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Citation: J. Chem. Phys. **118**, 8791 (2003); doi: 10.1063/1.1566949
View online: http://dx.doi.org/10.1063/1.1566949
View Table of Contents: http://jcp.aip.org/resource/1/JCPSA6/v118/i19
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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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(Received 4 November 2002; accepted 21 February 2003)

The np ($n=3-10$) and nf ($n=4-9$) Rydberg states of O_2 converging on $O_2^+\,X\,^2\Pi_{1/2,g}$ and $X\,^2\Pi_{3/2g}$ 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 $b\,^1\Sigma_{0g}^+$ 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 $n\leqslant 8$. The intensities of some of the $5f$ bands are anomalously high due to accidental resonances with the $3s\,d\,^1\Pi_{1g}$ 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 O_2 using two-photon excitation from single rotational levels of the metastable $b\,^1\Sigma_{0g}^+$ 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 $b\,^1\Sigma_{0g}^+$ state in a $(1+[(3')+1'])$ excitation pathway.

Reaching *ungerade* states from the *gerade* $b\,^1\Sigma_{0g}^+$ 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 $X\,^3\Sigma_g^-$, $a\,^1\Delta_{2g}$, and $b\,^1\Sigma_{0g}^+$ states[2–12] and in $(3+1)$ REMPI experiments from the $X\,^3\Sigma_g^-$ state.[13] By photolyzing O_3, Collins *et al.*[10] 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 $X\,^3\Sigma_{0g}^-$ 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 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.[15,16] While the effects of such interactions should diminish as *n* increases, at the same time the energy levels will become closer together, leading to a congested spectrum where single rovibronic bands will be hard to distinguish from an apparent continuum of blended bands.

To simplify the spectrum in this energy region we have used $(1+[(3')+1'])$ OODR/REMPI spectroscopy. This multiphoton excitation scheme has several advantages over single-photon excitation. Using three photons removes the need to generate the high-energy vacuum ultraviolet photons required to excite, in a single-photon transition, the *ungerade* Rydberg states that lie at energies above 75 000 cm^{-1}. Multiphoton excitation also allows access to higher-angular-momentum states that cannot be reached by single-photon transitions. Furthermore, since the OODR/REMPI spectrum is recorded via a single intermediate rotational level, only a few rotational levels of the Rydberg states can appear in the final spectrum, resulting in a less congested spectrum compared with absorption spectroscopy from the $a\,^1\Delta_{2g}$ or $b\,^1\Sigma_{0g}^+$ states, populated through photolysis of O_3 or discharge excitation of O_2, where a large number of rovibrational levels of the initial state are populated.

While the advantage of rotational selection for investigating the Rydberg states is clear, the two-color, multiphoton setup also allows for other excitation schemes which can complicate the spectrum. For example, the $3p\,f\,^1\Sigma_{0u}^+\,v=1$ level is detected through three different excitation schemes: at $\nu_{\text{probe}}=21\,690\,cm^{-1}$ through $(1+[(3')+1'])$, at $\nu_{\text{probe}}=25\,960\,cm^{-1}$ through $(1+[(2'+1)+1'])$, both via the $b\,^1\Sigma_{0g}^+$ state, and at $\nu_{\text{probe}}=26\,050\,cm^{-1}$ through $(3'+1')$, directly from the $X\,^3\Sigma_g^-$ state. Thus the three-photon signal from the states of interest may be affected in many ways. It can be concealed by competing resonances, enhanced by an additional resonance at the one- or two-photon levels, or diminished by ground-state depletion. In this last process, the population of the ground-state rotational level from which the OODR pathway begins can be depleted by a more favorable excitation involving the probe laser alone. Examples of

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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 $3p\,f\,^1\Sigma_{0u}^+$ state band positions[12] 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,[1] experimental results showed that the $3s$ and $3d$ states are best described by (Λ,S) coupling, while (Ω,ω) 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 $b\,^1\Sigma_{0g}^+$ state. First, strong transitions are observed to states which are singlet in the (Λ,S) coupling scheme or are linear combinations of equal weights of singlet- and triplet-spin states in the (Ω,ω) 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 $4s$ and $5s$ 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 $\leqslant$2 cm^{-1}. The same criteria will be used to interpret the $(3+1)$ REMPI spectra from the $b\,^1\Sigma_{0g}^+$ 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 $b \leftarrow X$ 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 $4f$ 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.

