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Resonance-enhanced multiphoton-ionization photoelectron spectroscopy of even-parity autoionizing Rydberg states of atomic sulphur

S. Woutersen,^{a)} J. B. Milan, W. J. Buma, and C. A. de Lange

Laboratory for Physical Chemistry, University of Amsterdam, Nieuwe Achtergracht 127,
1018 WS Amsterdam, The Netherlands

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Several previously unobserved Rydberg states of the sulphur atom above the lowest ionization threshold are identified and assigned using (2+1) resonance-enhanced multiphoton-ionization photoelectron spectroscopy. All states were accessed by two-photon transitions from either the 3P ground or the 1D excited state, prepared by *in situ* photodissociation of H_2S . The observed states derive from the $(^2D^o)5p$ and $(^2P^o)4p$ configurations. For the $(^2D^o)5p\ ^3F$ and $(^2P^o)4p\ ^3D$ triplets, extensive photoelectron spectroscopic studies enable a detailed comparison of the autoionization and photoionization rates of these states. © 1997 American Institute of Physics. [S0021-9606(97)01317-2]

I. INTRODUCTION

A detailed knowledge of the energy levels, oscillator strengths, and photoionization cross sections of the S atom is of fundamental interest for understanding the spectroscopy and dynamics of open-shell atoms,¹ and is of astrophysical relevance because of the high abundance of sulphur in the interstellar medium and in the sun.² Even- and odd-parity excited states of the atom have been extensively investigated by one-photon vacuum ultraviolet absorption^{3–5} and photoionization⁶ studies, and by (2+1) resonance enhanced multiphoton ionization (REMPI) spectroscopy.^{7–11} Recently we reported on a (2+1) REMPI-photoelectron spectroscopy (REMPI-PES) study of the S atom, in which Rydberg states converging upon the lowest ionic state were investigated.¹² In this study, some 20 hitherto unobserved even-parity Rydberg states belonging to the $(^4S^o)nf\ ^3F$ and $(^4S^o)np\ ^3P$ series have been characterized. Photoelectron spectroscopy and analysis of the quantum defects of the latter series clearly showed that it is perturbed around $n=7$ by the $(^2D^o)4p\ ^3P$ interloper state. Moreover, the extensive observation of the $(^4S^o)np\ ^3P$ series enabled the lowest ionization energy to be determined with improved accuracy as $83560.8 \pm 0.1\text{ cm}^{-1}$.

In the present study we shall be concerned with Rydberg states converging upon excited ionic states, and located in the energy region above the lowest ionization threshold. Here, new states have been observed that derive from the $(^2D^o)5p$ and $(^2P^o)4p$ configurations, and which include the $(^2D^o)5p\ ^3F$ and $(^2P^o)4p\ ^3D$ states, accessed from the 3P ground state. These states can decay into the $^4S^o$ continua, and as it turns out, the autoionization rates are small enough that at sufficient laser intensities, photoionization into the $^2D^o$ and $^2P^o$ continua will compete with autoionization. The observed ionic state branching ratios then reflect the relative magnitudes of the one-photon absorption and autoionization rates of these excited states. Apart from the transitions to the

$(^2D^o)5p\ ^3F$ and $(^2P^o)4p\ ^3D$ states, the excitation spectra show resonance enhancement as well from several other states deriving from the $(^2D^o)5p$ and $(^2P^o)4p$ configurations. Combination of photoelectron spectra obtained for ionization *via* these levels and the relative transition intensities leads to assignments of these states.

II. EXPERIMENTAL DETAILS

The experimental setup has been described elsewhere.¹³ In short, the frequency-doubled output of an excimer pumped dye laser is focused into the ionization chamber of a “magnetic bottle” electron spectrometer. With this electron spectrometer, REMPI spectroscopy is performed using either kinetic energy-resolved photoelectron detection or mass-resolved ion detection.¹⁴

The dye laser wavelength calibration was performed using two-photon transitions to known states of atomic sulphur and xenon, and resulted in an uncertainty of 0.3 cm^{-1} at the two-photon level in the line positions tabulated in the following.

Two kinds of experiments have been performed. First, excited states were located by scanning the excitation wavelength while simultaneously detecting either the S^+ ion signal or the electron current. Secondly, at a given excitation wavelength the photoelectrons were analyzed according to their kinetic energies.

Sulphur atoms are produced *in situ* by subsequent photodissociation of H_2S and HS , which results in the formation of $H(^2S)$ and $S(^3P, ^1D)$.¹⁵ The $S(^3P_2):S(^3P_1):S(^3P_0)$ fine-structure branching ratio for this process has been found to be only slightly colder than the statistical distribution 5:3:1.¹⁵

In the present study, photodissociation and subsequent REMPI spectroscopy are carried out with one laser only. The concentration of sulphur atoms in the ionization chamber may therefore depend on the excitation wavelength. However, the S concentration is expected to be a slowly varying function of the wavelength, allowing for the comparison of

^{a)}Present address: FOM-Institute for Atomic and Molecular Physics, Kruislaan 407, 1098 SJ Amsterdam, The Netherlands.

intensities of peaks lying within a limited excitation energy interval.

H₂S (99.6%, Messer Griesheim) is introduced into the ionization chamber using an effusive inlet. Typical operating pressure are 10⁻⁴ mbar in the ionization chamber and 10⁻⁶ mbar in the flight tube.

