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Identification of the nd Δ and Σ states and the $^{1,3}\Phi \leftarrow \leftarrow X \, ^3\Sigma_g^-$ transition of O_2 by resonant multiphoton ionization

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Spectra of the $3d$ Rydberg state region of O_2 have been obtained by two-photon resonant ionization of the ground electronic state. By varying the rotational distribution and radiation polarization, all observed bands were identified and attributed to excitation of Σ, Δ, and Φ states. Earlier assignments were corrected. The Δ and Φ assignments are complete while the Σ assignments are so far incomplete.

I. INTRODUCTION

The $4s$-$3d$ Rydberg states of O_2 have been the subject of several recent investigations.[1-5] The observed spectra due to the $2+1$ REMPI $3d \leftarrow \leftarrow a \, ^1\Delta_2$ transitions are now well understood, although a number of formally allowed transitions have not yet been observed. Rapid progress is now being made in interpreting the more complex spectra due to the $3d \leftarrow \leftarrow \, ^3\Sigma_g^-$ transitions. In this paper we report in detail on that part of the spectra due to transitions to Δ and Φ states and report progress in identification of Σ states.

II. EXPERIMENTAL

The apparatus described in Ref. 1 was used in this work with only minor changes. The most important is the substitution of a pulsed nozzle for the microwave discharge source. By varying timing, gas mixture, pressure and, most importantly, location of ionization in the molecular beam, spectra were taken at many different degrees of rotational cooling, although this cooling could not be controlled with any precision. The best cooling resulted in spectra with $> 90\%$ of the intensity due to transitions from the $N'' = 1$ levels. Warmer spectra were also taken with the use of a double and single rhomb to study polarization effects.

III. RESULTS

A. $^3\Delta$ states

In order to give an overall view, Figs. 1 and 2 show the $2+1$ REMPI spectra of the $3d$ Rydberg states of O_2 excited from the $X \, ^3\Sigma_g^-$ ground state for $v' = 0, 1, 2$ and 3 at different rotational temperatures. Tables of observed transition frequencies are available from Ref. 6. Spectra for all vibrational levels $v' = 0$-3 were nearly identical in respect to relative positions of the various bands, but differed considerably in respect to relative intensities. These spectra can be compared with those of Fig. 1 of Park *et al.*[1] and the upper part of Fig. 3 of Loo *et al.*[2] Band assignments made in this paper are also shown in this figure.

The greatest difficulty in detecting and assigning the transitions to the $^3\Delta$ states arises from the fact that for all observed vibrational levels ($v' = 0$-3) the bands are badly overlapped by more intense transitions to other states and many appear to be predissociated to various degrees. The problem of congestion could be alleviated by rotational cooling and, as discussed below, by the use of circularly polarized light. However, rotational cooling, as well as heterogeneous predissociation, decreased the number of spectral lines and thus made analysis more difficult.

The assignments were helped greatly by earlier work[4] in which the $3d\pi \, ^1\Delta_2'$ state was detected by two-photon REMPI from the $a \, ^1\Delta_2$ metastable state of O_2. The identification of that state was made definitively by rotational analysis and polarization effects. [The case (a)–case (a) selection rules[7] for two identical photons allow only a Q branch for those $\Delta\Omega = 0$ transitions occurring by virtue of the zero rank component of the transition moment tensor. Since this component vanishes with circularly polarized light, the intensity of the Q branch decreases, often dramatically, upon switching from linear to circular polarized light.] In the work of Park *et al.*,[4] the $3d\pi \, ^3\Delta_2$ state was also tentatively identified, but could not be rotationally analyzed due to its very low intensity. Instead the tentative assignment of the band depended solely on its polarization dependence and its position in the spectrum. Although nominally spin-forbidden it appeared weakly due to spin–orbit interaction with the strongly allowed $^1\Delta_2$ state.

In the present spectra both the $^1\Delta_2$ and the $^3\Delta_2$ states are found to occur at their previously observed energies. (See Fig. 2 and Table I.) A rotational analysis definitively confirms the identity of the $^3\Delta_2$ states. The case (b)–case (a) two-photon rotational selection rules and line strength factors were very useful in this respect and will be very briefly reviewed.

According to Mainos,[8] the multiphoton rotational line strength is proportional to the multiphoton rotational line factor defined by

$$\Theta_{k,\Delta\Lambda}^{(n)}(a-b) = (2J+1)(2J'+1)(2N'+1)$$
$$\times \begin{vmatrix} J' & S & N' \\ \Lambda'+\Sigma & -\Sigma & -\Lambda' \end{vmatrix}^2$$
$$\times \begin{vmatrix} J & k & J' \\ \Omega & -\Delta\Lambda & -\Lambda'-\Sigma \end{vmatrix}^2,$$

