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Two photon resonance enhanced multiphoton ionization spectroscopy of gas phase O_2 $a^1\Delta_g$ between 305–350 nm

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The resonance enhanced multiphoton ionization (REMPI) spectrum of O_2 $a^1\Delta_g$ between 305 and 350 nm is reported. The spectrum is compared to the REMPI spectrum of ground state molecular oxygen in the same electronic energy region, and a number of differences in the respective spectra are observed. Detection limits for O_2 $a^1\Delta_g$ by REMPI is calculated to be 5×10^9 molecule cm^{-3} in the ion source of the mass spectrometer.

INTRODUCTION

This paper reports the resonance enhanced multiphoton ionization (REMPI) spectrum of O_2 $a^1\Delta_g$ between 305 and 350 nm. The $a^1\Delta_g$ state of molecular oxygen plays an important role in the chemistry of terrestrial and extraterrestrial atmospheres.¹ A sensitive method of detecting O_2 $a^1\Delta_g$, such as REMPI, will aid in the further elucidation of important chemical reactions involving O_2 $a^1\Delta_g$.

The first observation of electronic states of oxygen in the 8.4–8.8 eV region was achieved by Cartwright *et al.*² using electron impact excitation. The states observed were assigned to the $(3s\sigma)^1\Pi_g$ and the $(3s\sigma)^3\Pi_g$ Rydberg states. More recently, Sur *et al.* examined these states using two photon resonant REMPI spectroscopy.^{3,4} They reported the rotational analysis of the $v' = 2$ band of the $(3s\sigma)^3\Pi_g \leftarrow \leftarrow^3\Sigma_g^-$ and the $v' = 0$ band of the $^1\Pi_g \leftarrow \leftarrow^3\Sigma_g^-$ two photon transitions. Evidence for a Rydberg–valence interaction was also given.

In this study we probe the same energy region as the work mentioned above. However, since the transitions originate from the $a^1\Delta_g$ state of oxygen, two photon absorption may prepare states inaccessible by two photon absorption from the ground state. Specifically, transitions to singlet states and transitions to states with orbital angular momentum quantum numbers of $\Lambda = 3$ and $\Lambda = 4$ (Φ and Γ states) are allowed. We find the cross section for the two photon transition from the $a^1\Delta_g$ state to the $(3s\sigma)^1\Pi_g$ Rydberg state of oxygen to be at least an order of magnitude greater than the transition from the $a^1\Delta_g$ state to the $(3s\sigma)^3\Pi_g$ state. The increased sensitivity for probing transitions to the $(3s\sigma)^1\Pi_g$ state allowed rotational analysis of the $(3s\sigma)^1\Pi_g$ ($v' = 3$) band. In addition, we report previously unobserved REMPI bands between 330–310 nm.

EXPERIMENTAL SECTION

The apparatus used in this study consisted of a flow tube, a microwave discharge which produced the excited O_2 ,

a Nd:YAG pumped dye laser, and a time-of-flight mass spectrometer. The excited oxygen produced in the discharge effused through a small orifice into the mass spectrometer ion source, where it was ionized by the laser beam. Pressures in the ion source were usually near 10^{-4} Torr. The m/z 32 ion current was recorded and processed by a computerized data acquisition system.

The frequency doubled output of the Nd:YAG pumped dye laser was focused into the ion source using a 250 mm focal length quartz lens. The doubled laser beam output characteristics were typically 5–10 mJ per pulse, a pulse duration of 10 ns, and a bandwidth of ~ 0.2 cm^{-1} FWHM. The data acquisition electronics were synchronized to the Q switch of the Nd:YAG laser which operated at a repetition rate of 10 Hz. The laser dyes used in this study were kiton red 620 (295–302), rhodamine 610 mixed with rhodamine 640 (301–306), rhodamine 640 (305–320), LDS 698 (310–330), oxazine 720 (330–340), LDS 722 (340–353), and Nile blue 690 (350–358). Laser wavelengths were calibrated optogalvanically using a neon hollow cathode lamp.⁵

The 2450 MHz microwave discharge which produced the excited oxygen molecules was operated at about 0.5 Torr of pure oxygen. Ultrahigh purity (99.98%) oxygen was used for these studies. When oxygen of lower purity was used, signals resulting from NO were observed at m/z 30. The presence of NO was also evidenced by visible luminescence downstream from the microwave discharge.