III. RESULTS AND DISCUSSION

A. General considerations

The ground-state electronic configuration of atomic sulphur is $1s^2 2s^2 2p^6 3s^2 3p^4$, which gives rise to the three terms 3P , 1D , and 1S in order of increasing energy. The 3P ground state is inverted, the 3P_1 and 3P_0 states lying 369.06 and 573.64 cm⁻¹ above the 3P_2 state, respectively; the energies of the 1D_2 and 1S_0 states are 9239.61 and 22 179.95 cm⁻¹.¹⁶ Removal of an outer electron produces the S⁺ ion in its lowest electronic configuration, ... $3p^3$, giving rise to the $^4S^o$ ground and $^2D^o$ and $^2P^o$ excited ionic states, which lie 83 559.1, 98 428 (mean value), and 108 107 cm⁻¹ (mean value) above the $S I$ ground state, respectively.

In the present study, two-photon transitions from the 3P ground and 1D excited state have been observed. Strict two-photon selection rules are $|\Delta J|=0,1,2$ with $J=0 \leftrightarrow J=1$ forbidden, and the parity selection rule *odd-odd, even-even*. For ($^2D^o$) $5p$ and ($^2P^o$) $4p$ states the principal quantum number is low enough to justify application of the *LS*-coupling scheme. In fact, the ($^2D^o$) $5p^1 F_3$ and ($^2D^o$) $5p^3 F_{2,3,4}$ states were found to lie ~ 70 cm⁻¹ apart, which is reasonably large compared to the spin-orbit splitting of ~ 30 cm⁻¹ in the $^2D^o$ ionic core. In the *LS*-scheme the additional two-photon selection rules $\Delta S=0$ and $|\Delta L|=0,1,2$ (with $L=0 \leftrightarrow L=1$ forbidden) apply.

B. ($^2D^o$) $5p^3 F$ and ($^2P^o$) $4p^3 D$ autoionizing states

1. Wavelength studies

The two-photon energy region from 83 600 cm⁻¹, just above the lowest ionization energy, up to 89 000 cm⁻¹ was scanned employing mass-resolved ion detection, monitoring the S⁺ channel. This region contains mostly transitions from the 1D_2 excited state to higher members of the ($^2D^o$) np and ($^2D^o$) nf Rydberg series, which have been extensively documented.¹¹ However, in the region from 87 200 to 89 000 cm⁻¹, shown in Fig. 1(a), several intense peaks corresponding to transitions from the 3P ground state are seen as well. These transitions have not been observed in Ref. 11, since in that experiment atomic sulphur was prepared by photodissociation of OCS, which yields mainly S(1D_2), and very little S(3P). Some of the transitions from the 3P state can in fact be seen as very weak features in the wavelength scans of Ref. 11, but they have not been commented on. Three other broad peaks in these spectra were attributed to transitions from the 3P state.¹¹ As these peaks could not be observed in the present experiments, it seems more probable that they derive from molecular resonances.

FIG. 1. Wavelength scans (not corrected for dye efficiency) covering the two-photon energy region from 87 000 to 89 000 cm⁻¹. Scan (a) has been recorded employing mass-resolved ion detection, monitoring the S⁺ channel. Scans (b) and (c) have been recorded employing kinetic energy-resolved photoelectron detection, monitoring electrons with kinetic energies of 1.8 eV in (b) and with kinetic energies larger than 2.5 eV in (c).

In the two-photon energy region from 88 000 to 89 000 cm⁻¹, the signal-to-noise ratios are rather low when mass-resolved ion detection is used. For this reason, excitation spectra employing kinetic energy-resolved electron detection were recorded as well. The resulting excitation spectra are shown in Figs. 1(b) and (c). When electrons with kinetic energies of 1.8 eV are monitored, transitions from the 1D_2 state to the strongly autoionizing ($^2D^o$) np and ($^2D^o$) nf Rydberg states reported previously¹¹ can be reproduced for $n=10-15$ [see Fig. 1(b)], though our measured transition energies differ systematically by about 1 cm⁻¹ from the ones reported in this study. When electrons with kinetic energies larger than 2.5 eV are monitored, the (2+1) REMPI transitions from the 3P_J ground state are observed [see Fig. 1(c)].

In Fig. 1(a) 13 intense peaks can be distinguished that correspond to transitions from the 3P_2 , 3P_1 , and 3P_0 ground-state fine-structure levels to two triplet states, which lie 87 820 cm⁻¹ and 88 800 cm⁻¹ above the 3P_2 ground state, respectively. The line positions of these transitions are listed in Table I. The initial state of every transition can be identified by observation of the $^3P_1 - ^3P_2$, and $^3P_0 - ^3P_2$ ground-state splittings in the spectrum. The linewidths of the resonances in Fig. 1 are 1.0 cm⁻¹, but can be reduced to 0.6 cm⁻¹ when lower laser powers are employed. Since the laser bandwidth and Doppler broadening are responsible for a contribution of ~ 0.6 cm⁻¹, it appears that there is little lifetime broadening, indicating slow autoionization rates.

On the basis of quantum defect considerations, the states in this energy region are expected to have either a ($^2D^o$) $5p$ or a ($^2P^o$) $4p$ configuration (at an energy of 88 800 cm⁻¹, the effective quantum number is 3.38 with

TABLE I. Observed transitions from the ground state to autoionizing triplet states. The uncertainty in the wave numbers is estimated to be 0.3 cm^{-1} . In the last three columns the ionic state branching ratios observed by photoelectron spectroscopy for ionization *via* the given levels are reported. Previously unobserved term levels are denoted by asterisks. All photoelectron spectra have been recorded with equal laser intensity.