where the primed quantities refer to the case (b) state, and $k = 0$ or 2 for two identical photons (except that k has only the value 2 for circularly polarized light), and the other symbols have their conventional meanings. For $k = 0$ the
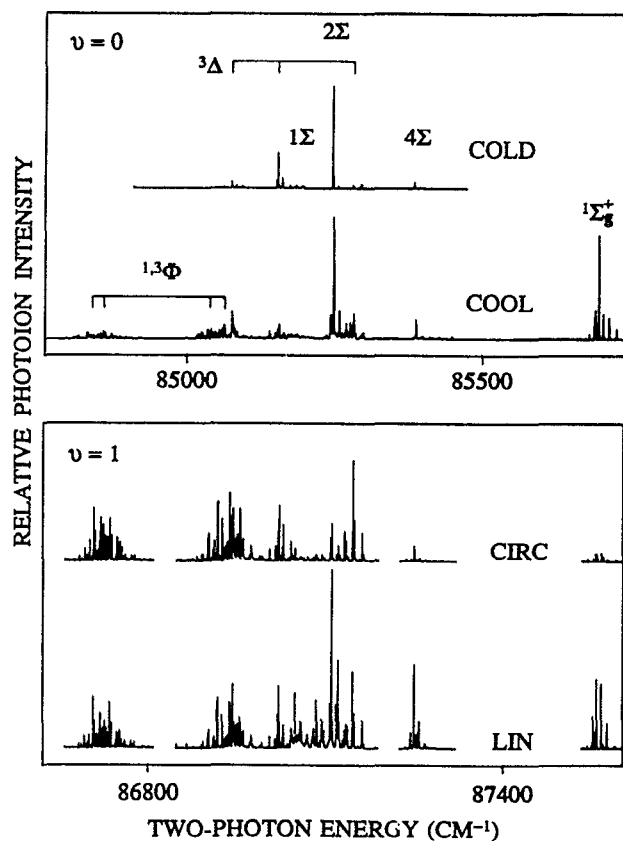
FIG. 1. Overall REMPI spectra of the $3d$ Rydberg states for $v'=0$ and 1. The $^3\Delta$ states are most clearly shown in the upper part of the $v'=0$ spectrum. The $^{1,3}\Phi$ states are also indicated and can be seen to "disappear" in the colder spectrum. For $v'=1$ the spectrum is shown for both linear and circular polarization. The energy scale of both spectra are the same so that corresponding bands are vertically aligned. Thus the identification shown for $v'=0$ can be extended vertically to $v'=1$. Similarly the linear-circular behavior (see text) shown for $v'=1$ supports the identification of Σ states given in $v'=0$. Relative intensities are approximate.
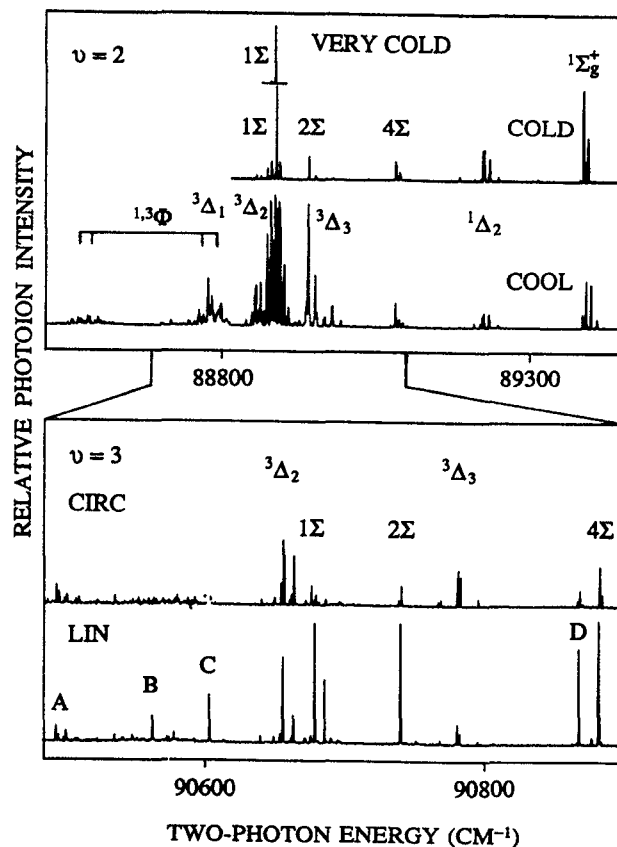
FIG. 2. REMPI spectra of $v'=2$ and 3 of the $3d$ Rydberg States. The $v'=3$ spectrum has an expanded energy scale as indicated. For $v'=2$ the $^1\Delta_2$ band is shown and its relation to the other $^3\Delta$ bands can be seen. The extreme spectral simplification achieved thru rotational cooling can be seen, especially for the 1Σ band. The $v'=3$ spectrum also contains four bands marked A–D which are $v'=0$ levels of $4d$ Rydberg states. The polarization behavior shows that A is non Σ in character while B–D are Σ in character. Band D has been assigned as $^1\Sigma_g^+$ by Pratt et al. Bands B and C appear to correspond to 1Σ and 2Σ in the $3d$ spectrum. Band A resembles the spectrum of $3d\pi$, $^3\Delta_1$.

second 3-j symbol is nonzero only for $\Delta\Lambda=0$, (instead of $\Delta\Omega=0$ when both states are case (a), and then only for $J'=J$, i.e., the Q branch only. Since the $k=0$ contribution vanishes for circularly polarized light (while the intensity

due to the $k=2$ term increases by a factor of 3/2 for all branches), a decrease of Q branch intensity is decisive evidence for Σ character of the states excited from the $^3\Sigma_g^-$ ground state of O_2. The detection and assignment of $^3\Delta$

TABLE I. Energy of lowest rotational level of state ($J'=\Omega'$) in cm^{-1}. See Sec. III E. vw=very weak, nm=not measured in this work, na=not applicable.

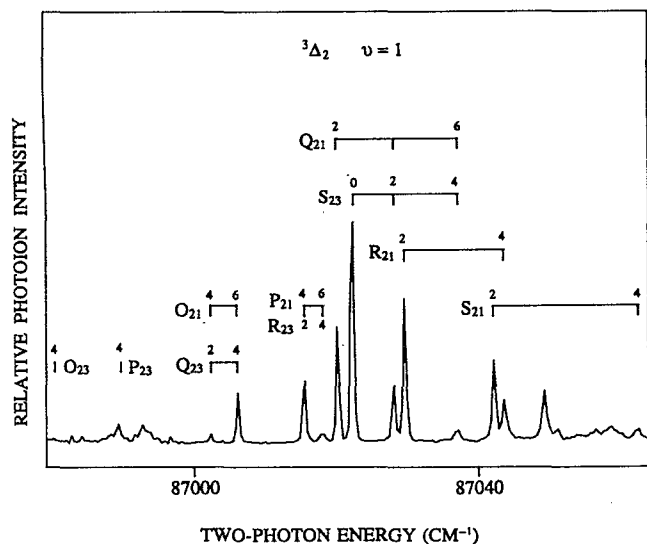|	$^{1,3}\Phi$ and $^{1,3}\Delta$ states								
v'	$^3\Phi_2$	$^3\Phi_3$	$^3\Phi_4$	$^1\Phi_3$	$^3\Delta_1$	$^3\Delta_2$	$^3\Delta_3$	$^1\Delta_2$	$^1\Sigma_0^+$
0	84 838	84 863	85 042	85 065	85 080	85 153	85 282	85 527	85 694
	1 879	1 877	1 877	1 876	1 867	1 866	1 867	1 863	1 862
1	86 717	86 740	86 919	86 941	86 947	87 021	87 149	87 390	87 556
	1 845	1 845	1 843	1 843	1 832	1 832	1 832	1 836	1 839
2	88 562	88 585	88 762	88 784	88 779	88 853	88 981	89 226	89 395
						1 802	1 802		
3	vw	vw	vw	vw	vw	90 655	90 783	nm	nm
ΔE^1									
Expt. avg.	na	na	na	na	-101	-27	101	345	512
Calc.	na	na	na	na	-101	-30	101	330	536
$4d(v'=0)$									
Expt.					90 495				
Calc.					90 510				