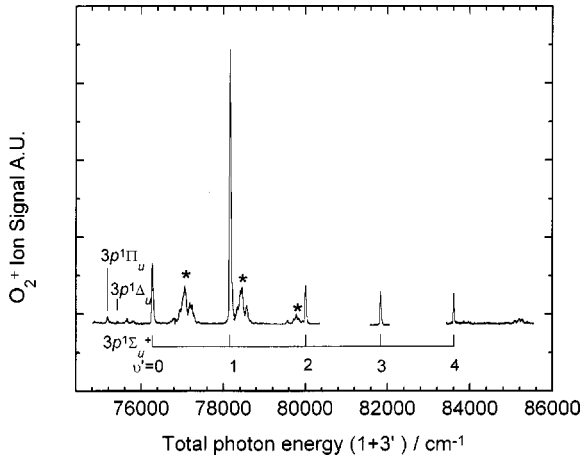

FIG. 1. OODR/REMPI spectrum of $v=0-4$ of the O_2 $3p\,f\,^1\Sigma_{0u}^+$ Rydberg state excited in a $(1+[(3')+1'])$ scheme via $b\,^1\Sigma_{0g}^+$ $(v=0,\ J=0)$. The broader features (starred) are $v=0-2$ of the $3d$ Rydberg-state cluster seen via $(4'+1')$ excitation of the $X\,^3\Sigma_g^-$ state.

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 $b\,^1\Sigma_{0g}^+$ $(v=0,\ J=0)$ is optically pumped from the ground state. The spectrum is dominated by the well-known[2–5,7,12] vibrational progression of the $3p\,f\,^1\Sigma_{0u}^+$ 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 (Λ,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 $3d$-state cluster.[17,18]

The OODR/REMPI spectrum recorded by scanning ν_{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.[13] The $3p\,f\,^1\Sigma_{0u}^+$ vibrational progression is seen strongly in this ν_{probe} region via $(1+[(2'+1)+1'])$ transitions, in which one pump and two

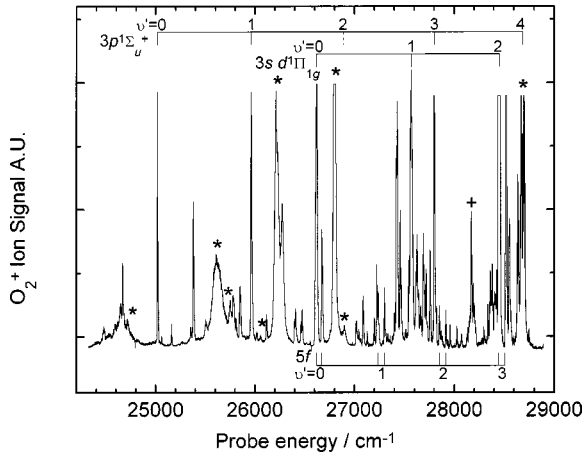

FIG. 2. OODR/REMPI spectrum of O_2 over the range $\nu_{\text{probe}} = 24\,400-29\,000\ \text{cm}^{-1}$. The energy scale shows probe photon energy rather than total energy in order to illustrate the occurrence of different excitation schemes. The $3s\,d\,^1\Pi_{1g}$ ($v=0-2$) bands are seen via a $(1+[(2')+2'])$ scheme, the $3p\,f\,^1\Sigma_{0u}^+$ ($v=0,1,3,4$) bands via a $(1+[(2'+1)+1'])$ scheme and the $5f$ states via a $(1+[(3')+1'])$ scheme, all excited via $b\,^1\Sigma_{0g}^+$ ($v=0$, $J=0$). Various $3p$ Rydberg states (starred) are observed via a $(3'+1')$ scheme from the $X\,^3\Sigma_g^-$ state. The $3s\,C\,^3\Pi_g$ ($v=2$) band (+) is seen via $(1+[(2')+2'])$ ionization.