$2h\nu \text{ (cm}^{-1}\text{)}$	Excited state energy ^a (cm^{-1})	Initial state	Excited state	$^4S^o(\%)^b$	$^2D^o(\%)$	$^2P^o(\%)$
87 251.1	87 824.7*	3P_0	$(^2P^o)4p \ ^3D_2$	90	1	9
87 428.8	87 824.9*	3P_1	$(^2P^o)4p \ ^3D_2$	87	0	13
87 433.6	87 829.7*	3P_1	$(^2P^o)4p \ ^3D_1$	72	4	24
87 440.2	87 836.3*	3P_1	$(^2P^o)4p \ ^3D_3$	10	8	82
87 824.7	87 824.7*	3P_2	$(^2P^o)4p \ ^3D_2$	89	1	10
87 829.7	87 829.7*	3P_2	$(^2P^o)4p \ ^3D_1$	80	4	16
87 835.9	87 835.9*	3P_2	$(^2P^o)4p \ ^3D_3$	25	7	68
88 226.1	88 799.7 ^c	3P_0	$(^2D^o)5p \ ^3F_2$	79	20	1
88 403.6	88 799.7 ^c	3P_1	$(^2D^o)5p \ ^3F_2$	72	27	1
88 421.2	88 817.3*	3P_1	$(^2D^o)5p \ ^3F_3$	57	43	0
88 799.6	88 799.6 ^c	3P_2	$(^2D^o)5p \ ^3F_2$	87	13	0
88 817.0	88 817.0*	3P_2	$(^2D^o)5p \ ^3F_3$	70	30	0
88 841.2	88 841.2*	3P_2	$(^2D^o)5p \ ^3F_4$	58	42	0

^aExcited state energy calculated with respect to the 3P_2 ground state.

^b $S^+(^4S^o)$ produced by autoionization of the excited state.

^cEnergy level reported previously⁹ to lie at $88\,799.2 \pm 2 \text{ cm}^{-1}$.

respect to the $^2D^o$ ionic limit and 2.38 with respect to the $^2P^o$ ionic limit). Photoelectron spectra obtained *via* these resonances (see Table I) unambiguously identify the ionic core as $^2D^o$ for the triplet at approximately $88\,800 \text{ cm}^{-1}$ and $^2P^o$ for the triplet at approximately $87\,820 \text{ cm}^{-1}$.

The $(^2D^o)5p$ triplet may be either a 3P , 3D , or 3F state. The 3P state, which can couple by electrostatic interaction to the $(^4S^o)\epsilon p \ ^3P$ continua, is expected to be strongly autoionizing, and the accompanying lifetime broadening will probably render this state unobservable by REMPI methods. In fact, in a study of atomic oxygen,¹⁷ the linewidth FWHM of the autoionizing $(^2D^o)3p \ ^3P$ state has been found to be 800 cm^{-1} . The linewidth of the $(^2D^o)5p \ ^3P$ state in atomic sulphur can be expected to be of the same order of magnitude. The observed resonances must therefore be attributed to either a 3D or 3F state. The fact that only two fine-structure levels of the triplet are observed to be accessible from the 3P_1 ground-state level (see the spectrum at $88\,400 \text{ cm}^{-1}$ in Fig. 1) strongly suggests that the triplet is 3F rather than 3D , since the 3F_4 level cannot be reached by a two-photon excitation from the 3P_1 level. In contrast, three transitions from the 3P_1 level would be expected if the triplet were a 3D state, since all three of the $^3D_{1,2,3}$ fine-structure levels are accessible from the 3P_1 level. Accordingly, the $(^2D^o)5p$ triplet is assigned as 3F . Using the two-photon selection rules, the 3F fine-structure levels can be assigned unambiguously. The state at $88\,841.2 \text{ cm}^{-1}$ must be assigned as the 3F_4 fine-structure level, as it is accessible from the 3P_2 level, but not from the 3P_1 level. Furthermore, the state at $88\,799.6 \text{ cm}^{-1}$ must be assigned to the 3F_2 level, as this is the only 3F level accessible by two-photon absorption from the 3P_0 state. The remaining state at $88\,817.0 \text{ cm}^{-1}$ must consequently be the 3F_3 level. Thus, the $^3F_{2,3,4}$ ordering is the same as for the first series member $(^2D^o)4p \ ^3F$. Furthermore, the fine-structure splitting decreases by a factor

of 0.7, going from $4p$ to $5p$, which is of the order of the expected factor $(4/5)^3 \approx 0.5$.

A detailed scan, shown in Fig. 2(a), was recorded in order to determine the relative line strengths of the fine-structure transitions. These can be compared with theoretical values for a $^3P \rightarrow ^3F$ two-photon transition, which can be calculated using the spherical tensor formalism described in Refs. 18 and 19. In the *LS*-approximation, both the Hamiltonian in the absence of the radiation field H_0 , and the dipole operator D , commute with the total spin operator S .²⁰ It can then be shown that for linearly polarized light the relative line strengths $I(J \rightarrow J')$ of a $\gamma LSJ \rightarrow \gamma' L'S'J'$ two-photon transition (where γ stands for all quantum numbers other than L , S , and J) are given by

FIG. 2. Detailed wavelength scans recorded employing mass-resolved ion detection, showing the transitions listed in Table I. The three scans of (a) were recorded with equal laser intensity; likewise for (b). The bars represent calculated two-photon line strengths for $^3P \rightarrow ^3F$ (a) and $^3P \rightarrow ^3D$ (b) fine-structure transitions (see the text for details).

TABLE II. Calculated relative line strengths for the ${}^3P_J \rightarrow {}^3F_{J'}$ transition. The values have been normalized w.r.t. the ${}^3P_1 \rightarrow {}^3F_3$ line strength.