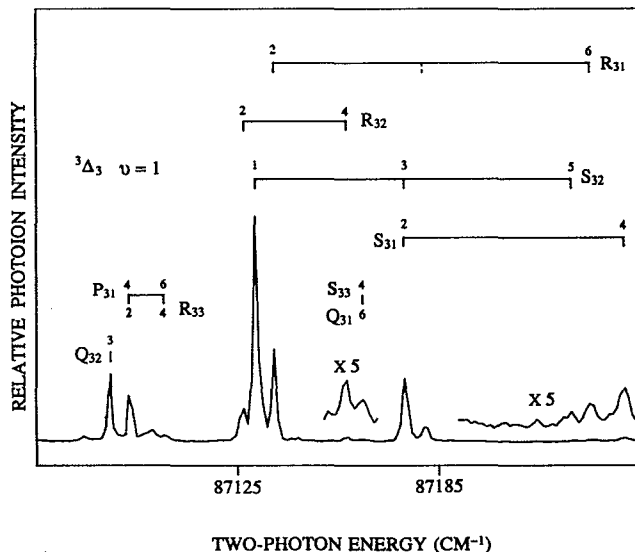FIG. 3. REMPI spectrum (circular polarization) of $^3\Delta_2$ ($v'=1$) with rotational assignments.

FIG. 5. REMPI spectrum (circular polarization) of $^3\Delta_3$ ($v'=1$) with rotational assignments. The region in which O branches should occur (off scale to the red) is strongly dominated by the 2Σ band.
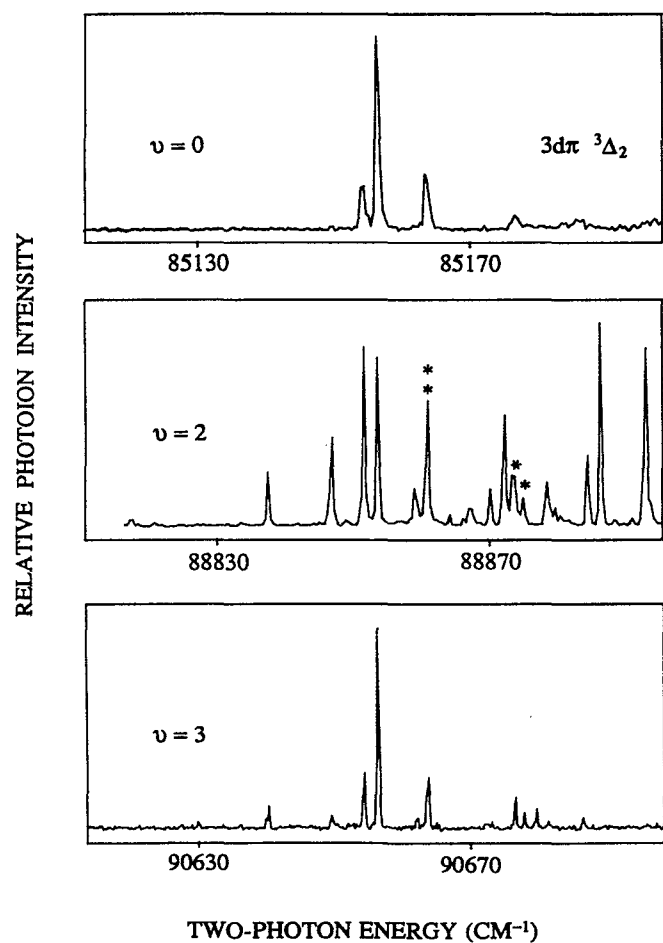
FIG. 4. REMPI spectra of $^3\Delta_2$ $v'=0$ (lin.), 2 (circ.), 3 (circ.) with the same energy scale as that of Fig. 3 so that rotational assignments can be made readily by comparison. For $v'=2$ note the peak marked with 2 stars. All the peaks to the blue of this peak which are not marked with a single star have been assigned as belonging to the 1Σ band.

FIG. 6. REMPI spectra (circular polarization) of $^3\Delta_3$ $v'=0,2,3$ aligned and presented on the same total energy scale as in Fig. 5 for ease of transferring rotational assignments.

FIG. 7. REMPI spectrum (linear polarization) of $^3\Delta_1$ ($v'=1$). Three bands overlap here and residuals belong to $^3\Phi_4$ and $^1\Phi_3$ (see Fig. 10).