probe photons coherently excite a three-photon transition from the $b\,^1\Sigma_{0g}^+$ state. The $v=0$ levels of the $3p\,^1\Pi_{1u}$ and $3p\,e\,^1\Delta_{2u}$ states, indicated in Fig. 3, are observed very weakly by the same excitation route. The $v=0-2$ levels of the $3s\,d\,^1\Pi_{1g}$ state[19] 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 $n^*=(n-\delta)$, as calculated from the Rydberg equation

$$T([\Omega_c]nl)=\text{IE}(\Omega_c)-R/[n-\delta(l)]^2,$$

where $T([\Omega_c]nl)$ is the term value of the electronic state origin, R is the Rydberg constant (109735.5 cm^{-1}), and $\text{IE}(\Omega_c)$ is the ionization energy of the relevant spin–orbit component of the $^2\Pi_g$ ion to which the Rydberg series converges. IEs for $O_2^+\,X\,^2\Pi_{1/2g}$ and $X\,^2\Pi_{3/2g}$ of 97 348 and 97 548 cm^{-1}, respectively, were used.[20,21] δ was found to be 0.73 ± 0.07 and 0.01 ± 0.04 for the np and nf 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.

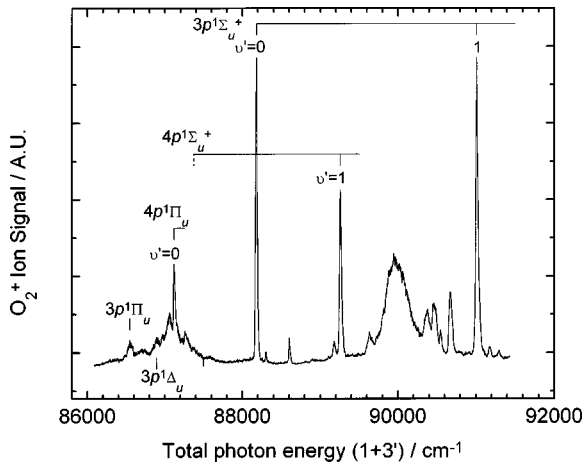

FIG. 3. OODR/REMPI spectrum of O_2 between 86 100 and 91 400 cm^{-1} excited via $b\,^1\Sigma_{0g}^+$ ($v=0$, $J=0$). The energy scale corresponds to $(1+3')$ excitation. The $3p$ states are seen by $(1+[(2'+1)+1'])$ ionization.

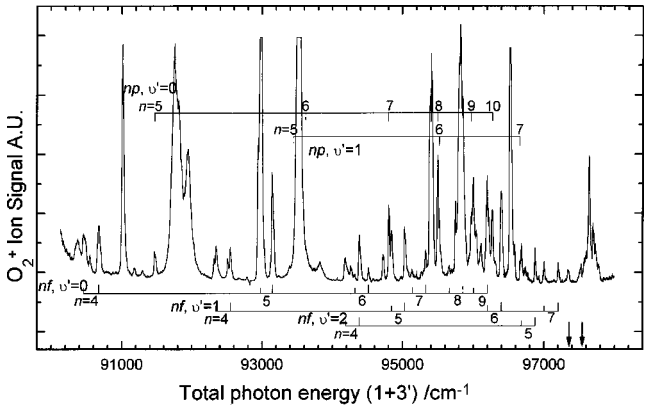

FIG. 4. OODR/REMPI spectrum of O_2 between 90 100 and 98 000 cm^{-1} excited via $b\,^1\Sigma_{0g}^+$ ($v=0$, $J=0$). The energy scale corresponds to $(1+3')$ excitation. The ionization energies of $O_2^+\,X\,^2\Pi_{1/2g}$ and $X\,^2\Pi_{3/2g}$ at 97 348 and 97 548 cm^{-1}, respectively, are arrowed.