J	J'	$I(J \rightarrow J')$
0	2	0.500
1	2	0.500
1	3	1.000
2	2	0.071
2	3	0.500
2	4	1.928

$$\begin{aligned}
 I(J \rightarrow J') &= \frac{1}{3} (2J' + 1)(2J + 1) \\
 &\times \left\{ \begin{matrix} L' & J' & S \\ J & L & 0 \end{matrix} \right\}^2 |\langle \gamma' L' \| Q^0 \| \gamma L \rangle|^2 \delta_{S'S} \\
 &+ \frac{2}{15} (2J' + 1)(2J + 1) \\
 &\times \left\{ \begin{matrix} L' & J' & S \\ J & L & 2 \end{matrix} \right\}^2 |\langle \gamma' L' \| Q^2 \| \gamma L \rangle|^2 \delta_{S'S}, \quad (1)
 \end{aligned}$$

where the reduced matrix elements $\langle \gamma' L' \| Q^0 \| \gamma L \rangle$ and $\langle \gamma' L' \| Q^2 \| \gamma L \rangle$ of the zero- and second-order irreducible tensor operators Q^k are defined in Ref. 18. If $L \neq L'$, the first $6j$ -symbol vanishes, and the relative line strengths can be calculated algebraically. The resulting values for a ${}^3P_J \rightarrow {}^3F_{J'}$ two-photon transition are given in Table II. In Fig. 2(a) they are compared with the experimentally determined line strengths. The scans in this figure were recorded using mass-resolved ion detection, with identical H_2S pressure and laser intensity. In the calculation the $S({}^3P_2):S({}^3P_1):S({}^3P_0)$ distribution was assumed to be 5:3:1, following Ref. 15. The agreement between the theoretical and experimental line strengths seems to justify the assignments of the 3F_J fine-structure levels. Closer inspection of Fig. 2(a) suggests that the $S({}^3P_2):S({}^3P_1):S({}^3P_0)$ distribution deviates slightly from the statistical distribution 5:3:1, showing a preference for $S({}^3P_1)$ and $S({}^3P_0)$. However, the deviations may also be due to changes in photodissociation cross sections of either SH or H_2S , or to dye gain effects.

The possible $({}^2P^\circ)4p$ triplet states are 3P and 3D . The $({}^2P^\circ)4p {}^3P$ state will be strongly autoionizing and can probably not be observed for reasons mentioned previously. It therefore seems that the triplet can only be a 3D state. This assumption is confirmed by the observed transitions. The spectrum shows that only one of the triplet fine-structure levels is accessible from the 3P_0 level, which is to be expected for a ${}^3D_{1,2,3}$ state, since the $J=3$ level cannot be reached from $J=0$, and $J=0 \rightarrow J=1$ two-photon transitions are strictly forbidden. All three of the ${}^3D_{1,2,3}$ fine-structure levels are accessible from the 3P_1 and 3P_2 levels, which is in agreement with the two triplet structures observed in the spectrum at 87 430 and 87 830 cm^{-1} . The assignments of the fine-structure levels are given in Table I. The state at 87 824.7 cm^{-1} can immediately be assigned as 3D_2 , as this is the only level accessible from the 3P_0 level. The assignment of the two remaining levels at 87 829.7 and 87 835.9 cm^{-1} , which must be the 3D_1 and 3D_3 states, is not

possible on the basis of two-photon selection rules. The theoretical values of the relative line strengths of a ${}^3P_J \rightarrow {}^3D_{J'}$ two-photon transition have been calculated before.²¹ Equation (1) reproduces the values given in this previous paper. From these calculated values it follows that the ${}^3P_2 \rightarrow {}^3D_3$ transition should be 6.2 times stronger than the ${}^3P_2 \rightarrow {}^3D_1$ transition. Since the resonance at 87 835.9 cm^{-1} is observed to be ~ 8 times stronger than the resonance at 87 829.7 cm^{-1} , it seems justified to assign the state at 87 835.9 cm^{-1} as 3D_3 and the state at 87 829.7 cm^{-1} as 3D_1 . As can be seen in the scan shown in Fig. 2(b), the observed fine-structure line strengths agree reasonably well with the values predicted on the basis of the present assignments.

In a previous REMPI-PES study of atomic sulphur,⁷ a resonance at 66 758 cm^{-1} has been attributed to a spin-forbidden ${}^1S_0 \rightarrow ({}^2P^\circ)4p {}^3D_2$ transition, which would place the $({}^2P^\circ)4p {}^3D_2$ state at an energy of 88 925 cm^{-1} . The fact that at 79 683.5 cm^{-1} a very strong transition from the 1D_2 excited state to the 88 925 cm^{-1} level is observed (see Table III), and that only very weak signals corresponding to transitions from the 3P_2 and 3P_1 levels can be observed [see Fig. 1(c) and Table III], suggests that this state must rather be assigned as a singlet state, possibly $({}^2P^\circ)4p {}^1D_2$ (see Sec. C).

It seems that none of the states given in Table I can be accessed from either the 1D_2 or the 1S_0 excited state, except for the level at 88 799.7 cm^{-1} , which is assigned here as $({}^2D^\circ)5p {}^3F_2$. In a previous REMPI study of atomic sulphur,⁹ a weak two-photon transition from the 1S_0 state to this level [which the authors have tentatively assigned as $({}^2P^\circ)4p {}^3D_2$] has been observed. In addition, in the present study a very weak transition from the 1D_2 excited state to the level at 88 799.7 cm^{-1} was observed at a two-photon energy of 79 561.0 cm^{-1} (see Table III). No other transitions from the 1D_2 state to any of the levels given in Table I are observed. The fact that such spin-forbidden transitions to the $({}^2D^\circ)5p {}^3F$ and $({}^2P^\circ)4p {}^3D$ do not occur or are very weak indicates that the LS -coupling scheme may be considered appropriate.

2. Photoelectron studies

Photoelectron spectra have been recorded for all the ${}^3P \rightarrow {}^3D$ and ${}^3P \rightarrow {}^3F$ transitions, and the observed ionic state branching ratios are given in Table I. As can be expected, the branching ratios for a given excited state are virtually independent of the initial 3P fine-structure state from which it is excited.