transitions in this research has been greatly facilitated by the supression of stronger overlapping Σ transitions with circularly polarized light as mentioned earlier.
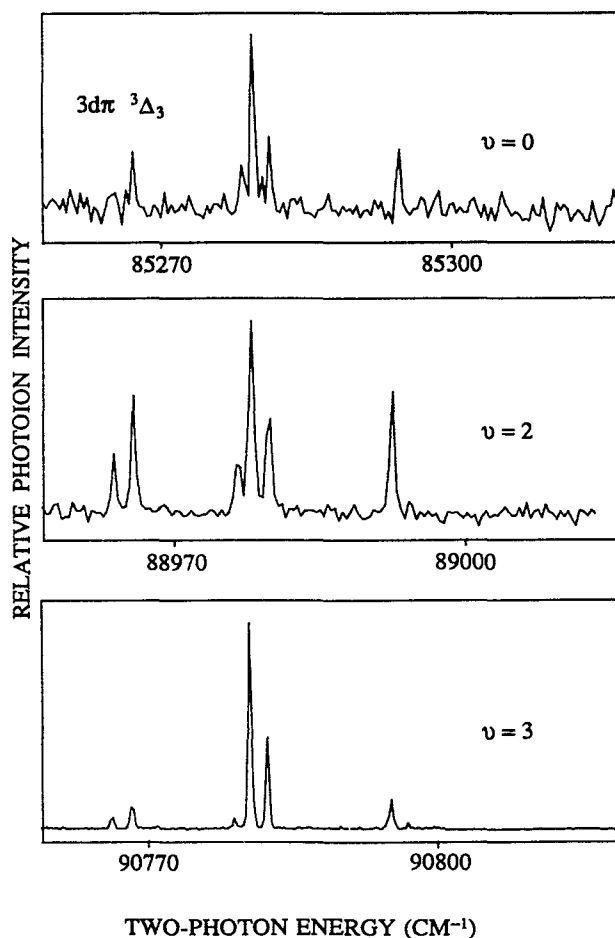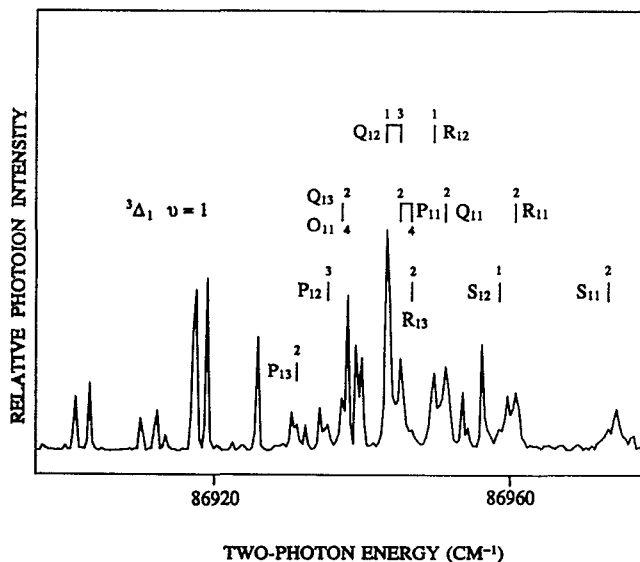
Another useful conclusion from the expression for the line strength factor is the following. For the $^3\Delta_2$ resonant state one has $\Sigma=0$ and therefore all zeros in the bottom row of the first 3-j symbol. The top row sum must then be even,[9] forbidding $J''=N''$ (i.e., transitions from F_2 levels of the ground state).

Figures 3 and 4 show the $^3\Delta_2$, $v'=0-3$ bands. All spectra, except for $v'=0$, are taken with circularly polarized light to suppress the partially overlapping 1Σ band. The $v'=0$ band of the 1Σ state is apparently very strongly predissociated and is very nearly absent in the spectrum. Only a single broadened line can be attributed to the 1Σ band. The rotational structures of all the $^3\Delta_2$ bands are very similar. The regular vibrational spacing, very nearly that of the ion, indicates no significant perturbation.

The bands for $^3\Delta_3$, $v'=0-3$ are shown in Figs. 5 and 6. The O branches are not shown as they are strongly overlapped by the 2Σ band even with the use of circularly polarized light. As with $^3\Delta_2$ the $^3\Delta_3$ bands are regularly spaced and show no significant perturbation.

The $^3\Delta_1$ state is the most difficult of the $^3\Delta$ states to identify purely spectroscopically since at moderate rotational temperatures ($> \sim 100$ K) its bands are badly overlapped by a complex spectrum immediately to the red which is not suppressed by circular polarization. Also the rotational lines are significantly broadened, probably due to predissociation. However, at the coldest rotational temperatures we were able to achieve, the bands were detectable for $v'=0-2$ and the spectra are shown in Figs. 7 and 8. The identification is strongly supported by the fact that these bands lie very nearly 200 cm^{-1} below those of $^3\Delta_3$ as expected from the value of the spin–orbit splitting of the ion core (200.33 cm^{-1}).[10] A band which is probably the $4d$
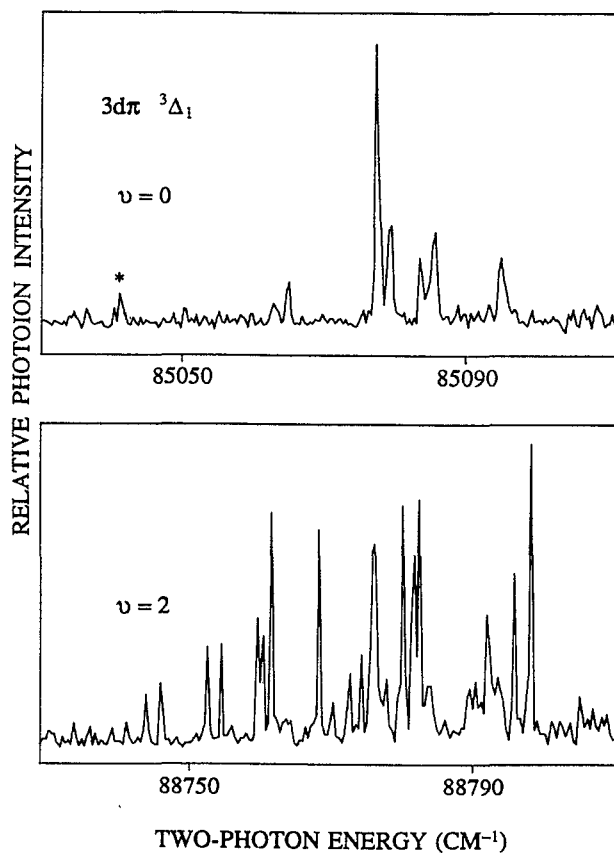

TWO-PHOTON ENERGY (CM^{-1})

FIG. 8. REMPI spectra (linear polarization) of $^3\Delta_1$ $v'=0$ and 2 ($v'=3$ is very weak) showing the effect of cooling on the Φ states spectrum. For $v'=0$ the Φ state spectrum shows only a transition starting in $N''=1$, the $S_{31}(2)$ line of $^3\Phi_4$ marked with a star. For $v'=2$ the rotational temperature is much higher and the spectrum is dominated by the Φ states. See Fig. 10 for the assignment of these states.