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 $np\,^1\Sigma_{0u}^+$ series, with $n=3-10$, converging on $O_2^+\,X\,^2\Pi_{3/2g}$ has been identified. 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 $O_2^+\,X\,^2\Pi_{1/2,3/2g}$, have also been identified.

B. *np* states

The three singlet $3p$ Rydberg states in (Λ,S) coupling, $3p\,f\,^1\Sigma_{0u}^+$, $3p\,^1\Pi_{1u}$, and $3p\,e\,^1\Delta_{2u}$, have all been observed previously. $v=0-4$ of the sharp $3p\,f\,^1\Sigma_{0u}^+$ state have been seen via a strong one-photon transitions from the $b\,^1\Sigma_{0g}^+$ state.[12] The $3p\,^1\Pi_{1u}\,v=0$ level around 75 170 cm^{-1} has been seen via strong one-photon transitions from the $a\,^1\Delta_{2g}$ and $b\,^1\Sigma_{0g}^+$ states.[10,12] The $3p\,e\,^1\Delta_{2u}\,v=0$ 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 $3p\,^1\Pi_{1u}$ and $3p\,e\,^1\Delta_{2u}$ states were seen as diffuse bands, showing that they are predissociated. The $v=0$ bands of the $3p\,^1\Pi_{1u}$ and $3p\,e\,^1\Delta_{2u}$ 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 $4p\,j\,^1\Sigma_{0u}^+$ state have been seen via strong, rotationally sharp, one-photon transitions from the $b\,^1\Sigma_{0g}^+$ state.[12] Although a strong transition to $v=1$ of the $4p\,j\,^1\Sigma_{0u}^+$ 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, $4p\,h\,^1\Pi_{1u}$ (87 121 cm^{-1}) and $4p\,i\,^1\Delta_{2u}$ (87 128 cm^{-1}) have

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 $(1+[(3')+1'])$ 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^+ $X\ ^2\Pi_{1/2g}$ and $X\ ^2\Pi_{3/2g}$ of 97 348 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 $n\geqslant 4$ refer to unresolved components.

$\Omega_c=1/2$		v				
nl	n^*	0	1	2	3	
$4f$	3.98	90430	92318	94172		
$4f$	3.99	90454	92347	94185		
$4f$	4.00	90470	92368	94201	96002	
$5f$	4.99	92943	94839	96676		
$6f$	5.97	94313	96197			
$7f$	7.03	95131	96996			
$8f$	8.06	95659	97528			
$9f$	9.02	96002				

$\Omega_c=3/2$		v				
nl	n^*	0	1	2	3	4
$3p\ ^1\Pi_{1u}$	2.21	75170[a]				
$3p\ ^1\Delta_{2u}$	2.23	75390[b]				
$3p\ ^1\Sigma^+_{0u}$	2.27	76263.7[c]	78153.0[c]	80001.8[c]	81824.1[c]	83600.8[c]
$4p\ ^1\Pi_{1u}$	3.24	87121[d]				
$4p\ ^1\Sigma^+_{0u}$	3.28	87370.0[c]	89264.5[c]			
$4f$	3.99	90635	92512	94374		
$4f$	3.99	90655	92548	94384		
$4f$	4.00	90667	92564	94403	96199	
$5p\ ^1\Sigma^+_{0u}$	4.25	91474				
$5f$	5.00	93160	95031	96873		
$6p\ ^1\Sigma^+_{0u}$	⋯	⋯	95518			
$6f$	6.01	94509	96392			
$7p\ ^1\Sigma^+_{0u}$	6.32	94799	96655			
$7f$	7.03	95325	97194			
$8p\ ^1\Sigma^+_{0u}$	7.31	95496	97345			
$8f$	7.92	95800				
$9p\ ^1\Sigma^+_{0u}$	8.34	95971				
$9f$	9.01	96197				
$10p\ ^1\Sigma^+_{0u}$	9.26	96269				

[a]Literature (Ref. 12) transition energy.
[b]Literature (Ref. 10) transition energy.
[c]Literature (Ref. 12) term values for $J'=0$.
[d]Literature (Ref. 6) transition energy.

