5f$ bands are anomalously high due to accidental resonances with the $3s\,d^1\Pi_{1/2}$ Rydberg state at the two-photon level. © 2003 American Institute of Physics. [DOI: 10.1063/1.1566949]

I. INTRODUCTION

In a companion paper, we report the use of optical–optical double resonance with resonance enhanced multiphoton ionization (OODR/REMPI) to excite gerade $ns$ and $nd$ Rydberg states of O$_2$ using two-photon excitation from single rotational levels of the metastable $b^1\Sigma^+_0$ valence state in a $(1\!+\![2'+1'])$ excitation pathway (the OODR notation has been described previously). We now apply the same technique to excite ungerade $np$ and $nf$ Rydberg states using three-photon excitation from single rotational levels of the $b^1\Sigma^+_0$ state in a $(1\!+\![3'+1'])$ excitation pathway.

Reaching ungerade states from the gerade $b^1\Sigma^+_0$ state requires an odd number of photons. A few, short, vibrational progressions of $np$ Rydberg states have been identified for $n=3–4$ in a range of one-photon absorption experiments from the $X^3\Sigma^+_g$ and $a^1\Delta_{2g}$, and $b^1\Sigma^+_g$ states and in (3+1) REMPI experiments from the $X^3\Sigma^+_g$ state. By photolyzing $O_3$, Collins et al. were able to prepare O$_2$ in the $a^1\Delta_{2g}$ state, virtually in the absence of the $X^3\Sigma^+_g$ state, and hence were able to observe $np$ series up to $n=10$. In addition, they also tentatively identified some $nf$ series where $n=4–9$. However, these bands were generally broad and in some cases probably represent unresolved components based on the two spin–orbit components of the core. One-photon transitions from the $X^3\Sigma^+_g$ state to $v=0$ of the $4f$ complex have also been reported, and eight states with sharp structure were rotationally analyzed.

The $l=0$ part of the $O_2$ spectrum has been much studied, but it has been difficult to interpret because of strong Rydberg–valence interactions which predissociate and shift the low-$n$ Rydberg states. While the effects of such inter-

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this ground-state depletion are described in Sec. III E.

A further disadvantage of the technique is that the peaks are power broadened as a consequence of the high-power densities that are required to excite a nonresonant three-photon transition. Previous work with our experimental arrangement has demonstrated that the observed maximum of a signal is shifted towards higher energy as the power broadening increases. Comparisons with the known $3p f 1\Sigma_{0}^{+}$ state band positions indicate that our results overestimate the energy by up to 10 cm$^{-1}$ even after calibration. Thus all of the transition energies quoted here are subject to a similar offset.

In a companion paper, experimental results showed that the 3$s$ and 3$d$ states are best described by ($\Lambda$,S) coupling, while ($\Omega$,$\omega$) coupling becomes more appropriate as $n$ increases. Those results also highlighted two criteria that were crucial for the observation of strong (2+1) REMPI signals from the essentially singlet $b^3\Sigma_{0}^{+}$ state. First, strong transitions are observed to states which are singlet in the ($\Lambda$,S) coupling scheme or are linear combinations of equal weights of singlet- and triplet-spin states in the ($\Omega$,$\omega$) coupling scheme (the remaining states being pure triplets in this scheme). Second, it was shown that strong transitions are only observed to states which are not predissociated. This was exemplified by the 4$s$ and 5$s$ states where only very weak transitions were observed to the former, which are predissociated with a linewidth of $\sim$6 cm$^{-1}$, whereas strong transitions were observed to the latter, which have linewidths of $\leq$2 cm$^{-1}$. The same criteria will be used to interpret the (3+1) REMPI spectra from the $b^3\Sigma_{0}^{+}$ state recorded in the present study.

II. EXPERIMENT

The pump and probe photons were produced by two independently tunable dye lasers (Lambda Physik FL 3002 and Lambda Physik FL 2002) pumped by a XeCl excimer laser (Lambda Physik EMG201MSC). The (0,0) band of the $b^3\Pi$ transition, at 13 118.0 cm$^{-1}$, was pumped using R700. The probe photons for the (1+[3$'$$+$$'$]+1$'$) scheme were generated using the dyes DMQ, QUI, DPS, S3, and C47 to cover the region 345–485 nm. The counterpropagating pump and probe laser beams were focused to an overlapping point in a differentially pumped ionization chamber using lenses of focal length 6 cm and intersected, at 90°, the pulsed molecular beam generated using a backing pressure of 600 Torr of O$_2$. The resulting ions were ejected into a linear time-of-flight mass spectrometer, and the ion current from the microchannel plate detector was processed by a boxcar integrator and stored on a PC.