Apart from photoelectron peaks due to $(2 + 1)$ REMPI, all the photoelectron spectra show a peak at a photoelectron energy of $2h\nu - 10.36$ eV, which is due to autoionization of the excited state into the $({}^4S^\circ)\epsilon l$ continua. In fact, the two processes compete, and the excited state can either decay by autoionization, leaving the ion in the ${}^4S^\circ$ ground state, or absorb another photon and subsequently ionize, leaving the ion in one of the two excited ionic states or the ground ionic state. As the photoionization probability is proportional to the photon flux, the relative branching ratios are expected to

TABLE III. Observed excited state levels and ionic state branching ratios in the energy region 87 000–89 000 cm⁻¹ and tentative assignments. Previously unobserved levels are denoted by asterisks.

$2h\nu$ (cm ⁻¹)	Excited state energy (cm ⁻¹) ^a	Initial state	Lit. value	² D ^o (%)	² P ^o (%)	Assignment
78 385.6	87 624.2	¹ D ₂	87 624 ^b	12	88	(² P ^o)4p ¹ P ₁
79 561.0	88 799.6	¹ D ₂	88 799 ^c	81	19	(² D ^o)5p ³ F ₂
79 638.7	88 877.3	¹ D ₂	88 876 ^d	68	32	(² D ^o)5p ³ D ₂
79 649.5	88 888.1*	¹ D ₂		100	0	(² D ^o)5p ¹ F ₃
79 668.7	88 907.3*	¹ D ₂		45	55	(² D ^o)5p ³ D ₃
79 683.5	88 922.1	¹ D ₂	88 925 ^d	-	-	(² P ^o)4p ¹ P ₁
81 882.7	91 121.3	¹ D ₂	91 123 ^c	3	97	(² P ^o)4p ¹ S ₀
87 227.3	87 623.4	³ P ₁	87 624 ^b	20	80	(² P ^o)4p ¹ P ₁
87 414.2	87 810.3*	³ P ₁		11	89	(² P ^o)4p ³ S ₁
87 624.1	87 624.1	³ P ₂	87 624 ^b	12	88	(² P ^o)4p ¹ P ₁
87 810.5	87 810.5*	³ P ₂		23	77	(² P ^o)4p ³ S ₁
88 303.1	88 876.7	³ P ₀	88 876 ^d	62	38	(² D ^o)5p ³ D ₂
88 466.2	88 862.3*	³ P ₁		74	26	(² D ^o)5p ³ D ₁
88 481.2	88 877.3	³ P ₁	88 876 ^d	64	36	(² D ^o)5p ³ D ₂
88 492.2	88 888.3*	³ P ₁		100	0	(² D ^o)5p ¹ F ₃
88 510.6	88 906.7*	³ P ₁		71	29	(² D ^o)5p ³ D ₃
88 526.5	88 922.6	³ P ₁	88 925 ^d	13	87	(² P ^o)4p ¹ D ₂
88 861.6	88 861.6*	³ P ₂		76	24	(² D ^o)5p ³ D ₁
88 877.2	88 877.2	³ P ₂	88 876 ^d	71	29	(² D ^o)5p ³ D ₂
88 906.3	88 906.3*	³ P ₂		77	23	(² D ^o)5p ³ D ₂
88 922.7	88 922.7	³ P ₂	88 925 ^d	13	87	(² P ^o)4p ¹ D ₂

^aExcited state energy calculated with respect to the ³P₂ ground state.^bExcited state energy previously reported by Appling *et al.* (Ref. 10).^cExcited state energy previously reported by Ventikachalam *et al.* (Ref. 9).^dExcited state energy previously reported by Steadman and Baer (Ref. 7).

depend on the laser power, the ⁴S^o branching ratio diminishing as the laser power increases. This power dependence is indeed observed, as can be seen in Figs. 3(a) and (b), which show photoelectron spectra recorded for ionization *via* the (²P^o)4p ³D₁ level at a two-photon energy of 87 829.7 cm⁻¹ (see Table I), employing low laser power in (a) and high laser power in (b). Although comparison of the peak heights in Figs. 3(a) and (b) is not allowed, as the peaks in Fig. 3(b) are broadened by space charge effects, careful

determination of the integrated intensities shows that in Fig. 3(b) the ²P^o and ²D^o branching ratios are indeed significantly larger than in Fig. 3(a), whereas the ²P^o:²D^o ratio stays the same, as expected. A similar power dependence of ionic state branching ratios has been reported previously for (2 + 1) REMPI *via* autoionizing states of atomic oxygen.²²

The ionic state branching ratios for ionization *via* the (²P^o)4p ³D_J states show a strong *J* dependence. An example is shown in Fig. 4, where the photoelectron spectra for

FIG. 3. Photoelectron spectra following excitation of the (²P^o)4p ³D₁ state employing low (a) and high (b) laser intensities.

