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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 $1\Sigma^0g^+$ valence state
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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 b¹Σ⁺₀g valence state

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The np (n = 3–10) and nf (n = 4–9) Rydberg states of O₂ converging on O₂⁺ X²Π₁/₂g and X²Π₁/₂g 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 b¹Σ⁺₀g valence state was used to access these states. The nf states show a strong tendency towards (Ω,ω) coupling for all values of n, whereas the np states appear to be best described by (Λ,S) coupling for n ≈ 8. The intensities of some of the 5f bands are anomalously high due to accidental resonances with the 3s d¹Π₁g Rydberg state at the two-photon level. © 2003 American Institute of Physics. [DOI: 10.1063/1.1566949]

I. INTRODUCTION

In a companion paper,¹ 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 O₂ using two-photon excitation from single rotational levels of the metastable b¹Σ⁺₀g valence state in a (1⁺[(2')⁺⁺1]) excitation pathway (the OODR notation has been described previously).¹ We now apply the same technique to excite ungerade np and nf Rydberg states using three-photon excitation from single rotational levels of the b¹Σ⁺₀g state in a (1⁺[(3')⁺⁺1]) excitation pathway.

Reaching ungerade states from the gerade b¹Σ⁺₀g state requires an odd number of photons. A few, short, rotational progressions of np Rydberg states have been identified for n = 3–4 in a range of one-photon absorption experiments from the X³Σ⁻₀g, a¹Δ₂g, and b¹Σ⁺₀g states²–¹² and in (3 + 1) REMPI experiments from the X³Σ⁻₀g state.¹³ By photolyzing O₃, Collins et al.¹⁰ were able to prepare O₂ in the a¹Δ₂g state, virtually in the absence of the X³Σ⁻₀g 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 X³Σ⁻₀g state to v = 0 of the 4f complex have also been reported,¹⁴ and eight states with sharp structure were rotationally analyzed.

The low-n part of the O₂ 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.¹⁵,¹⁶ 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 $3p^1 \Sigma^+_{0u}$ state band positions\textsuperscript{12} indicate that our results overestimate the energy by up to $10 \text{ cm}^{-1}$ even after calibration. Thus all of the transition energies quoted here are subject to a similar offset.

In a companion paper\textsuperscript{1}, experimental results showed that the $3s$ and $3d$ 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 $b^1 \Sigma^+_0$ 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 $4$ 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 $(1+[3'(3')]+1')$ OODR/REMPI spectrum over the range $75\,000–86\,000 \text{ cm}^{-1}$. In this spectrum, and all of those shown in this work, the intermediate state $b^1 \Sigma^+_{0g}$ ($v=0$, $J=0$) is optically pumped from the ground state. The spectrum is dominated by the well-known\textsuperscript{2–5,7,12} vibrational progression of the $3p^1 \Sigma^+_{0u}$ state. In this progression, each vibronic band [full width at half maximum (FWHM) $\sim 30 \text{ cm}^{-1}$] is comprised of unresolved $R$ and $T$ branches which are separated by $17 \text{ cm}^{-1}$, 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 $3p^1 e^1 \Delta_{2u}$ states, are only seen very weakly in the spectrum shown in Fig. 1. The $v=1$ level of the $3p^1 e^1 \Delta_{2u}$ 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 $3d$-state cluster.\textsuperscript{17,18}

The OODR/REMPI spectrum recorded by scanning $\nu_{\text{probe}}$ 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 $X^3 \Sigma^-_g$ ground state to $3p$ Rydberg states.\textsuperscript{13} The $3p^1 \Sigma^+_{0u}$ vibrational progression is seen strongly in this $\nu_{\text{probe}}$ region via $(1+[2'(3')+1'])$ transitions, in which one pump and two
The 3$^1P_g$ origin, 3$^1S_u$ and 3$^3S_u$ states are seen via strong, rotationally sharp, one-photon transitions 3$^P_g$ and 3$^1S_u$ states, respectively. These agree closely with the values of 0.77±0.06 and 0.0±0.01 for the np and nf states of atomic oxygen, respectively.

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 $^1S_{0_u}$ series, with $n=3–10$, converging on O$_2^+$ $^2X^2\Pi_{3/2}$ 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 O$_2^+$ $^2X^2\Pi_{3/2,3/2}$, have also been identified.