The wavelength of the probe laser was calibrated by simultaneously recording the neon optogalvanic spectrum. However, the main source of error in the measurements was the power broadening, discussed above, which results in the quoted experimental transition energies being up to 10 cm$^{-1}$ higher than the true values.

With the possible exception of $v=0$, 1, and 2 of the 4$f$ states, the observed vibronic bands could not be fully rotationally resolved and may be blends of two or three lines (e.g., $S$ and $T$ branch lines). Hence term values for the observed Rydberg states could not be obtained. The data presented are therefore, strictly, transition energies.

III. RESULTS AND DISCUSSION

A. Overview

Figure 1 shows the (1+[3$'$$+$$'$]+1$'$) OODR/REMPI spectrum over the range 75 000–86 000 cm$^{-1}$. In this spectrum, and all of those shown in this work, the intermediate state $b^3\Sigma_{0}^{+}$ ($v=0, J=0$) is optically pumped from the ground state. The spectrum is dominated by the well-known 3$'$–5$'$, 5$'$–7$'$, 7$'$–9$'$ vibrational progression of the $3p f 1\Sigma_{0}^{+}$ state. In this progression, each vibronic band [full width at half maximum (FWHM) $\sim$30 cm$^{-1}$] is comprised of unresolved $R$ and $T$ branches which are separated by 17 cm$^{-1}$, but are blended as a result of power broadening. Previous VUV absorption studies have shown that these bands have well-resolved rotational structure with sharp lines.

The $v=0$ bands of the other two singlet $3p$ Rydberg states in ($\Lambda$,S) coupling, $3p ^{1}\Pi_{1u}$ and $3p e ^{1}\Delta_{2u}$ states, are only seen very weakly in the spectrum shown in Fig. 1. The $v=1$ level of the $3p e ^{1}\Delta_{2u}$ state is hidden by one of the broader features which result from one-color four-photon transitions from the ground state to $v=0$, 1, and 2 of the 3$d$-state cluster.$^{17,18}$

The OODR/REMPI spectrum recorded by scanning $\nu_{probe}$ between 24 500 and 29 100 cm$^{-1}$ is shown in Fig. 2. The spectrum in Fig. 2 is shown in expanded form and rescaled to give the (1+3$'$) four-photon energy, in Figs. 3 and 4. As Fig. 4 is a composite of two spectra, neither of which is power normalized, only a broad overview of the relative intensities of the peaks can be obtained.

The bands shown in Fig. 2 are observed via several different excitation pathways. Most of the broad signals are caused by (3$'$$+$$'$)+1$'$ transitions from the $X^1\Sigma_{g}^{+}$ ground state to $3p$ Rydberg states.$^{13}$ The $3p f 1\Sigma_{0}^{+}$ vibrational progression is seen strongly in this $\nu_{probe}$ region via (1+[(2$'$+1)+1$'$]) transitions, in which one pump and two
FIG. 2. OODR/REMPI spectrum of O₂ over the range ν₂, = 24 400–29 000 cm⁻¹. The energy scale shows probe energy rather than total energy in order to illustrate the occurrence of different excitation schemes. The 3s d⁻¹ Π₁,₂, (ν = 0–2) bands are seen via a (1+[(2')+2']) scheme, the 3p f⁻¹ Π₂,₃, (ν = 0,1,3,4) bands via a (1+([2']+1')) scheme and the 5f states via a (1+[(3')+1']) scheme, all excited via b⁻¹ Σ₄, (ν = 0, J = 0). Various 3p Rydberg states (starred) are observed via a (3'+1') scheme from the X³Σ₁ₙ state. The 3s C⁻¹ Π₄, (ν = 2) band (+) is seen via (1+[(2')+2']) ionization.

Probe photons coherently excite a three-photon transition from the b⁻¹ Σ⁺₀, state. The ν = 0 levels of the 3p⁻¹ Π₁,₂, and 3p e⁻¹ Δ₂, states, indicated in Fig. 3, are observed very weakly by the same excitation route. The ν = 0–2 levels of the 3s d⁻¹ Π₁,₂, state are observed via (1+[(2')+2']) transitions. Most of the remaining bands have been assigned to (1+[(3')+1']) Rydberg resonances and are discussed below.