FIG. 4. Photoelectron spectra observed following excitation of the $(^2P^\circ)4p\ ^3D_1$ (a) and $(^2P^\circ)4p\ ^3D_3$ (b) fine-structure states.

ionization *via* the 3D_1 and 3D_3 components are displayed, recorded with equal laser intensities at two-photon energies of 87 433.6 and 87 440.2 cm^{-1} , respectively (see also Table I). Ionization *via* the 3D_1 and 3D_2 components is observed to produce mainly $^4S^\circ$ ions, whereas ionization *via* the 3D_3 component produces only 10% $^4S^\circ$ ions and 80% $^2P^\circ$ ions, providing an interesting example of state-selective photoionization. Under the assumption that the photoionization cross section is independent of J , this would imply that the autoionization rate for the 3D_3 component is at least an order of magnitude smaller than for the other two components. This effect can be understood on the basis of the autoionization selection rules.²³ As there are no even-parity 3D continua associated with the $^4S^\circ$ core, the 3D state cannot autoionize electrostatically and must autoionize entirely through spin interactions, possibly spin-orbit coupling. The selection rules for such a coupling would allow for the interaction with several $^4S^\circ$ ionization continua. The observation that the $(^2P^\circ)4p\ ^3D_3$ state, however, has a considerably smaller autoionization rate than the $(^2P^\circ)4p\ ^3D_1$ and 3D_2 states, suggests that the dominant interaction concerns spin-orbit coupling with the $(^4S^\circ)\epsilon p\ ^3P$ continua. As the 3P continua have no $J=3$ component, and since autoionization can only occur with $\Delta J=0$, only the 3D_1 and 3D_2 states can autoionize into these continua, while the 3D_3 state is expected to remain unaffected.

All the photoelectron spectra for ionization *via* the $(^2P^\circ)4p\ ^3D$ levels show a small peak corresponding to the production of $S^+(^2D^\circ)$. This is probably due to configuration interaction of these states with the $(^2D^\circ)5p\ ^3D$ state (see Sec. C).

The photoelectron spectra for ionization *via* the $(^2D^\circ)5p\ ^3F$ states show only transitions to the $^2D^\circ$ and $^4S^\circ$ ionic states, the latter being accessed by autoionization. The $^4S^\circ$ branching ratio depends weakly on the J quantum number, being larger for 3F_2 than for 3F_3 and 3F_4 . This suggests that the autoionization process proceeds partly

through spin-spin interactions with the $(^4S^\circ)\epsilon p\ ^3P$ continua, which can affect the 3F_2 component, but not the 3F_3 and 3F_4 components. However, as the $^4S^\circ$ branching ratios are still appreciable for the 3F_3 and 3F_4 components, the most important autoionization channel is probably electrostatic interaction with the $(^4S^\circ)\epsilon f\ ^3F$ continua.

C. Other $(^2P^\circ)4p$ and $(^2D^\circ)5p$ states in the energy region 87 000–89 000 cm^{-1}

In addition to the transitions discussed above, many other resonances can be seen in Fig. 1, corresponding to transitions from the 3P ground state to energy levels in the region from 87 000 to 89 000 cm^{-1} . Most of these resonances are weak. Also, transitions from the 1D_2 state to some of these excited states are observed at two-photon energies of about 80 000 cm^{-1} . The transitions from the 1D_2 state can easily be recognized as such by their photoelectron spectra.⁷ The line positions of the transitions are given in Table III. Some of the energy levels have been reported previously, accessed from either the 1D_2 or 1S_0 excited state. When this is the case, the reported energy is also given in the table. Photoelectron spectra have been recorded for all but one of the transitions. In general, these spectra show a peak deriving from autoionization into the $^4S^\circ$ continua and $(2+1)$ ionization into the $^2D^\circ$ and $^2P^\circ$ continua. Since in this section we are primarily interested in the identification of states responsible for the resonance enhancement in the excitation spectra, and since the branching ratio to the $^4S^\circ$ autoionization continua is dependent on the intensity of the excitation laser, Table III only contains such ratios for the $^2D^\circ$ and $^2P^\circ$ ionic states.

In Table III tentative assignments are given, which are based on the relative intensities of the transitions and the observed ionic state branching ratios. As has been mentioned above, the excited states in this energy region are expected to have either a $(^2D^\circ)5p$ or a $(^2P^\circ)4p$ configuration. Since ionization of a Rydberg state should in principle occur with

core preservation, the photoelectron spectra should give an unambiguous identification of the ionic core. However, $(^2D^o)5p$ and $(^2P^o)4p$ states having the same angular momentum composition (L, S, J) are likely to show substantial configuration interaction. Furthermore, the photoionization matrix elements may differ considerably for different cores, and a strong peak in the photoelectron spectrum may well be due to a minor contribution in the wave function. This makes the assignment a delicate matter. In what follows, each of the tentative assignments given in Table III will be discussed separately.

The state at $87\,624\text{ cm}^{-1}$ has been reported previously¹⁰ and has been assigned as $(^2D^o)5p\ ^1P_1$. The fact that no transition from the 3P_0 level to this state was observed in the present study, and that no transitions from the 1S_0 state have occurred in previous two-photon excitation studies,⁷ confirms the assignment of this state as 1P_1 . However, the photoelectron spectra recorded at two-photon energies of $87\,624.1$ and $78\,385.6\text{ cm}^{-1}$ both show a $^2D^o:2P^o$ ratio of 1:7, which suggests that the configuration is $(^2P^o)4p$ rather than $(^2D^o)5p$. In Ref. 10, a photoelectron spectrum has also been recorded, which only showed $S^+(^4S^o)$, probably because of the lower laser powers employed in the experiment. Accordingly, the state is reassigned here as $(^2P^o)4p\ ^1P_1$.