The rotational constants were determined by computer simulations of the experimental REMPI spectra. The computer program input parameters were varied to give the best visual agreement between the simulated spectrum and the 312 nm band. The rotational line positions were calculated using the equations

$$E_{\text{line}} = E_{\text{upper}} - E_{\text{lower}},$$

$$E_{\text{upper}} = E''_{00} + [B' - D'J'(J' + 1)]J'(J' + 1),$$

$$E_{\text{lower}} = E''_{00} + [B'' - D''J''(J'' + 1)]J''(J'' + 1).$$

E_{lower} was calculated using the following parameter values: $E''_{00} = 7882.4$ cm^{-1} , $B'' = 1.4179$ cm^{-1} , and $D'' = 4.9 \times 10^{-6}$ cm^{-1} .⁶ The lower electronic state was assumed to have a Boltzmann distribution of rotational states. Other

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variables in the simulation are the peak width, the sample temperature, and the number of laser photons simultaneously absorbed by the molecule.

RESULTS

The composite REMPI spectrum of 300 K $O_2 a^1\Delta_g$ is shown in Fig. 1. The m/z 32 REMPI signal is plotted as a function of laser wavelength. The spectra used to construct Fig. 1 were chosen such that the laser energy is nearly constant over the entire wavelength range. The spectrum encompassed 11 REMPI bands, both discrete and unresolved, labeled *A* through *K*. A summary of these bands is given in Table I.

All of the m/z 32 REMPI signals shown in Fig. 1 displayed an intensity dependence that was proportional to the oxygen concentration. When the microwave discharge was extinguished, they vanished. This behavior indicates that these bands originate from either vibrationally or electronically excited states of oxygen.

Under conditions similar to those used in these experiments, microwave discharges produce $O_2 a^1\Delta_g$ and $O_2 b^1\Sigma_g^+$ with yields of 10% and 0.001%, respectively.⁷ When we assume total transmission of the excited oxygen from the microwave discharge into the ion source, the resulting concentration of $O_2 b^1\Sigma_g^+$ in the ion source would be about 10^7 molecule cm^{-3} , which seems too low to account for the strong m/z 32 signals. The concentration of $O_2 a^1\Delta_g$ would be about 10^{11} molecule/ cm^{-3} . To verify that none of the observed m/z 32 signal was due to $O_2 b^1\Sigma_g^+$, CO_2 was added to the flow downstream from the discharge. CO_2 is known to rapidly quench $O_2 b^1\Sigma_g^+$ ($k_q = 2 \times 10^8$ ℓ molecule $^{-1}$ s $^{-1}$) but only slowly quenches $O_2 a^1\Delta_g$ ($k_q = 10^2$ ℓ molecule $^{-1}$ s $^{-1}$).⁷ A 5:1 mixture of CO_2 to O_2 failed to strongly attenuate the m/z 32 signal. This result limits assignment of the m/z 32 spectral carriers of Fig. 1 to $O_2 a^1\Delta_g$ and to vibrationally excited $O_2 X^3\Sigma_g^-$ molecules.

A composite REMPI spectrum of 300 K ground state molecular oxygen is shown in Fig. 2. In this spectrum the m/z 32 signal is not scaled to correct for laser energy variations. The top abscissa plots the state energy (cm^{-1}). State energy is the energy at which the resonant state of a REMPI transition resides. In Fig. 2, state energy is simply the energy sum of two laser photons.

