

Auger Spectra of Highly Ionized Oxygen and Fluorine

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The energies of some metastable states of ionized oxygen and fluorine with three, four, or five electrons are computed. The spectra of Auger electrons, emitted during the autoionization of these states, are obtained and compared with the experimental measurements of Pegg *et al.* The energies of some of the associated x-ray transitions are tabulated.

I. INTRODUCTION

Multiply charged ions have been detected recently in plasma discharges,¹⁻⁴ and are believed to be active components of the solar corona.⁵⁻⁸ Ions of this type can be studied through beam-foil spectroscopy. Sellin and co-workers,⁹⁻¹² have recently bombarded carbon foils with fast ions and observed the spectrum of Auger electrons which are emitted from various positions along the path of the beam beyond the foil. They have shown¹⁰ that 60-MeV argon ions can be stripped of at least 15 electrons by foils with a thickness of $15 \mu\text{g}/\text{cm}^2$. In another experiment,^{9, 12} Auger spectra were obtained from oxygen and fluorine ions with energies between 2 and 30 MeV. These spectra are the subject of this paper.

The Auger spectra observed from oxygen and fluorine ions each contain several prominent peaks which correspond to states previously calculated by Holøien and Geltman.¹³ These peaks arise from the decay of doubly excited states of three-electron ions, with configurations such as $(1s)(2s)(3s)^4S^e$, $(1s)(2s)(2p)^4P^o$, and $(1s)(2p)^2^4P^e$. These states are metastable against autoionization, which can occur only through non-Coulombic interactions. The lifetimes of these states can be larger than 10^{-8} sec,¹⁴ so that the ions may travel several centimeters past the foil before electron emission occurs. Holøien and Geltman calculated the energies of nine states of this type. However, there are several unexplained features of the observed spectrum. First, there is a broad peak, called peak A by Sellin *et al.*,⁹ with a width of ~ 8 eV, which occurs near 438 eV in the oxygen spectrum and near 555 eV in the fluorine spectrum. A second broad peak, called peak B, occurs near 449 eV for O and 573 eV for F. Third, there is a narrow peak at 531 eV in the oxygen spectrum. The closest calculated line occurs at 529 eV. This difference of 2 eV may be significant in view of

the fact that improvements in the calculated energy levels would lead to a lower energy for the emitted electron. Fourth, more recent observations by Pegg *et al.*¹² show evidence of further structure near 445 and 522 eV in oxygen, which does not correspond to any of the calculated states.

Sellin *et al.*⁹ suggest that some of the spectral features may be due to the decay of four-electron ions, and point out that there are additional three-electron states for which the energies are unknown. We have therefore computed the energy levels of a large number of states of these ions, with three, four, or five electrons. The results of these calculations are given in Secs. II and III. In Sec. II we compare our results with the previous calculations, and in Sec. III we discuss the computed Auger spectrum.

X-ray emission has been observed from some of the three-electron states calculated here, and the X-ray energies will be discussed in Sec. IV.

II. COMPUTATION OF ENERGY LEVELS

The energy levels of many states of ionized oxygen and fluorine were obtained by variational calculations, using the nonrelativistic Hamiltonian which includes only Coulomb interactions. With this Hamiltonian the states of interest appear as bound states, and can be computed by the standard Rayleigh-Ritz variational method. The trial wave functions consist of linear combinations of products of single-particle Slater orbitals, combined with spin functions to give the proper over-all symmetry. Each Slater orbital contains an exponent which can be varied. Our trial functions are thus less flexible than those used by Holøien and Geltman,¹³ who included terms which were defined explicitly in terms of the interelectronic distances, r_{ij} .

Our aim in these calculations was not to improve the results of Holøien and Geltman, but rather to

TABLE I. Energies of metastable states of O^{5+} and F^{6+} .

State	Oxygen energies (a.u.)		Fluorine energies (a.u.)		Major configuration
	This work	Ref. 9	This work	Ref. 9	
$^4P^o$ (1)	-43.830	-43.869	-56.022	-56.071	1s 2s 2p
$^4P^o$ (2)	-40.649	-40.706	-51.814	-51.896	1s 2s 3p
$^4P^o$ (3)	-40.491	-40.495	-51.648	-51.659	1s 2p 3s
$^4P^e$ (1)	-43.384	-43.391	-55.517	-55.524	1s 2p 2p
$^4P^e$ (2)	-40.370	-40.377	-51.513	-51.519	1s 2p 3p
$^4P^e$ (3)	-39.433	-39.338	-50.247	-50.137	1s 2p 4p
$^4S^e$ (1)	-40.782	-40.863	-51.973	-52.077	1s 2s 3s
$^4S^e$ (2)	-40.382	-40.370	-51.522	-51.506	1s 2p 3p
$^4S^e$ (3)	-39.693	-39.775	-50.529	-50.637	1s 2s 4s
$^2P^e$ (1)	-43.124	...	-55.207	...	1s 2p 2p
$^2P^e$ (2)	-40.420	...	-51.569	...	1s 2p 3p
$^2P^e$ (3)	-40.179	...	-51.287	...	1s 2p 3p