both been observed following one-photon transitions from the $X\ ^3\Sigma_g^-$ state[6] and the $a\ ^1\Delta_{2g}$ state,[22] respectively. The $4p\ h\ ^1\Pi_{1u}$ Rydberg state has been shown[6] to contain only one unpredissociated rotational level $J=1$, while the sharpness of the $4p\ i\ ^1\Delta_{2u}$ state was not specified. The narrow peak observed at 87 121 cm^{-1} in Fig. 3 is probably due to a transition to $v=0$, $J=1$ of the $4p\ h\ ^1\Pi_{1u}$ Rydberg state. However, on the basis of the line position, a transition to $v=0$ of the $4p\ i\ ^1\Delta_{2u}$ state cannot be discounted.

The $v=0$ levels of the $np\ ^1\Sigma^+_{0u}$ series are identified up to $n=10$. Weak bands are observed at ~225 cm^{-1} to low energy of the $n=8-10$ members of this series. These may be due to the $np\ ^3\Sigma^-_{0u}$ series to which the $np\ ^1\Sigma^+_{0u}$ 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 $^1\Sigma^+_{0u}$ in (Λ,S) coupling can mix with the $^3\Sigma^-_{0u}$ series as a result of spin–orbit coupling in the core. However, it is known that $n=3$ and 4 of the $^3\Sigma^-_{0u}$ series undergo avoided crossings with the $B\ ^3\Sigma^-_{0u}$ 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 $^1\Sigma^+_{0u}$ 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 $^3\Sigma^-_{0u}$ series becomes observable for $n\geqslant 8$ is correct, this implies that spin–orbit coupling has become dominant for these states.

The $v=14$, 15, and 19 vibrational levels of the $f'\ ^1\Sigma^+_{0u}$ 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 $v=14$ 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 $f'\ ^1\Sigma^+_{0u}$ 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 $n=4-9$, which appear in pairs with a spacing of $\sim$200 cm^{-1}, corresponding to the splitting of $O_2^+ X\,^2\Pi_{1/2,3/2g}$, have been identified. This suggests that the nf states, even for the lowest, $n=4$ cluster, can be effectively described by (Ω,ω) coupling and are presented accordingly in Table I. The current assignments call into question the previous identification[10] of some broadbands seen in the one-photon absorption spectra from the $a\,^1\Delta_{2g}$ state as higher-nf states.

In these assignments we have only specified Ω_c, n_{Ry}, and l_{Ry}. The different possible orientations of the f orbital with respect to the core (i.e., λ_{Ry}) will result in a cluster of states that can each be further characterized by an Ω value. If spin is to be conserved, only transitions from the singlet $b\,^1\Sigma_{0g}^+$ state to states that, in (Ω,ω) coupling, are linear combinations of singlet- and triplet-spin states will be allowed. The 4 possible configurations of $(^2\Pi_g)nf\lambda_{\mathrm{Ry}}$ will produce 16 such states, 8 for each Ω_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 Ω_c (transitions to the 0^- and Γ 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 $v=1$ $(^2\Pi_{1/2,g})4f$ and $(^2\Pi_{3/2,g})4f$, 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 $4f\,^{1,3}\Pi_{1u}$ and two $4f\,^{1,3}\Delta_{2u}$ coupled pairs will only be observed very weakly. As the $4f\,^{1,3}\Phi_{3u}$ 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 $4f\,^{1,3}\Pi_{1u}$ coupled pairs from $b\,^1\Sigma_{0g}^+$ ($v=0$, $J=0$) should consist of R, S, and T branches while those to the two $4f\,^{1,3}\Delta_{2u}$ coupled pairs should consist