In Fig. 2 two REMPI band progressions are observed which correspond to the REMPI bands reported by Sur *et al.*^{3,4} from two photon REMPI spectra of supersonically cooled oxygen at ~ 5 K. The stronger progression with bands centered at 306, 295, 287.7, and 280.5 nm were assigned by Sur *et al.* to two photon $(3s\sigma)^3\Pi_g (v' = 0, 1, 2, 3) \leftarrow X^3\Sigma_g^- (v'' = 0)$ transitions. The weaker progression with bands centered at 301.2, 293, 285, and 278 nm was assigned to the $(3s\sigma)^1\Pi_g (v' = 0, 1, 2, 3) \leftarrow X^3\Sigma_g^- (v'' = 0)$ transitions. Sur *et al.* also noted that a band corresponding to another electronic state lies near the $(3s\sigma)^1\Pi_g (v' = 2)$ state which complicates the rotational structure.³ They proposed that this band arises from a valence $^1\Pi_g$ upper state. *Ab initio* calculations⁸ predict this valence $^1\Pi_g$ state to lie at 67 500 cm^{-1} . In the present 300 K spectrum (Fig. 2) the two photon REMPI band of this proposed

TABLE I. Summary of bands observed in the REMPI spectrum of microwave discharge excited O_2 molecule.

Band	Wavelength (nm)	State energy (cm^{-1})	Comments
<i>A</i>	331.3	68 230	$(3s\sigma)^1\Pi_g (v' = 1) \leftarrow a^1\Delta_g (v'' = 0)$
<i>B</i>	330.9	68 305	Possible new state with $a^1\Delta_g (v'' = 0)$ as the initial state
<i>C</i>	324.8	69 440	$(3s\sigma)^3\Pi_g (v' = 2) \leftarrow a^1\Delta_g (v'' = 0)$
The <i>DEFG</i> band system incorporates transitions from $(3s\sigma)^1\Pi_g (v' = 0) \leftarrow a^1\Delta_g (v'' = 0)$			
<i>D</i>	321.6	70 045	Broadband, degraded to red with unresolved rotational structure
<i>E</i>	321.3	70 110	Intense symmetric peak; 10 cm^{-1} FWHM
<i>F</i>	320.8	70 210	Unresolved fine structure which includes six bands separated by ~ 5 cm^{-1}
<i>G</i>	320.5	70 265	Six bands separated by ~ 10 cm^{-1}
<i>H</i>	320.0	70 365	Possible new state with $a^1\Delta_g (v'' = 0)$ as the initial state
<i>I</i>	319.6	70 440	Possible new state with $a^1\Delta_g (v'' = 0)$ as the initial state
<i>J</i>	312.2	71 925	$(3s\sigma)^1\Pi_g (v' = 3) \leftarrow a^1\Delta_g (v'' = 0)$. $B_v = 1.169$ cm^{-1}
<i>K</i>	311.3	66 345	$(3s\sigma)^3\Pi_g (v' = 0) \leftarrow X^1\Sigma_g^- (v'' = 1)$. Resolved rotational structure

valence $^1\Pi_g$ state is not conspicuous but is probably merged with the rotational envelope of the $(3s\sigma)^3\Pi_g (v' = 2) \leftarrow X^3\Sigma_g^- (v'' = 0)$ band.

In Fig. 1 the bands labeled *A*, *DEFG*, and *J* form a progression which has the same pattern as the $v' = 1, 2, 3$ progression of the $(3s\sigma)^1\Pi_g \leftarrow (v'' = 0) X^3\Sigma_g^-$ transitions in Fig. 2 except that each corresponding band lies ~ 7883 cm^{-1} lower than the energy sum of two laser photons. Since the T_0 of $O_2 a^1\Delta_g$ is approximately 7883 cm^{-1} and we have determined that the REMPI bands in Fig. 1 originate either from $O_2 a^1\Delta_g$ or from $O_2 X^3\Sigma_g^- (v' > 0)$ initial states, we assign bands *A* and *J* to $(3s\sigma)^1\Pi_g (v' = 1, 3) \leftarrow a^1\Delta_g (v'' = 0)$ two photon transitions, respectively. Below a state energy of 68 000 cm^{-1} , which includes the $(3s\sigma)^1\Pi_g (v' = 0) \leftarrow a^1\Delta_g (v'' = 0)$ band, no intense m/z 32 signals were observed. Bands *DEFG* display complex structure which seems to involve at least two different electronic states. The $(3s\sigma)^1\Pi_g (v' = 2) \leftarrow a^1\Delta_g (v'' = 0)$ two photon transition can account for part of the structure seen in bands *DEFG*. Presumably two photon transitions to neighboring high lying states (including the proposed valence $^1\Pi_g$ state³) from the $a^1\Delta_g$ initial state can account for the balance of the structure in bands *DEFG*.