Several np and nf states are assigned. These were identified mainly on the basis of their effective quantum number n* = (n − δ), as calculated from the Rydberg equation

T[(Ω, n)] = IE(Ω) − R[(n − δ)(l)]²,

where T[(Ω, n)] is the term value of the electronic state origin, R is the Rydberg constant (10 9735.5 cm⁻¹), and IE(Ω) is the ionization energy of the relevant spin–orbit component of the ²Π₁₉ ion to which the Rydberg series converges. IEs for O₂⁺ X²Π₁₂, and X²Π₁₃, of 97 348 and 97 548 cm⁻¹, respectively, were used.δ

The transition energies for the observed np and nf Rydberg state vibronic levels and the effective quantum numbers of their electronic origins are presented in Table I. It can be seen that the np⁻¹ Σ⁺₀, series, with n = 3–10, converging on O₂⁺ X²Π₁₂, has been identified. The nf Rydberg state clusters, for n = 4–9, which appear in pairs with a spacing of ~200 cm⁻¹, corresponding to the splitting of O₂⁺ X²Π₁₂, have also been identified.

B. np states

The three singlet 3p Rydberg states in (A, S) coupling, 3p f⁻¹ Σ⁺₀, 3p⁻¹ Π₁,₂, and 3p e⁻¹ Δ₂, have all been observed previously. ν = 0–4 of the sharp 3p⁻¹ Σ⁺₀, state have been seen via a strong one-photon transitions from the b⁻¹ Σ⁺₀, state. The 3p⁻¹ Π₁,₂, ν = 0 level around 75 170 cm⁻¹ has been seen via strong one-photon transitions from the a⁻¹ Δ₂, state, around 75 390 and 77 230 cm⁻¹ and via weak three-photon transitions from the X³Σ⁺₀, state, around 70 400 and 77 200 cm⁻¹. In previous studies, both the 3p⁻¹ Π₁,₂, and 3p e⁻¹ Δ₂, states were seen as diffuse bands, showing that they are predissociated. The v = 0 bands of the 3p⁻¹ Π₁,₂, and 3p e⁻¹ Δ₂, states are only seen very weakly in the spectrum shown in Fig. 1. The observation that these states are predissociated explains, at least in part, why they are seen so weakly here.

The v = 0 and 1 bands of the 4p⁻¹ Σ⁺₀, state have been seen via strong, rotationally sharp, one-photon transitions from the b⁻¹ Σ⁺₀, state. Although a strong transition to v = 1 of the 4p⁻¹ Σ⁺₀, state can be seen in Fig. 3, the v = 0 band is absent. This will be discussed further in Sec. III E. The other two singlet 4p Rydberg states, 4p⁻¹ Π₁,₂, and 4p⁻¹ Δ₂, have been seen via strong, rotationally sharp, one-photon transitions from the b⁻¹ Σ⁺₀, state.
TABLE I. Experimental transition energies, in cm$^{-1}$, for those $np$ ($n=5-10$) and $nf$ ($n=4-9$) Rydberg states of O$_2$ observed in the $1+(3^3S')+1'$ OODR/REMPI spectrum and literature values for those $3p$ and $4p$ states which are also observed in the present study. The effective quantum numbers $n^*$ were calculated using ionization energies of O$_2$, $X^1\Pi_{1u}$, and $X^2\Pi_{3/2}$, of 97.34 and 97.548 cm$^{-1}$, respectively (Refs. 20 and 21). See text for discussion of the $4f$ cluster. For each core state, the values for $nf$ states with $n\geq 4$ refer to unresolved components.

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*Literature (Ref. 12) transition energy.
$^a$Literature (Ref. 10) transition energy.
$^b$Literature (Ref. 16) term values for $J' = 0$.
$^c$Literature (Ref. 6) transition energy.

both been observed following one-photon transitions from the $X^3\Sigma_g^-$ state$^3$ and the $a^1\Delta_g$ state,$^22$ respectively. The $4p\,^1\Pi_{1u}$ Rydberg state has been shown$^9$ to contain only one unpredissociated rotational level $J=1$, while the sharpness of the $4p\,^1\Delta_{2u}$ state was not specified. The narrow peak observed at 87 121 cm$^{-1}$ in Fig. 3 is probably due to a transition to $\nu=0$, $J=1$ of the $4p\,^1\Pi_{1u}$, Rydberg state. However, on the basis of the line position, a transition to $\nu=0$ of the $4p\,^1\Delta_{2u}$ state cannot be discounted.