($v'=0$) level of $^3\Delta_1$ is seen at 90 495 cm^{-1}. This band is marked with an uppercase "A" in Fig. 2. Preliminary calculations (see Sec. III E) support our assignment. The rotational assignment gives a B' value of ≈ 1.43 which is lower than the average B' value (1.6) of the $3d$ $^3\Delta$ states, very probably due to increasing uncoupling with increasing n.

B. $^{1,3}\Phi$ states

At the low energy side of the spectra of Fig. 1 lie two clusters of bands approximately 200 cm^{-1} apart. The high energy cluster badly overlaps the $^3\Delta_1$ band except at the very lowest rotational temperatures. These bands behave very anomalously. In our initial experiments they seemed to *disappear* upon cooling (see Figs. 1 and 8). In fact they cannot be seen in the spectra of Park et al.[1] which were taken under conditions of strong cooling, while they are very prominent in the spectra of Loo et al.[2] whose measurements were carried out at room temperature. This behavior suggests that they appear as a result of a rotational interaction which allows them to "borrow oscillator strength" from some relatively intense allowed transition. Loo et al.[2] assign these bands as due to transitions to the
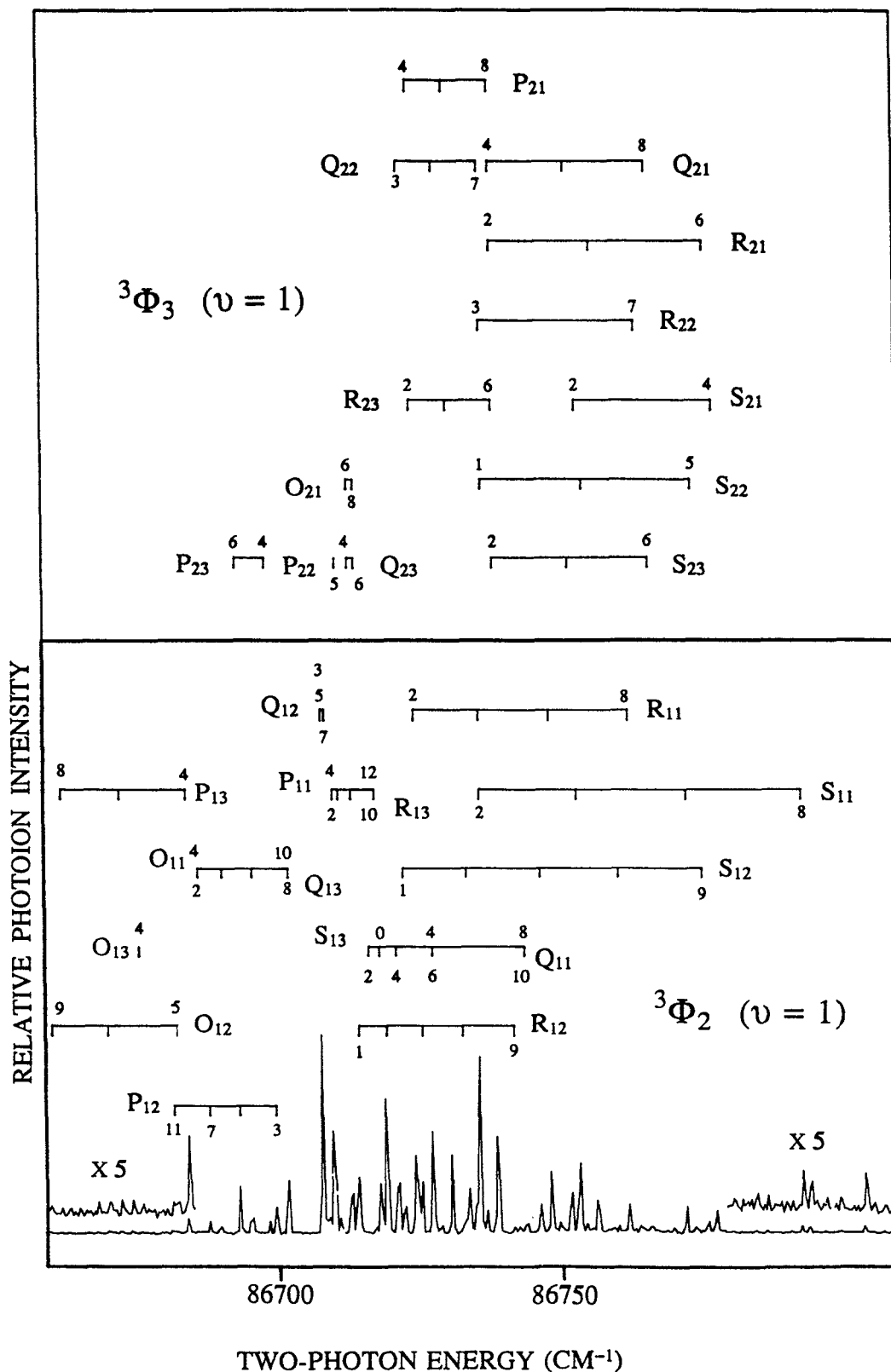
FIG. 9. REMPI spectrum of the overlapped $^3\Phi_2$ and $^3\Phi_3$ ($v'=1$) bands with rotational assignments. Of 30 possible branches 28 were strong enough to use in the determination of the upper state levels and are shown here. Most of the peaks are composite features. Spectra of $v'=0$ and 2 are very similar and $v'=3$ is too weak for reliable analysis.
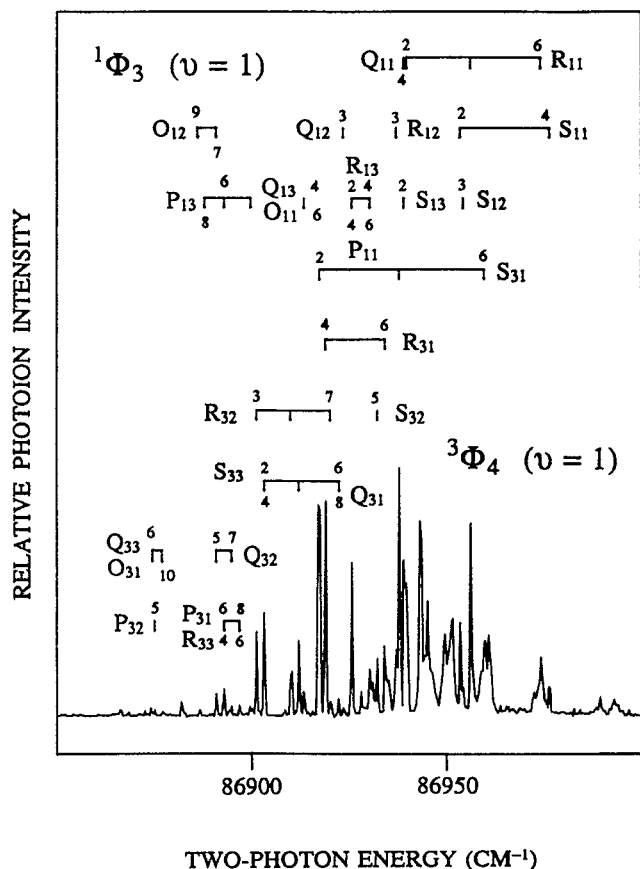
FIG. 10. REMPI spectrum of overlapping $v'=1$ bands of the $^3\Phi_4$, $^1\Phi_3$, and $^3\Delta_1$ states with rotational assignments for the Φ states. Note the difference in linewidth between the Φ and Δ states.