The state energy (cm^{-1}) plotted in the upper abscissa of Fig. 1 shows the energy of the resonant state when the initial state is $O_2 a^1\Delta_g$, i.e., in Fig. 1 state energy is the energy sum of two laser photons plus the T_0 of $a^1\Delta_g$ ($= 7883$ cm^{-1}). Although the laser wavelength intervals differ between Fig. 1 and Fig. 2, both spectra encompass the same state energy range when the initial state is $a^1\Delta_g (v'' = 0)$ in Fig. 1 and $X^3\Sigma_g^- (v'' = 0)$ in Fig. 2. This convention simplifies direct comparison of the spectra between Figs. 1 and 2.

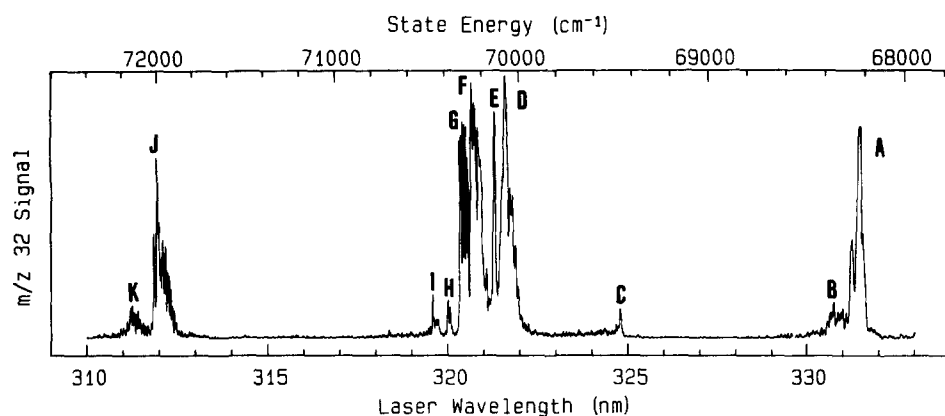


FIG. 1. Composite spectrum of $O_2\ a\ ^1\Delta_g$. State energy (cm^{-1}) is the energy sum of two laser photons plus the T_0 of the $O_2\ ^1\Delta_g$ state.

The intensity patterns of the REMPI bands observed in Fig. 1 and Fig. 2 support the spectral assignments. The selection rule $\Delta S = 0$ permits transitions between states of the same multiplicity. Transitions between states of differing multiplicities ($\Delta S \neq 0$) are formally forbidden and become allowed only through configurational mixing. Thus, in Fig. 2 transitions from the $X^3\Sigma_g^-$ to the $(3s\sigma)^3\Pi_g$ states are generally more intense than transitions to the $(3s\sigma)^1\Pi_g$ states. But when the initial state is the $a\ ^1\Delta_g$ state, the pattern of weak and strong bands is reversed. As shown in Fig. 1, transitions to the $(3s\sigma)^1\Pi_g$ states are intense because the $(3s\sigma)^1\Pi_g \leftarrow a\ ^1\Delta_g$ transitions ($\Delta S = 0$) are allowed. Most of the formally forbidden singlet-triplet transitions are absent. The only $\Delta S \neq 0$ spectral feature which appears in the spectrum of $O_2\ a\ ^1\Delta_g$ is band C which appears weakly at 324.8 nm (Fig. 1). Band C is assigned to the two photon $(3s\sigma)^3\Pi_g$ ($v' = 2$) $\leftarrow a\ ^1\Delta_g$ ($v'' = 0$) transition because its two photon energy is $\sim 7883\text{ cm}^{-1}$ lower than two photon energy of the $(3s\sigma)^3\Pi_g$ ($v' = 2$) $\leftarrow X^3\Sigma_g^-$ ($v'' = 0$) band at 287.7 nm (Fig. 2).