The $\nu=0$ levels of the $np\,^1\Sigma_{u+}^-$ series are identified up to $n=10$. Weak bands are observed at $\sim 225$ cm$^{-1}$ to low energy of the $n=8-10$ members of this series. These may be due to the $np\,^3\Sigma_{u+}^-$ series to which the $np\,^1\Sigma_{u+}^-$ series is coupled by spin–orbit interaction. However, such an assignment must remain tentative.

Clearly, the core–Rydberg coupling of the $np$ states is very different from that in the $ns$ and $nd$ states. The strong series $^1\Sigma_{u+}^-$ in ($\Lambda,S$) coupling can mix with the $^3\Sigma_{u+}^-$ series as a result of spin–orbit coupling in the core. However, it is known that $n=3$ and 4 of the $^3\Sigma_{u+}^-$ series undergo avoided crossings with the $B^1\Sigma_{u+}^-$ valence state.$^9$ This very strong interaction [$~4000$ and 2000 cm$^{-1}$ for $n=3$ and 4, respectively (Ref. 16)] dominates any spin–orbit coupling with the $^1\Sigma_{u+}^-$ Rydberg state ($~200$ cm$^{-1}$). The strength of the Rydberg–valence interaction will continue to decrease as $n$ increases. If the tentative assignment that the $^3\Sigma_{u+}^-$ series becomes observable for $n\geq 8$ is correct, this implies that spin–orbit coupling has become dominant for these states.

The $\nu=14, 15$, and 19 vibrational levels of the $f^1\Sigma_{u+}^-$ valence state with origins at 88 313.7, 88 631.0, and 88 975.4 cm$^{-1}$, respectively, have been previously observed, in the energy region covered by Fig. 3, in one-photon absorption experiments from the $X^3\Sigma_g^-$ state.$^{23}$ Two weak bands at 88 304 and 88 604 cm$^{-1}$ are now seen in the region of the $\nu=14$ and 15 levels in the spectrum in Fig. 3. However, it seems very unlikely that these two weak bands can be assigned as the $\nu=14$ and 15 levels of the $f^1\Sigma_{u+}^-$ valence
state since they are observed at lower energies than the literature values (power broadening would move the bands to higher energy). Therefore these two bands, along with a third at 89 183 cm$^{-1}$, remain unassigned.

**C. nf states**

The nf Rydberg state clusters, for $n = 4\ldots9$, which appear in pairs with a spacing of $\sim 200$ cm$^{-1}$, corresponding to the splitting of $O_2^+ \chi \Pi_{1/2,3/2}\Sigma_{u^+}$, have been identified. This suggests that the nf states, even for the lowest, $n = 4$ cluster, can be effectively described by $(\Omega, \omega)$ coupling and are presented accordingly in Table I. The current assignments call into question the previous identification$^{10}$ of some broadband seen in the one-photon absorption spectra from the $1\Delta_2\Sigma_g^-$ state as higher-nf states.

In these assignments we have only specified $\Omega_\epsilon$, $n_{Ry}$, and $l_{Ry}$. The different possible orientations of the $f$ orbital with respect to the core (i.e., $\lambda_{Ry}$) will result in a cluster of states that can each be further characterized by an $\Omega$ value. If spin is to be conserved, only transitions from the singlet $b^1\Sigma_{0g}^+$ state to states that, in $(\Omega, \omega)$ coupling, are linear combinations of singlet- and triplet-spin states will be allowed. The 4 possible configurations of $(2\Pi)_{nf\lambda_{Ry}}$ will produce 16 such states, 8 for each $\Omega_\epsilon$, (see Table I of Ref. 1). Three-photon transitions from the $b^1\Sigma_{0g}^+$ state to 12 of these are allowed, 6 for each $\Omega_\epsilon$ (transitions to the $0^-$ and $\Gamma$ states are still forbidden).