### B. np states

The three singlet 3p Rydberg states in (A,S) coupling, $3p$ $^3P_{1_u}$, $3p$ $^1P_{1_u}$, and $3p$ $^1D_{2u}$, have all been observed previously, $v=0–4$ of the sharp $3p$ $^1S_{0_u}$ state have been seen via a strong one-photon transitions from the $b^1\Sigma_{0_u}^+$ state.$^{12}$ The $3p$ $^1P_{1_u}$, $v=0$ level around 75 170 cm$^{-1}$ has been seen via strong one-photon transitions from the $a^1\Delta_{2g}$ and $b^1\Sigma_{0_u}^+$ states.$^{10,12}$ The $3p$ $^1D_{2u}$, $v=0$ and 1 levels have been seen via strong one-photon transitions from the $a^1\Delta_{2g}$ state,$^{10,12}$ around 75 390 and 77 230 cm$^{-1}$ and via weak three-photon transitions from the $X^3\Sigma_{g}^-$ state,$^{13}$ around 75 400 and 77 200 cm$^{-1}$. In previous studies, both the $3p$ $^1P_{1_u}$ and $3p$ $^1D_{2u}$ states were seen as diffuse bands, showing that they are predissociated. The $v=0$ bands of the $3p$ $^1P_{1_u}$ and $3p$ $^1D_{2u}$ 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 $4p$ $^1\Sigma_{0_u}^+$ state have been seen via strong, rotationally sharp, one-photon transitions from the $b^1\Sigma_{0_u}^+$ state.$^{12}$ Although a strong transition to $v=1$ of the $4p$ $^1\Sigma_{0_u}^+$ 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, $4p$ $^3P_{1_u}$ (87 121 cm$^{-1}$) and $4p$ $^1\Delta_{2u}$ (87 128 cm$^{-1}$) have
both been observed following one-photon transitions from the \( X^3\Sigma^– \) state\(^6\) and the \( \alpha^1\Delta_2 \) state\(^22\) respectively. The \( 4p \ h^1\Pi_1 \) Rydberg state has been shown\(^8\) to contain only one unpredissociated rotational level \( J = 1 \), while the sharpness of the \( 4p \ h^1\Delta_2 \) state was not specified. The narrow peak observed at \( 87121 \text{ cm}^{-1} \) in Fig. 3 is probably due to a transition to \( v = 0, J = 1 \) of the \( 4p \ h^1\Pi_1 \) Rydberg state. However, on the basis of the line position, a transition to \( v = 0 \) of the \( 4p \ h^1\Delta_2 \) state cannot be discounted.

The \( v = 0 \) levels of the \( np \ \Sigma^+ \) \( \Omega = \frac{1}{2} \) series are identified up to \( n = 10 \). Weak bands are observed at \( \sim 225 \text{ cm}^{-1} \) to low energy of the \( n = 8–10 \) members of this series. These may be due to the \( np \ \Sigma^+ \) series to which the \( np \ \Sigma^+ \) 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 \( \Sigma^+ \) in \( (\Lambda,S) \) coupling can mix with the \( \Sigma^+ \) series as a result of spin–orbit coupling in the core. However, it is known that \( n = 3 \) and \( 4 \) of the \( \Sigma^+ \) series undergo avoided crossings with the \( B^3\Sigma^0_u \) valence state.\(^9\) This very strong interaction \([\sim 4000 \text{ and } 2000 \text{ cm}^{-1} \text{ for } n = 3 \text{ and } 4, \text{ respectively (Ref. 16)}]\) dominates any spin–orbit coupling with the \( \Sigma^+ \) Rydberg state \( (~200 \text{ cm}^{-1} \text{)}. \) The strength of the Rydberg–valence interaction will continue to decrease as \( n \) increases. If the tentative assignment that the \( \Sigma^+ \) series becomes observable for \( n \geq 8 \) is correct, this implies that spin–orbit coupling has become dominant for these states.

The \( v = 14, 15, \) and \( 19 \) vibrational levels of the \( \Sigma^+ \) \( \Omega = \frac{1}{2} \) valence state with origins at \( 88313.7, 88631.0, \) and \( 88975.4 \text{ cm}^{-1} \), respectively, have been previously observed, in the energy region covered by Fig. 3, in one-photon absorption experiments from the \( X^3\Sigma^– \) state.\(^23\) Two weak bands at \( 88304 \) and \( 88604 \text{ cm}^{-1} \) are now seen in the region of the \( v = 14 \) and \( 15 \) levels in the spectrum in Fig. 3. However, it seems very unlikely that these two weak bands can be assigned as the \( v = 14 \) and \( 15 \) levels of the \( \Sigma^+ \) valence state.
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 $n=4-9$, which appear in pairs with a spacing of $\sim 200$ cm$^{-1}$, corresponding to the splitting of $O_2^+ X^2\Pi_{1/2,3/2}$, 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 of some broad bands seen in the one-photon absorption spectra from the $\alpha \Delta_{2\mu}$ state as higher-nf states.