In Fig. 1, band K is centered at 311.3 nm and does not lie 7883 cm^{-1} to the red of any corresponding band in Fig. 2. Band K cannot be assigned to a transition from the $O_2\ a\ ^1\Delta_g$ state; instead, it is assigned to the two photon $(3s\sigma)^3\Pi_g$ ($v' = 0$) $\leftarrow X^3\Sigma_g^-$ ($v'' = 1$) transition (the state energy abscissa of Fig. 1 does not apply to band K).

Bands B, H, and I centered at 330.9, 321.1, and 319.7 nm do not correlate with any feature in the spectrum of $X^3\Sigma_g^-$. In addition, these bands do not have reasonable as-

signments as hot bands from the $O_2\ a\ ^1\Delta_g$ or $X^3\Sigma_g^-$ states. We believe that bands B, H, and I may arise from previously uncataloged states accessible from the $a\ ^1\Delta_g$ state. An alternate assignment of bands H and I would be as rotational branches associated with the *DEGF* complex.

Figure 3(a) shows the rotationally resolved REMPI spectrum of band J. Figure 3(b) shows a computer generated simulation of this band based upon $(3s\sigma)^1\Pi_g \leftarrow a\ ^1\Delta_g$ ($v'' = 0$) transitions. The rotational analysis of band J gave a rotational constant B'_v of 1.169 cm^{-1} and a centrifugal distortion constant of $9 \times 10^{-5}\text{ cm}^{-1}$. The spectrum displays a decrease in intensity with increasing J' at a rate greater than can be accounted for by a Boltzmann distribution in the initial state; therefore, a loss term was included in the simulation to exponentially decrease the transition strength as a function of the upper state rotational energy.

The signal intensities observed in the spectrum could not be accounted for by applying the two photon Honl-London formulas in the simulation.⁹ The two photon Honl-London formulas do not accurately describe the REMPI signal intensities when the laser radiation is intense enough to cause saturation of the resonant molecular state in the REMPI transition, nor when the laser beam intensity and pulse duration are sufficient to deplete the total population of the resonant rovibronic state.¹⁰ Considering the large laser intensities used during these studies both circumstances seem likely.

In the previous work by Sur *et al.*³ the REMPI band at 278 nm (Fig. 2) was assigned to $(3s\sigma)^1\Pi_g$