$^{1,3}\Delta$ complex, for which one would not expect this anomalous behavior. On the other hand, these bands appear at approximately the positions expected for transitions to the $^{1,3}\Phi$ complex identified earlier in transitions from the a $^1\Delta_g$ state of O_2.[5] As mentioned earlier, these bands show no decrease in intensity with change from linear to circular polarized light. From calculations reported in the earlier works,[2,5] it appeared possible that the resonant states in question might belong to the $^{1,3}\pi$ complex which is expected in this energy region. However, those transitions are not expected to have the observed anomalous behavior. Upon careful measurement of spectra taken at moderate temperatures it is now certain that the observed states are members of the $^{1,3}\Phi$ complex. Figures 9 and 10 show these bands for $v'=1$ together with rotational line assignments which give upper state levels which coincide within experimental error with those of the $^{1,3}\Phi$ states identified in the earlier works. An important upper state rotational level observed in this work, but not in the earlier work[5] is the $J'=2$ level of the $^3\Phi_2$ state (see Fig. 9). This level was not observed in the earlier work since the $^3\Phi_2$ state in that case became allowed by an s-uncoupling interaction with the $^3\Phi_3$ state for which $J'=2$ does not exist. Its observation in the present work confirms the identification and supports the proposed transition mechanism.

The assignment of these bands to the $^{1,3}\Phi$ complex also explains their anomalous behavior, since they are nominally forbidden in two photon transitions which are restricted to $\Delta\Lambda\leqslant2$. The transitions become allowed by a J' dependent l-uncoupling interaction with members of the allowed $^{1,3}\Delta$ complex. Within the Φ complex, mixing by spin–orbit interaction and spin–uncoupling is also important. The strong spin–orbit mixing of the $^1\Delta_2$ and $^3\Delta_2$ states identified in this work is readily apparent from the relative positions of the $^3\Delta_{1,2,3}$ levels.

Another relevant characteristic of the $^{1,3}\Phi$ complex observed in the earlier work[5] is the lack of evidence for predissociation, except possibly for very weak predissociation of the $^1\Phi_3$ state, as inferred from the deviation of measured line intensities from calculated values. Those bands observed in this work which are assigned to the excitation of the $^{1,3}\Phi$ complex are composed of lines which are all laser bandwidth limited in contrast to those of all other bands observed in this work. This can be readily seen in Fig. 10 by comparing the widths of the lines ascribed to the Φ system with those ascribed to the $^3\Delta_1$ band. Many of the vibrational bands of the $^3\Delta$ system exhibit similar amounts of broadening as did the $^1\Delta_2$ bands observed in the earlier work.[4] In the latter case, the most probable predissociating state was identified as the repulsive 1 $^1\pi_g$ valence state as calculated most recently by Guberman[11] as well as others.[12–14] The $^3\Delta$ states are probably predissociated by the repulsive 1 $^3\pi_g$ valence state. Of the 62 valence states arising from 2 oxygen atoms in the ground configuration, Guberman has eliminated 31 with most important configurations which differ by more than two orbitals from the primary configuration of the ground state of the ion plus a free electron and therefore of the Rydberg states converging to the ground state of the ion. According to Guberman,[11] only the remaining 31 can interact significantly with these Rydberg states. Of these 31 states only two gerade states, 1 $^1\pi_g$ and 1 $^3\pi_g$ have potential curves so situated as to effectively predissociate the lower vibrational levels of the $3d$ Rydberg states. If this is indeed the case, π states can be expected to be strongly homogeneously predissociated (which may be one reason for their nonappearance in MPI), Σ and Δ states moderately heterogeneously predissociated, and Φ states very weakly predissociated by interaction with the predissociated Rydberg Δ states. All observations on the $3d$ Rydberg states are at least qualitatively in accord with these expectations. For example, J dependence of peak widths for the $^3\Delta$ states is easily seen in Fig. 3. A quantitative determination of this dependence was not attempted and many of the observed lines are composite features. It should be noted that Δ state levels with the lowest possible value of J can be predissociated by π states, since the square of the interaction matrix element is proportional to