In an attempt to identify different components of the 4f cluster, the 4f ($v = 0$, 1, and 2) bands were recorded under higher resolution using a lower probe laser power and a slower scan speed. In the resultant spectra, shown in Fig. 5, the linewidth is reduced to $\sim 10$ cm$^{-1}$ and many more peaks are observed. For instance, the two bands near 92 400 and 92 600 cm$^{-1}$, shown in Fig. 4, and assigned to $v = 1 (2\Pi_{1/2})_{4f}$ and $(2\Pi_{3/2})_{4f}$, respectively, are now seen to consist of at least three peaks in Fig. 5(b).

Using the relative intensities of the $3p$ states, shown in the spectrum in Fig. 1, an attempt can be made to predict which 4f states will be observed. Thus it might be expected that the 4f $^1\Sigma_{0u}^+/^3\Sigma_{0u}^-$ coupled pair will be observed strongly, whereas the two 4f $^1\Pi_{1/2}$ and two 4f $^1\Delta_{2u}$ coupled pairs will only be observed very weakly. As the 4f $^1\Delta_{2u}$ coupled pair has no equivalent 3p states (they involve the $f\delta$ orbital), its intensity cannot be predicted.

Transitions to the 4f $^1\Sigma_{0u}^+/^3\Sigma_{0u}^-$ coupled pair of states from $b^1\Sigma_{0g}^+$ ($v = 0$, $J = 0$) should consist of $R$ and $T$ branches separated by 17 cm$^{-1}$, assuming a typical $B$ value of 1.7 cm$^{-1}$. The separation of the two highest-energy peaks in each triad in Fig. 5(b) is equal to this value to within the experimental uncertainties. Furthermore, the observed separations of the equivalent peaks in the $v = 0$ and 2 spectra in Figs. 5(a) and 5(c) are not significantly different. Thus the two highest-energy peaks in each triad are tentatively assigned to $R$ and $T$ branches of transitions to the 4f $^1\Sigma_{0u}^+/^3\Sigma_{0u}^-$ coupled pair of states.

Transitions to the two 4f $^1\Pi_{1u}$ coupled pairs from $b^1\Sigma_{0g}^+$ ($v = 0$, $J = 0$) should consist of $R$, $S$, and $T$ branches while those to the two 4f $^1\Delta_{2u}$ couples pairs should consist of $S$ and $T$ branches since $J$ must be $\geq \Omega$. If the experimental linewidth is 10 cm$^{-1}$, then the branches will not be resolved in either case. The unresolved branches will produce a single peak which is much broader than any observed in Fig. 5(b). This appears to confirm that the two 4f $^1\Pi_{1u}$ and two 4f $^1\Delta_{2u}$ coupled pairs are not seen strongly.

The transitions to the $^1\Delta_{3u}$ coupled pair of states from $b^1\Sigma_{0g}^+$ ($v = 0$, $J = 0$) should only consist of an $S$ branch. Thus the lowest-energy peak in each of the triads observed in Fig. 5 can be tentatively assigned to a transition to the $^1\Delta_{3u}$ coupled pair of states. A further peak, for which we have no assignment, is observed between the triplets in the spectra of the $v = 0$ and $v = 2$ levels, but not in that of the $v = 1$ level.

One-photon transitions from the $X^3\Sigma_g^-$ state to eight rotationally sharp states of the $4f^0P = 0$ complex have been reported. Because of the experimental uncertainties, it is not possible to determine which, if any, of these eight states are observed in the present experiments. Thus, although the present assignments of peaks to different components of the 4f cluster are consistent with the experimental observations, they are still speculative. Indeed, it may not be possible to associate the observed features with any specific electronic substates.

**D. Signal enhancement by the 3s $^1\Pi_{1g}$ Rydberg state**

It can be seen from Fig. 2 that the $v = 0$ and 3 bands of the 5f series, particularly those converging on the lower
energy $O_2^+ X^2\Pi_{1/2g}$, have considerably higher intensity than the other $nf$ peaks. These two intense peaks coincide, at the two-photon level, with $v = 0$ and 2 of the $3s\,d^1\Pi_{1g}$ Rydberg state, respectively. The simultaneous two- and three-photon resonances produce a more intense and complex signal than either transition would be expected to do on its own. By contrast, $v = 1$ of the $3s\,d^1\Pi_{1g}$ state appears with only medium intensity as its signal is not resonantly enhanced at the three-photon level. No assignment has been made for the band with medium intensity at 95 380 cm$^{-1}$, which also appears to be involved in some form of accidental resonance.