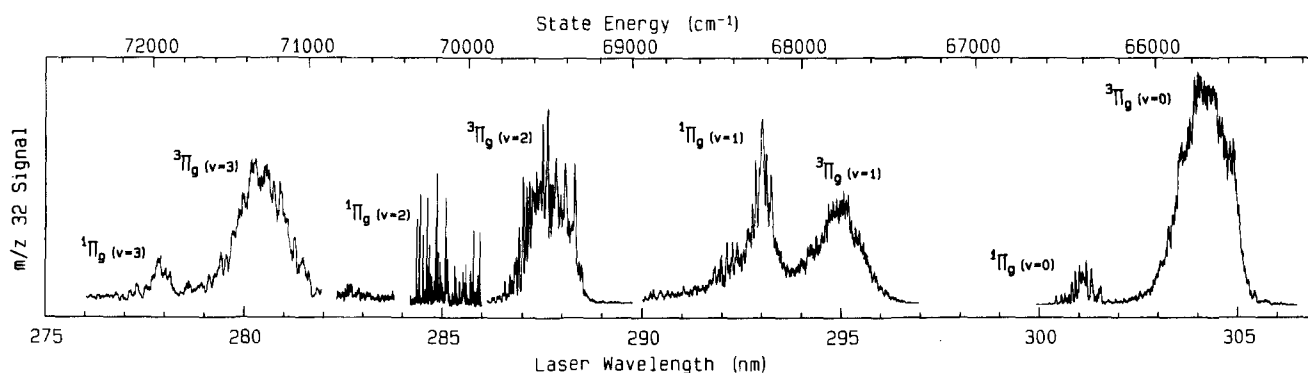


FIG. 2. Composite spectrum of $O_2\ ^3\Sigma_g^-$. State energy (cm^{-1}) is the energy sum of two laser photons.

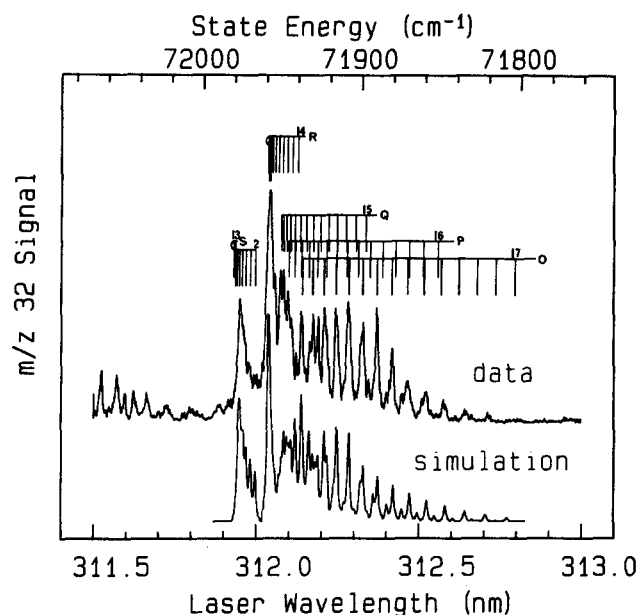


FIG. 3. Top trace: Spectrum of band *J*. Lower trace: Computer simulated spectrum of band *J* based upon two photon $(3s\sigma)^1\Pi_g (v' = 3) \leftarrow a^1\Delta_g (v'' = 0)$ transitions.

$(v' = 3) \leftarrow (v'' = 0) X^3\Sigma_g^-$ transitions because it fit a vibrational progression. They determined that the $(3s\sigma)^1\Pi_g (v' = 0)$ member of this progression exhibited a rotational constant of 1.68 cm^{-1} . In this work, band *J* allows a view of these same upper states by excitation from the $a^1\Delta_g$ state. In view of the large change in the rotational constants between the $v' = 0$ and $v' = 3$ levels in the $(3s\sigma)^1\Pi_g$ state, we wished to use the computer simulations to independently verify assignment of the upper state of band *J* to the $(3s\sigma)^1\Pi_g (v'' = 3)$ state. If band *J* did not arise from the $(3s\sigma)^1\Pi_g (v'' = 3)$ state, possibly candidates for band *J* would be selected from other two photon accessible Σ_g , Π_g , Δ_g , Φ_g , or Γ_g ($\Lambda = 0, 1, 2, 3, 4$) states. Since band *J* is observed near $71\,925 \text{ cm}^{-1}$ from both $O_2 X^3\Sigma_g^-$ and $O_2 a^1\Delta_g$ states, alternative assignment choices are limited to Σ_g , Π_g , and Δ_g ($\Lambda = 0, 1, 2$). Spin statistics permit Σ states of $^{16}O_2$ to have only half of the rotational levels ($N = \text{odd}$ for Σ^- ; $N = \text{even}$ for Σ^+ states) that states of $\Lambda > 0$ do. Thus, spectra of Σ_g states will display fewer rotational lines than spectra of states with $\Lambda > 0$. The complexity of band *J* emphatically rules out any possibility that band *J* originates from transitions to a Σ_g state. We could resolve between Π_g and Δ_g ($\Lambda = 1, 2$) final states by observing the lowest rotational lines present in band *J*. Unfortunately, spectral congestion thwarts an independent verification of or rejection of the presently accepted $^1\Pi_g$ state symmetry.