The state at $88\,878\text{ cm}^{-1}$ has been reported previously⁷ at an energy of $88\,876 \pm 2\text{ cm}^{-1}$, and has been assigned as $(^2P^o)4p\ ^3P$. This is rather unlikely, since the 3P state is expected to be strongly autoionizing, and no $S^+(^4S^o)$ was observed in the photoelectron spectrum.⁷ Here, an alternative assignment is proposed. The fact that the excited state is observed to be accessible from the 3P_2 , 3P_1 , and 3P_0 levels implies that it must have a total angular momentum $J=2$ ($J=0 \leftrightarrow J=1$, two-photon transitions are strictly forbidden). Furthermore, the transition from the 1D_2 level to the excited state is very weak compared to other transitions from the 1D_2 level in the same energy region, suggesting that the excited state is a triplet level. For reasons already mentioned, it is unlikely that it is a $(^2D^o)5p\ ^3P_2$ or a $(^2P^o)4p\ ^3P_2$ level. The $(^2D^o)5p\ ^3F_2$ and $(^2P^o)4p\ ^3D_2$ levels have already been assigned (see previous section), and the only remaining triplet state with $J=2$ is therefore $(^2D^o)5p\ ^3D_2$. For this reason the excited state is reassigned as $(^2D^o)5p\ ^3D_2$. Note that this assignment is supported by the photoelectron spectrum.

A consequence of such an assignment is that the $(^2D^o)5p\ ^3D$ state would lie above the $(^2D^o)5p\ ^3F$ state, whereas for the $(^2D^o)4p\ ^3F$ and $(^2D^o)4p\ ^3D$ states the ordering has been found to be reversed. An explanation for this effect might be configuration interaction between the $(^2D^o)5p\ ^3D$ and $(^2P^o)4p\ ^3D$ states, causing the $(^2D^o)5p\ ^3D$ level to shift towards higher energy, while the $(^2D^o)5p\ ^3F$ state remains unaffected, as there is no 3F state associated with the $(^2P^o)4p$ configuration. Such a configuration interaction nicely explains the $^2P^o:2D^o$ branching ratio of 1:2 observed for ionization of the presumed $(^2D^o)5p\ ^3D_2$ state. In the previous section it was observed that all the photoelectron spectra obtained for $(2+1)$ ionization of the $(^2P^o)4p\ ^3D_2$ level showed contributions of ion-

FIG. 5. Detailed wavelength scans showing some of the transitions listed in Table III. The scans were recorded employing kinetic-energy resolved electron detection, monitoring electrons with kinetic energies $>2.5\text{ eV}$. All scans were recorded with equal laser intensity. The bars represent calculated two-photon line strengths for $^3P \rightarrow ^3D$ fine-structure transitions (see the text for details).

ization to the $^2D^o$ ionic state. This can now be understood, as the effects of configuration interaction between the $(^2D^o)5p\ ^3D_2$ and the $(^2P^o)4p\ ^3D_2$ levels will similarly be visible in the photoelectron spectra of the latter level. The present assignment leads to the conclusion that the $^3P \rightarrow (^2D^o)5p\ ^3D$ transitions are much weaker than the $^3P \rightarrow (^2D^o)5p\ ^3F$ transitions, implying that for the latter the absolute two-photon absorption cross sections are significantly larger. At present no calculations of these cross sections are available, but *ab initio* calculations on oxygen²⁴ have shown that for this atom the two-photon absorption cross sections for $^3P \rightarrow (^2D^o)3p\ ^3D$ are indeed five times smaller than for $^3P \rightarrow (^2D^o)3p\ ^3F$.

The other two components of the 3D triplet may be expected to lie near the $(^2D^o)5p\ ^3D_2$ state. For the $(^2D^o)5p\ ^3D$ state the splittings are expected to be smaller by a factor $(\frac{4}{5})^3 \approx 0.5$ as compared to the $4p$ series member. It therefore appears that the term levels at $88\,906.3$ and $88\,861.6\text{ cm}^{-1}$, the photoelectron spectra of which show $^2P^o:2D^o$ branching ratios of $\sim 1:3$, might be the 3D_1 and 3D_3 components. This assumption is supported by the observation that neither of these states is accessed from the 3P_0 level. Detailed wavelength scans employing kinetic energy-resolved electron detection were recorded in order to obtain accurate estimates for the relative intensities of the transitions from the 3P_1 and 3P_2 levels to these states (see Fig. 5). Comparison of the theoretical values for the relative line strengths for a $^3P \rightarrow ^3D$ transition²¹ and the observed intensities suggests that the level at $88\,861.6\text{ cm}^{-1}$ might be assigned as 3D_1 and the level at $88\,906.3\text{ cm}^{-1}$ as 3D_3 .

A strong transition from the 1D_2 state is observed at a two-photon energy of $79\,649.5\text{ cm}^{-1}$, corresponding to an energy of $88\,888.1\text{ cm}^{-1}$ for the excited state. No transitions from the 3P_2 or 3P_0 ground-state levels to this excited state are observed, but a weak transition at a two-photon energy of $88\,492.2\text{ cm}^{-1}$, which has no 3P_2 or 3P_0 counterparts, is tentatively assigned as a transition from the 3P_1 level to this

excited state. The state is likely to be a singlet, since the transition from the 1D_2 state is very strong and the transition from the 3P_1 state is rather weak. The photoelectron spectra show that $(2+1)$ ionization occurs exclusively to the $^2D^o$ ionic state, implying that the configuration is $(^2D^o)5p$ and that the state possesses no $(^2P^o)4p$ character whatsoever. The possible $(^2D^o)5p$ singlet states are 1P_1 , 1D_2 , and 1F_3 . 1P_1 and 1D_2 states can also arise from the $(^2P^o)4p$ configuration, which implies that if the excited state were either $(^2D^o)5p\ ^1P_1$ or $(^2D^o)5p\ ^1D_2$, at least some $(^2P^o)4p$ character would be expected to mix in and show up in the photoelectron spectra. Therefore, the state is assigned as $(^2D^o)5p\ ^1F_3$. This assignment implies that the 1F_3 – 3F_3 splitting has decreased by a factor $88/200 \approx 0.44$ compared to the previous series member, which is indeed of the order of the expected factor $(\frac{4}{5})^3 \approx 0.5$.