The broad band around $v_{probe} = 28 200$ cm$^{-1}$ is due to $v = 2$ of the $3s\,C^3\Pi_{g}$ Rydberg state seen by $(1 + [(2') + 2'])$ ionization. The $\Omega = 1$ component is observed due to spin-orbit interaction ($\sim 98\% \, 1\Pi_{1g}, 2\% \, 1\Pi_{3g}$) with the two-photon spin-allowed $3s\,d^1\Pi_{1g}$ state. A two-photon transition to the same vibronic level from the singlet $a^1\Delta_{2g}$ state has also been reported.\textsuperscript{24}

**E. Ground-state depletion**

The sharp band with medium intensity at $v_{probe} = 25 400$ cm$^{-1}$ in Fig. 2 is due to $(1 + [(3') + 1'])$ ionization via $v = 1$ of the rotationally sharp $4p\ j^1\Sigma_{0u}^+$ level.\textsuperscript{12} However, $v = 0$ of the same state, which is also rotationally sharp and should appear around $v_{probe} = 24 750$ cm$^{-1}$, is not observed. Similarly, the $v = 2$ band of the $3f\ j^1\Sigma_{0u}^+$ state which, when excited via a $(1 + [(2' + 1') + 1'])$ pathway, should appear at $v_{probe} = 26 880$ cm$^{-1}$ is also missing although the same level is seen via a $(1 + [(3') + 1'])$ scheme. It is known that three photons of this probe energy will excite $v = 3$ of the $3p\ e^3\Sigma_{g}^-$ state of the $X^3\Sigma_g^-$ state.\textsuperscript{13} It thus appears that even this very weak three-photon transition can compete effectively with the strongly forbidden one-photon $b^1\Sigma_{0g}^+ \rightarrow \text{X}\,\Sigma_{g}^-$ transition and deplete the OODR/REMPI signal. More specifically, it is $v = 0$, $J = 1$ of the $X^3\Sigma_g^-$ state that is uniquely pumped in the OODR experiment, and hence it must be this rotational level that is effectively depleted by the three-photon resonance.

As can be seen from Fig. 2, $v_{probe} = 24 750$ cm$^{-1}$, which should excite $v = 0$ of the $4p\ j^1\Sigma_{0u}^+$ state in a $(1 + [(3') + 1'])$ ionization scheme, also gives rise to a weakly structured probe-only signal from $X^3\Sigma_g^-$. This transition must also be effective in depleting $v = 0$, $J = 1$ of the $X^3\Sigma_g^-$ state at $v_{probe} = 24 750$ cm$^{-1}$. In contrast, the $(1 + [(3') + 1'])$ 4$p\ h\,\Pi_{1u}$ signal is observed, superimposed on the same weakly structured background at $v_{probe} = 24 666$ cm$^{-1}$.

**IV. CONCLUSION**

We have used two-color optical–optical double resonance with $(3 + 1)$ REMPI via the metastable $b^1\Sigma_{0g}^+$ state to study ungerade Rydberg states converging on $O_2^+ X^2\Pi_{1/2g}$. The spectra clearly show two series of $nf$-state clusters, one converging on $O_2^+ X^2\Pi_{1/2g}$ and one on $O_2^+ X^2\Pi_{3/2g}$, with quantum defects very close to zero. One strong $np\ j^1\Sigma_{0u}^+$ series ($n = 3 – 10$) converging on $X^2\Pi_{3/2g}$ has also been observed. $(\Omega, \omega)$ coupling appears to describe the $nf$ states most accurately, but only becomes dominant, if at all, for $n \geq 8$ members of the $np$ series. The signal from the $4f$ Rydberg states can be resolved into several bands. It is suggested that, by analogy with the $np$ series where the $1\Pi_{1u}$ and $1\Delta_{2u}$ states are missing, transitions to the $1\Sigma_{0u}^+ - 3\Sigma_{0u}^-$ and $1\Sigma_{3u}^- - 3\Sigma_{0u}^-$ coupled pairs of states are observed.

The $v = 0$ and 3 bands of the $5f$ series have considerably higher intensity than the other $nf$ peaks as a result of accidental resonances at the two-photon level with $v = 0$ and 2 of the $3s\,d^1\Pi_{1g}$ Rydberg state. In contrast, some OODR transitions are not observed at all due to depletion of the initial rotational level in the excitation pathway by probe-laser-only transitions.

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