During this study we noted that the m/z 32 signal magnitudes observed in $O_2 a^1\Delta_g$ were comparable to those obtained from ground state oxygen. Since the concentration of $O_2 a^1\Delta_g$ is less than 10% of the ground state O_2 concentration, the REMPI cross section for $O_2 a^1\Delta_g$ is at least an order of magnitude greater than that of ground state O_2 .

REMPI spectroscopy appears to be a very sensitive and selective method of detecting $O_2 a^1\Delta_g$ molecules. Between

330–310 nm two photon REMPI detection of $O_2 a^1\Delta_g$ is relatively free of interfering bands from $O_2 X^3\Sigma_g^-$. We estimate a one laser pulse detection limit for $O_2 a^1\Delta_g$ of better than $5 \times 10^9 \text{ molecule cm}^{-3}$ in the ion source. The estimate of the detection limit is an upper limit since we have assumed 10% conversion of the oxygen to $a^1\Delta_g$, and total transmission of the $O_2 a^1\Delta_g$ to the ion source.

DISCUSSION

Comparison of the spectrum of $O_2 a^1\Delta_g$ and the spectrum of ground state molecular oxygen reveals a number of interesting features. The two photon energies of the bands *A*, *DEFG*, and *J* of the $O_2 a^1\Delta_g$ spectrum correspond to two photon transition energies reported by Sur *et al.*,³ who assigned these states to the $v' = 1, 2$, and 3 levels of the $(3s\sigma)^1\Pi_g$ Rydberg state. The $(3s\sigma)^1\Pi_g (v' = 0)$ level of this state, observed at an energy of $66\,445 \text{ cm}^{-1}$ above the ground state, is not seen in the spectrum of $O_2 a^1\Delta_g$. We would expect this transition to be located at 340 nm. However, at laser wavelengths greater than 336 nm, four photons are required to ionize $O_2 a^1\Delta_g$. Therefore, a 2 + 2 REMPI process is necessary to probe the $v' = 0$ level of the $(3s\sigma)^1\Pi_g$ state. The cross section for the four photon process may be much less than for the 2 + 1 REMPI process operative at shorter wavelengths. It should also be noted that a dissociative state of oxygen is known to lie at the energy sum of three $\sim 340 \text{ nm}$ photons.¹¹ After formation of the $(3s\sigma)^1\Pi_g (v' = 0)$ state by absorption of two 340 nm photons, absorption of one more photon can dissociate O_2 . Thus, at 340 nm the one photon dissociation process may compete effectively with the two photon ionization process, eliminating any REMPI signal.

Transitions from the $a^1\Delta_g$ state to the $(3s\sigma)^3\Pi_g$ Rydberg state of oxygen are extremely weak or absent. This is surprising in light of the fact that no strong spin multiplicity dependence is observed in transitions from the triplet ground state to the $(3s\sigma)^1\Pi_g (v' = 0, 1, 2, 3)$ Rydberg state of O_2 .³ Differences in the structure of the ground state and the $a^1\Delta_g$ state of oxygen seem insufficient to cause such an effect. Perhaps, there is considerable difference in the structure of the $(3s\sigma)^3\Pi_g$ and the $(3s\sigma)^1\Pi_g$ Rydberg states brought on by differences in the interaction of the Rydberg states with nearby valence states. Some evidence for this difference is found in the vibrational spacings observed in the respective states. The $(3s\sigma)^3\Pi_g$ state has a spacing of 2010 cm^{-1} between the $v' = 0$ and the $v' = 1$ vibrational levels while this spacing is only 1870 cm^{-1} in the $(3s\sigma)^1\Pi_g$ state. Information from the spacings of the remaining vibrational levels is clouded by the existence of additional states near the $(3s\sigma)^1\Pi_g (v' = 2)$ band. Bands *DEFGHI* extend over an energy range of 500 cm^{-1} , and the precise location of $(3s\sigma)^1\Pi_g (v' = 2)$ band center is not clear.