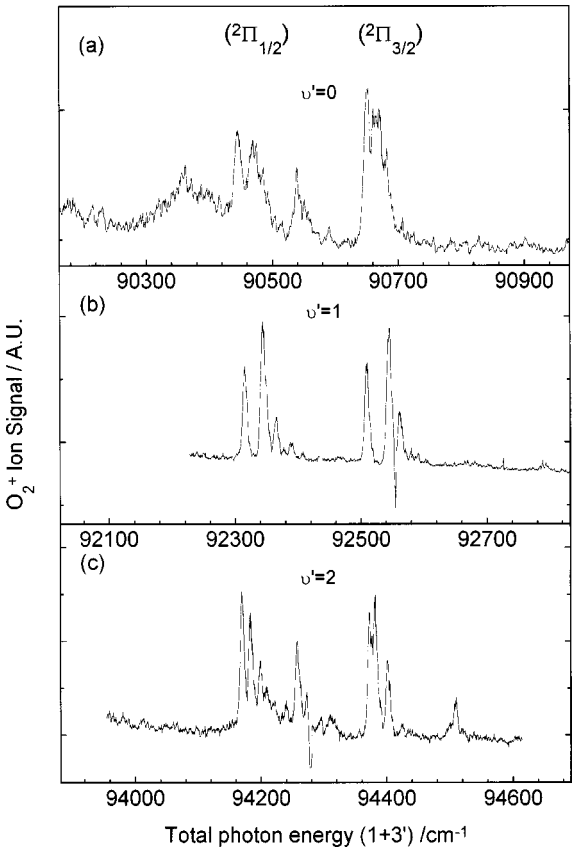

FIG. 5. Higher-resolution spectra of the lowest vibrational levels of the $4f$ Rydberg states of O_2: (a) $v=0$, (b) $v=1$, (c) $v=2$. The broad structure below $(^2\Pi_{1/2,g})4f$ ($v=0$) is a one-color signal.

of S and T branches since J must be $\geqslant\Omega$. 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 $4f\,^{1,3}\Pi_{1u}$ and two $4f\,^{1,3}\Delta_{2u}$ coupled pairs are not seen strongly.

The transitions to the $^{1,3}\Phi_{3u}$ 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 $^{1,3}\Phi_{3u}$ 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 $4f$ $v=0$ complex have been reported.[14] 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 $3s\,d\,^1\Pi_{1g}$ 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-

ergy $O_2^+ X\,^2\Pi_{1/2g}$, 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.[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 $\nu_{probe}=28\,200\,cm^{-1}$ 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 ($\sim 98\%\,^3\Pi_{1g}$,$2\%\,^1\Pi_{1g}$) 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.[24]

E. Ground-state depletion

The sharp band with medium intensity at $\nu_{probe}=25\,400\,cm^{-1}$ in Fig. 2 is due to $(1+[(3')+1'])$ ionization via $v=1$ of the rotationally sharp $4p\,j\,^1\Sigma_{0u}^+$ level.[12] However, $v=0$ of the same state, which is also rotationally sharp and should appear around $\nu_{probe}=24\,750\,cm^{-1}$, is not observed. Similarly, the $v=2$ band of the $3p\,f\,^1\Sigma_{0u}^+$ state which, when excited via a $(1+[(2'+1)+1'])$ pathway, should appear at $\nu_{probe}=26\,880\,cm^{-1}$ 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.[13] Thus it appears that even this very weak three-photon transition can compete effectively with the strongly forbidden one-photon $b\,^1\Sigma_{0g}^+ \leftarrow X\,^3\Sigma_g^-$ 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, $\nu_{probe}=24\,750\,cm^{-1}$, which should excite $\nu=0$ 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 $\nu_{probe}=24\,750\,cm^{-1}$. In contrast, the $(1+[(3')+1'])$ $4p\,h\,^1\Pi_{1u}$ signal is observed, superimposed on the same weakly structured background at $\nu_{probe}=24\,666\,cm^{-1}$.

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 $O_2^+ X\,^2\Pi_g$. 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. (Ω,ω) coupling appears to describe the nf states most accurately, but only becomes dominant, if at all, for $n\geqslant 8$ 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 $^{1,3}\Phi_{3u}$ 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.

ACKNOWLEDGMENTS

The authors would like to thank Professor M. L. Ginter for detailed comments on the manuscript. A.M.S. would like to thank the Göran Gustafsson foundation for a scholarship.

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