At two-photon energies of 87 414.2 and 87 810 cm^{-1} , two peaks are observed that correspond to transitions from the 3P_1 and 3P_2 levels to a state at 87 811.5 cm^{-1} . The fact that a transition from the 3P_0 level is not observed suggests that the excited state has either $J=1$ or $J=3$. No transition from the 1D_2 level to this state is observed either, suggesting that it is a triplet state. Inspection of the photoelectron spectra obtained after excitation of this state shows that ionization occurs preferentially to the $^2P^o$ ionic state. If we assume that this state is indeed built upon the $^2P^o$ ionic core, we have to conclude that its assignment is $(^2P^o)4p\ ^3S_1$. Such an assignment is supported by the observation that the state seems to have only a single level, but would violate the *LS*-coupling selection rule that $L=0 \leftrightarrow L=1$ transitions are forbidden. This would imply that for this state *LS*-coupling is not strictly valid. The fact that a significant ionization to the $^2D^o$ ionic state is observed indicates that the 3S_1 state is coupled to a state with a $^2D^o$ ionic core and $J=1$, from which it obtains transition probability.

The resonance at 81 882.7 cm^{-1} corresponds to a transition from the 1D_2 state to a state at 91 121 cm^{-1} , which has been reported previously^{7,25} and assigned as $(^2P^o)4p\ ^1S_0$. Since the photoelectron spectrum recorded at 81 882.7 cm^{-1} shows a $^2P^o:2D^o$ branching ratio of 30:1, this assignment was assumed in Table III. As the $(^2P^o)4p\ ^1P_1$ and $(^2P^o)4p\ ^1S_0$ states have now both been assigned, the only $(^2P^o)4p$ singlet state left to be found is $(^2P^o)4p\ ^1D_2$. The state at 87 810 cm^{-1} can be excluded, as it is observed not to be accessible from the 1D_2 state. The only remaining observed state with a high $^2P^o$ branching

ratio is the state at 88 923 cm^{-1} , which shows a $^2P^o:2D^o$ branching ratio of 7:1. A strong transition at 79 683.5 cm^{-1} from the 1D_2 state to this level suggests that it is in effect a singlet state. Accordingly, it is assigned as $(^2P^o)4p\ ^1D_2$. As has already been mentioned in the previous section, a transition from the 1S_0 state to this level has been observed, and assigned as $(^2P^o)4p\ ^3D_2$.⁷ However, the present study shows that the $(^2P^o)4p\ ^3D$ state lies at a much lower energy.

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- ¹Z. Altun, J. Phys. B **25**, 2279 (1992).
- ²R. P. Wayne, J. Photochem. Photobiol. A-Chemistry **62**, 379 (1992).
- ³G. Tondello, Astrophys. J. **172**, 771 (1972).
- ⁴V. N. Sarma and Y. N. Joshi, Physica C **123**, 349 (1984).
- ⁵Y. N. Joshi, M. Mazzoni, A. Nenecioni, W. H. Parkinson, and A. Cantu, J. Phys. B **20**, 1203 (1987).
- ⁶S. T. Gibson, J. P. Greene, B. Ruscić, and J. Berkowitz, J. Phys. B **19**, 2825 (1986).
- ⁷J. Steadman and T. Baer, J. Chem. Phys. **89**, 5507 (1988).
- ⁸P. Brewer, N. van Veen, and R. Bersohn, Chem. Phys. Lett. **91**, 126 (1982).
- ⁹T. V. Ventikachalam and A. S. Rao, Appl. Phys. B **52**, 102 (1991).
- ¹⁰J. R. Appling, M. R. Harbol, and R. A. Edgington, J. Chem. Phys. **97**, 4041 (1992).
- ¹¹S. T. Pratt, Phys. Rev. A **38**, 1270 (1988).
- ¹²S. Woutersen, J. B. Milan, W. J. Buma, and C. A. de Lange, Phys. Rev. A **54**, 5126 (1996).
- ¹³E. de Beer, C. A. de Lange, and N. P. C. Westwood, Phys. Rev. A **46**, 5653 (1992).
- ¹⁴B. G. Koenders, D. M. Wieringa, K. E. Drabe, and C. A. de Lange, Chem. Phys. **118**, 113 (1987).
- ¹⁵C.-W. Hsu, C. L. Liao, Z.-X. Ma, P. J. H. Tjossem, and C. Y. Ng, Chem. Phys. Lett. **199**, 78 (1992).
- ¹⁶W. C. Martin, R. Zalubas, and A. Musgrove, J. Phys. Chem. Ref. Data **19**, 820 (1990).
- ¹⁷A. V. Smith, T. D. Raymond, and M. E. Riley, Phys. Rev. A **45**, 4688 (1992).
- ¹⁸G. Grynberg, F. Biraben, E. Giacobino, and B. Cagnac, J. Phys. (Paris) **38**, 629 (1977).
- ¹⁹B. Cagnac, G. Grynberg, and F. Biraben, J. Phys. (Paris) **34**, 845 (1973).
- ²⁰I. Sobelman, *Atomic Spectra and Radiative Transitions* (Springer Verlag, New York, 1979).
- ²¹P. Das, G. Ondrey, N. van Veen, and R. Bersohn, J. Chem. Phys. **79**, 724 (1983).
- ²²S. T. Pratt, P. M. Dehmer, and J. L. Dehmer, Phys. Rev. A **43**, 282 (1991).
- ²³P. Feldman and R. Novick, Phys. Rev. **160**, 143 (1967).
- ²⁴R. P. Saxton and J. Eichler, Phys. Rev. A **34**, 199 (1986).
- ²⁵M. Kawasaki, H. Sato, Kobayashi, and T. Arikawa, Chem. Phys. Lett. **146**, 101 (1988).