$$[J(J+1)-\Omega(\Omega-1)].$$

C. Σ states

Most of the two-photon MPI signal intensity in the $3d$ region belongs to transitions to Σ states as determined by

the polarization dependence. Theoretical calculations,[2,5] including effects of spin–orbit coupling, place six Σ states in this region. See Fig. 1 of Ref. 5 and Table IX of Ref. 2. The Σ state of highest energy, the $^1\Sigma_0^+$ state, has been firmly identified[2,3] and the assignment can be seen in Fig. 4 of Loo et al.[2] and Figs. 1–4 of Park et al.[3] Of the remaining Σ states, the $^3\Sigma_1^-$ state is calculated by both Park et al.[5] and Loo et al.[2] to be the next highest, and the $^3\Sigma_0^-$ state to be about 60 cm^{-1} lower in energy. Transitions to both these states are allowed by two-photon selection rules. If we assume that the Σ state next lowest in energy with respect to the $^1\Sigma_0^+$ is indeed the $^3\Sigma_1^-$ state, we may then determine the so-called Recknagel parameters[2,15] which will give the position of the remaining $3d\pi$ Rydberg states. The next lowest observed Σ band is that indicated as the " * band" in Figs. 3 and 6 of Ref. 2 and as 4Σ in this work. A polarization study of this band by these authors was described as inconclusive and they tentatively suggested that it might correspond to a transition to a $^3\pi$ level but that there was "some chance that the transition could be due to a state possessing some $^3\Sigma_g^-$ character." Our polarization study of this band shows clearly that it corresponds to excitation of a Σ state as may be seen in Figs. 1 and 2. A rotational analysis suggests that the state has the value $\Omega = 1$, which would support an assignment as $^3\Sigma_1$.

The most intense Σ bands lie between the $^3\Delta_2$ and $^3\Delta_3$ bands. In the spectra of Loo et al.[2] a large complex band in this region (see their Fig. 3) was labeled series 5 and ascribed to transitions to $^3\Sigma_0^-$ and $^3\Sigma_1^-$, the latter state being higher in energy. In our spectra it can be seen that there are at least two Σ bands (labeled 1Σ and 2Σ) in this region, the lower energy one (1Σ) being the more complex. A preliminary rotational analysis suggests strongly that the lower (1Σ) band corresponds to excitation to a $^3\Sigma_1^-$ and the upper (2Σ) to a $^3\Sigma_0^-$ state,[16] contrary to the energy ordering predicted by calculations. Several of the intense Σ bands exhibit some unexplained anomalies possibly due to state mixing or continuum effects at the three-photon level.

In addition to the relatively intense Σ bands described above, a very weak band (3Σ), which was strongly suppressed with circular polarization, was found between the $^3\Delta_3$ and the "* band" (4Σ). This band, seen clearly only for $v' = 0$–2, remained in the same position relative to the $^1\Sigma_0^+$ within a few cm^{-1} for all vibrational levels. Therefore, it almost certainly corresponds to a $3d$ Rydberg state with significant Σ character. There are too few observed lines to permit a confident state assignment and the weakness of the band makes it uncertain that it still appears at the lowest rotational temperatures.

For the high-lying $^1\Sigma_0^+$ band (as also for the $^{1,3}\Delta$ and $^{1,3}\Phi$ states) the rotational structure varies little between vibrational levels. However, that is far from true for the 1–4 Σ states. Within a particular state, a rotational analysis which fits one vibrational level is not always easily transferred to the other vibrational levels. For this reason we plan more experimental work to ascertain the cause of these effects and to make assignments more certain. Despite the aforementioned difficulties it is possible to make electronic assignments of the Σ states which are strongly

supported by the tentative rotational assignments, relative transition intensities, and by the spin–orbit coupling calculations. (See Sec. III E.)

D. π states

It is now certain that none of the bands in the $4s$-$3d$ region clearly observed in the MPI spectrum excited from the $X^3\Sigma_g^-$ and $a^1\Delta_g$ states of O_2 correspond to excitation of π states, although such excitations are allowed by two-photon selection rules. A number of very weak ($\ll 1\%$ of major peaks) and sometimes broad features remain unidentified in the spectra but they are too few and too overlaid by intense bands to give much hope of analysis. Since all Φ, Δ, and at least five of the six Σ states arising from the $3d$ configuration have been seen, these weak features may correspond to π states although other possibilities exist (e.g., high rotational levels of an observed band or a forbidden Σ band, three-photon autoionizing resonances, etc.). Especially puzzling is the nonobservation of the $4s$ $^3\pi$ Rydberg states since the $3s\pi$ states have been observed[17–19] though many of the vibrational levels are strongly predissociated by the π valence states discussed earlier. Normally one expects the electronic factor for predissociation to decrease as $(n^*)^{-3}$ and that at least some vibrational levels would be detectable. However, this simple scaling of the electronic factor may not be a reasonable approximation here since the $4s$ (unlike the $3s$) states can have a very significant admixture of $3d\sigma$ as in the case for NO for instance.[20]

E. Calculations

Recknagel[15] has described the splitting between the terms arising from the configuration $\pi\pi'$ using the parameters a, b, and c. Loo et al. have extended this treatment to include the effects of spin–orbit interaction by means of the additional parameter a_π. If the "* band" (4Σ) is assigned to the $^3\Sigma_1^-$ state, we may use the procedure described by Loo et al.[2] and calculate the Recknagel parameters to fit our experimental data for $v' = 0$. Our experimental values of band origins are (in cm^{-1}): $^1\Delta_2$–85 527; $^3\Delta_1$–85 080; $^3\Delta_2$–85 155; $^3\Delta_3$–85 282; $^1\Sigma_0^+$–85 694; and $^3\Sigma_1^-$ (4Σ)–85 389. The Recknagel parameters which reproduce these energies (in cm^{-1}) are given in Table II and are compared with those of Loo et al.[2] and the ab initio values which were obtained by Lefebvre-Brion and were used to calculate the state energies given in Ref. 5. Note that both our set of values and the ab initio values have $a > b$ which must be true as discussed in Ref. 5.