Detailed rotational analysis at each vibrational level is needed to further characterize the $(3s\sigma)^1\Pi_g$ state. Unfortunately, we were only able to successfully analyze the $v' = 3$ vibrational level, band *J*. The $v' = 1$ vibrational level, band *A*, is not rotationally resolved, and the $v' = 2$ vibrational level which lies within band *DEFG* is complicated by adjacent

states. The $(3s\sigma)^1\Pi_g$ ($v' = 0$) rotational structure at 5 K was analyzed by Sur *et al.*,³ who calculated a B_0 of 1.68 cm^{-1} ($r_e = 1.12\text{ \AA}$). We obtain a B_0 of 1.169 cm^{-1} ($r_e = 1.35\text{ \AA}$) for the $v' = 3$ vibrational level of the same state. (In the $X^3\Sigma_g^-$ state, $r_e = 1.21\text{ \AA}$.)

The large difference between the rotational constants observed in different vibrational levels of the $(3s\sigma)^1\Pi_g$ state is remarkable. Initially this sparked speculation that band J was a new electronic state and unrelated to the $(3s\sigma)^1\Pi_g$ Rydberg state. However, if this were the case, we should have also observed an additional REMPI band near 312 nm from $(3s\sigma)^1\Pi_g$ ($v' = 3$) \leftarrow $a^1\Delta_g$ transitions. No additional band is observed. Therefore, it appears likely that a strong Rydberg–valence interaction is responsible for the change in rotational constants between the $(3s\sigma)^1\Pi_g$ ($v' = 1$) and ($v' = 3$) states. Sur *et al.* have given evidence for Rydberg–valence interactions in the $(3s\sigma)^3\Pi_g$ Rydberg state.⁴ However, this interaction is relatively weak and resulted only in selective broadening of the spectral linewidths. Theoretical calculations performed by Michaels⁸ predict that a number of valence states of oxygen with $^1\Pi_g$ symmetry lie in the same energy region as the $(3s\sigma)^1\Pi_g$ Rydberg state. These valence states may be capable of interaction with the $(3s\sigma)^1\Pi_g$ Rydberg state. The interaction may be in the form of an avoided crossing of the respective potentials to form two new adiabatic states or the interaction may be specific to the individual vibrational levels of the $(3s\sigma)^1\Pi_g$ Rydberg state.¹² Since no rotational analysis of the $v' = 1$ or $v' = 2$ levels of the $(3s\sigma)^1\Pi_g$ Rydberg state was possible, we can provide no better specification of the perturbing interaction.

The bands appearing around 321 nm, bands *DEFGHI*, clearly originate from more than one electronic state. A number of bound electronic states with symmetries appropriate to allow observation by two photon absorption are predicted to reside in this energy region.⁸ However, since several states appear at coincident energies, and no vibra-

tional progressions originating from these states are observed it is not possible to obtain the spectroscopic information that would allow the successful assignment of these states from our current data.

In summary, we have shown that the $(3s\sigma)^1\Pi_g$ Rydberg state differs greatly from the corresponding $(3s\sigma)^3\Pi_g$ Rydberg state. In the $(3s\sigma)^1\Pi_g$ Rydberg state rotational analysis reveals large changes in the equilibrium nuclear distance between the $v' = 0$ to the $v' = 3$ vibrational levels. We suggest that these structural changes arise from differences in the interactions of these Rydberg states with nearby valence states. This study also demonstrates that REMPI spectroscopy is very sensitive method of detecting $O_2 a^1\Delta_g$ molecules. Undoubtedly the application of this technique will lead to a better understanding of reactions which involve $O_2 a^1\Delta_g$.

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