In these assignments we have only specified $\Omega_c$, $n_{Ry}$, and $l_{Ry}$. The different possible orientations of the f orbital with respect to the core (i.e., $l_{Ry}$) 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 $(^2\Pi)_{n_f} \lambda_{Ry}$ will produce 16 such states, 8 for each $\Omega_c$, (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 $\Omega_c$ (transitions to the $0^-$ and $\Gamma$ states are still forbidden).

In an attempt to identify different components of the 4f cluster, the 4f ($v=0, 1, 2$) 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. 5, 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 $4f\, (^1\Sigma_{0u}^+)^{1/2}\Sigma_{0u}^-$ coupled pair will be observed strongly, whereas the two $4f\, (^1\Pi_{1/2})_{v}$ and two $4f\, (^1\Delta_{2u})_{v}$ coupled pairs will only be observed very weakly. As the $4f\, (^1\Delta_{3u})_{3a}$ coupled pair has no equivalent 3p states (they involve the $f\delta$ orbital), its intensity cannot be predicted.

Transitions to the $4f\, (^1\Sigma_{0u}^+)^{1/2}\Sigma_{0u}^-$ 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 ascribed to $R$ and $T$ branches of transitions to the $4f\, (^1\Sigma_{0u}^+)^{1/2}\Sigma_{0u}^-$ coupled pair of states.

Transitions to the two $4f\, (^1\Pi_{1/2})_{1a}$ coupled pairs from $b^1\Sigma_{0g}^+$ ($v=0, J=0$) should consist of $R, S$, and $T$ branches while those to the two $4f\, (^1\Delta_{2a})_{v}$ coupled 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 $4f\, (^1\Pi_{1a})_{v}$ and two $4f\, (^1\Delta_{2a})_{v}$ coupled pairs are not seen strongly.

The transitions to the $1\, ^3\Phi_{3a}$ 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 $1\, ^3\Phi_{3a}$ 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 2 levels, but not in that of the $v=1$ level.

One-photon transitions from the $X^2\Sigma_{e}^-$ state to eight rotationally sharp states of the $4f\, v=0$ 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 substrates.

D. Signal enhancement by the 3s $d\, ^1\Pi_{1g}$ 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 en-
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.\textsuperscript{19} 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 $v_{\text{probe}} \approx 28$ 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 ($\sim 98\% \, \Pi_{1g}, 2\% \, \Pi_{1g'}$) 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 $v_{\text{probe}} = 25$ 400 cm$^{-1}$ in Fig. 2 is due to $(1 + [(3') + 1')]$ ionization via $v = 1$ of the rotationally sharp $4p \, j \, \Sigma_{0u}^+$ level.\textsuperscript{12} However, $v = 0$ of the same state, which is also rotationally sharp and should appear around $v_{\text{probe}} = 24 750$ cm$^{-1}$, is not observed. Similarly, the $v = 2$ band of the $3f \, \Sigma_{0u}^+$ state which, when excited via a $(1 + [(2'+1') + 1'])$ pathway, should appear at $v_{\text{probe}} = 26 880$ 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 $3p \, e^3 \Delta_u$ state from the $X^3 \Sigma_g^-$ state.\textsuperscript{13} It appears that even this very weak three-photon transition can compete effectively with the strongly forbidden one-photon $b^1 \Sigma_{0g}^- \rightarrow X^3 \Sigma_g^-$ 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, $v_{\text{probe}} = 24 750$ cm$^{-1}$, which should excite $v = 0$ of the $4p \, j \, \Sigma_{0u}^+$ 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 $v_{\text{probe}} = 24 750$ cm$^{-1}$. In contrast, the $(1 + [(3') + 1'])$ $4p \, h \, \Pi_{1u}$ signal is observed, superimposed on the same weakly structured background at $v_{\text{probe}} = 24 666$ 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 $np^1 \Sigma_{0u}^+$ 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 $1\Delta_u$ states are missing, transitions to the $1\Sigma_{0u}^+ \rightarrow 3\Sigma_{0u}^+$ and $1\Phi_{3u}$ 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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