When these parameters are used to calculate the energies of the remaining Σ states the results are: $^1\Sigma_0^-$–(85 070), $^3\Sigma_1^+$–(85 167), $^3\Sigma_0^+$–(85 292), $^3\Sigma_0^-$–(85 299), $^3\Sigma_1^-$–(85 389). [The states are labeled according to their dominant case (a) character.] A comparison with the experimental energies given in Table II does not lead to a convincing set of assignments.

A second set (#2) of Recknagel parameters can be determined by assigning the 1Σ band, (instead of the 4Σ band) as due to the $^3\Sigma_1^-$ state as suggested by its intensity

TABLE II. Energy of strongest peak in band.

Band assignment	1Σ $^3\Sigma_1^-$	2Σ $^3\Sigma_0^-$	3Σ $^3\Sigma_0^+$	4Σ $^3\Sigma_1^+$	$E(J'=0)$ $^1\Sigma_0^+$
$v'=0$	85 187	85 247	85 340	85 389	85 694
Interval	1 863	1 863	1 864	1 861	1 862
$v'=1$	87 049	87 111	87 204	87 250	87 556
Interval	1 837	1 829	1 839	1 837	1 839
$v'=2$	88 886	88 940	89 043	89 087	89 395
Interval	1 794	1 801		1 796	
$v'=3$	90 680	90 741	vw	90 883	nm
ΔE Expt. avg.	4	63	159	206	512
ΔE Calc.	1	64	155	203	536
$4d$ ($v'=0$)	90 562	90 603	vw	vw	90 869
ΔE Expt.	−48	−7			259
ΔE Calc.	−57	−9			261

	Recknagel parameters			
	a	b	c	a_π
Loo et al.	95	95	280	197
Lefebvre-Brion (ab initio)	100	24	243	200
This work (set #1)	110	61	158	200
This work (set #2) $3d$	166	48	150	200
$4d$	70	20	63	200

and rotational structure. Such a set has been chosen to optimize agreement with Δ as well as Σ states. This set is shown in Table II. When this set is used, a very satisfactory assignment occurs for each observed band as can be seen in Table II. The comparison between calculated and experimental values can be made by comparing the values of ΔE given in the table. The significance of ΔE is as follows: In the Recknagel parameter treatment as applied to Loo et al.,[2] the zero of energy is taken as the average energy of the $^3\Delta_1$ and $^3\Delta_3$ states. (Accidentally, this nearly coincides with the experimental energy of the 1Σ state.) In Table II the average of the experimental values of the Σ states relative to that zero of energy is given for $v'=0-3$ and compared to the values calculated from the Recknagel parameters. Agreement between experimental and calculated values is quite satisfactory given the approximations of the treatment. The assignments are very plausible and in agreement with observed intensities. We note that Loo et al.[2] also assigned their badly overlapped spectrum of this region to the $^3\Sigma_0^-$ and $^3\Sigma_1^-$ states but in the opposite energetic order. The assignments of Table II leave only the $^1\Sigma_1^-$ state unobserved. Transitions to this state from the $^3\Sigma_g^-$ ground state of O_2 should be very weak. It might be expected to be more intense in the two-photon spectrum of the a $^1\Delta_g$ state of O_2. Loo et al.[2] assign a set of bands in their a $^1\Delta_g$ spectrum to the $^1\Sigma_0^- - ^3\Sigma_0^+$ mixed states, but these bands have been shown[5] to belong to excitation of the $^{1,3}\Phi$ band system. Earlier work[3–5] done in this laboratory produced no spectrum which could be assigned to the $^1\Sigma_0^-$ state and it remains the only unobserved Σ state of the $3d$ Rydberg states of O_2. Our calculations with parameter set #2 place the $v'=1$ band of this state at 86 893 cm^{-1}. As can be seen on Fig. 1 there are two peaks in this region which disappear when switching to circularly polarized light. We plan a more thorough reexamination of this area, perhaps using two colors and the a $^1\Delta_g$ ground state.

The Recknagel parameters are constants related to integrals involving the wave functions of Rydberg and core electrons[15] and should scale approximately as $(n^*)^{-3}$ in the familiar manner for Rydberg states. When the $3d$ Recknagel parameters (set #2) are roughly scaled by $(3/4)^3$ and $(3/5)^3$ to obtain approximate parameters for the $4d$ and $5d$ states the agreement with experiment is encouraging. The results for the $4d$ states are in Table II. For energies of the $5d$ states one can refer to the spectra of Pratt et al.[21] (see their Fig. 1). There are two main bands, 218 cm^{-1} apart, converging to $\Omega^+=3/2$ and 1/2 respectively. Pratt et al.[21] assign the high energy feature as the $5d$ $^1\Sigma_0^+$ state converging to $\Omega^+=3/2$. Our simply scaled $5d$ parameters predict that the $^3\Sigma_0^-$ (2Σ) band would lie 220 cm^{-1} below $^1\Sigma_0^+$. This is good energetic agreement and consistent with the strong intensity of the 2Σ band for the $3d$ and $4d$ levels. It is therefore plausible that the strong feature observed converging to $\Omega^+=1/2$ is the $^3\Sigma_0^-$ state. This assignment is also consistent with the rotational analysis of Pratt et al.[21] shown in Fig. 7 of Ref. 21. Their rotational analysis shows no P or R branches and no transitions from $F''=2$, all of which are forbidden by the case (a)–case (b) two-photon selection rules for an upper state of $^3\Sigma_0^-$ symmetry. Also, a correlation diagram for the $\pi\pi'$ configuration, similar to that given for the (inverted) π $^3\pi'$ configuration by Lefebvre-Brion et al.[22] (see their Fig. 1), shows that the $^3\Sigma_0^-$ and $^1\Sigma_0^+$ states correlate to the $^2\pi_{1/2}$ and $^2\pi_{3/2}$ levels of the ion respectively. However, the details of the variation of coupling and transition intensities in the converging series remain to be described.

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