obtain the energies for a large number of states, involving three, four, and five electrons. We therefore included fewer terms in each wave function, with a maximum of 12 terms, in contrast to the 30 terms used by Holþien and Geltman. The calculation of each level was accomplished in the following manner. For the N th lowest state of a given symmetry, a set of orbital exponents was chosen, the secular equations were set up, and the N th lowest eigenvalue was computed. The orbital exponents were then varied, one by one, until this particular eigenvalue achieved its minimum value. This value is then an upper limit to the energy of the state of interest.

In order to test the adequacy of our trial wave functions, we calculated the positions of some of the three-electron states previously studied by Holþien and Geltman. The results are shown in Table I. The energies of three states of the series $^2P^e(1s)(2p)(np)$ are also given in Table I. The number of terms included in the trial wave functions for these states was seven for the $^4S^e$ and $^4P^e$ states, and ten for the $^4P^o$ and $^2P^e$ states. For the states with major configurations containing both (1s) and (2s) electrons, our calculated energies are higher than the previous values by amounts up to 2 eV in O^{5+} , and 3 eV in F^{6+} . The poorest results are obtained for the states with configurations made up from three s orbitals. Thus we conclude that the major deficiency in our wave function is that it does not adequately allow for correlation of (1s) and (2s) orbitals. For states with major configurations which do not include both (1s) and (2s), our results are significantly better, and in some cases our energies are lower than those of Holþien and Geltman.

We have calculated the energies of several more members of the four series discussed above, and have studied four further series of O^{5+} and F^{6+}

that have not been studied previously. The additional series, together with the major configuration of the lowest member, are $^2D^o(1s2p3d)$, $^4D^o(1s2p3d)$, $^4D^e(1s2s3d)$, $^4F^o(1s2p3d)$. The energies of these states are not tabulated explicitly, but can be derived from the Auger electron spectrum given in Sec. III.

We have also computed the energy levels of several metastable states of O^{4+} , F^{5+} , O^{3+} , and F^{4+} . The four-electron states form five series whose lowest members can be characterized as $1s(2p)^3{}^3S^o$, $1s2s2p3p{}^5S^e$, $1s(2p)^3{}^5S^o$, $1s2s(2p)^2{}^5P^e$ and $1s2s2p3s{}^5P^o$. The five-electron states belong to the series ${}^6S^o$, of which the lowest member is $1s2s(2p)^3$.

The total number of states that we have computed is 66, but we have by no means exhausted the list of metastable states which could contribute to the Auger spectra. Obvious omissions are the four-electron states with angular momentum greater than 1 and the five-electron series with angular momentum greater than zero. Nevertheless, we believe we have determined sufficient energy levels to show the richness of the Auger spectra and to permit a comparison of theory and experiment.

III. SPECTRUM OF AUGER ELECTRONS

All the states under consideration in this paper contain a vacancy in the 1s shell which can be filled only through the action of spin-orbit or spin-spin forces. When the vacancy is filled the energy released often leads to the ejection of an electron. For the three-electron states the residual ion must have the configuration $(1s)^2$. However, the decay of a four-electron state can leave an ion in either the state $(1s)^2 2s{}^2S$ or $(1s)^2 2p{}^2P$. The difference in the energy of these two final states is 12.0 eV for oxygen and 14.0 eV for fluorine. Thus

TABLE II. Energies of the final ionic states after electron emission.

No. of electrons in residual ion	Final state designation	Oxygen	Fluorine
2	(1s) ²	-59.195	-75.596
3	(1s) ² (2s) ² S ^e	-64.271	-82.401
3	(1s) ² (2p) ² P ^o	-63.830	-81.887
4	(1s) ² (2s)(2p) ³ P ^o	-68.082	-87.736
4	(1s) ² (2p) ² ³ P ^e	-67.482	-87.031

each metastable state with four electrons can lead to two lines in the Auger spectrum. The five-electron states can lead to any of six possible final states with symmetry ¹S^e, ¹S^e, ¹P^o, ¹D^e, ³P^o, and ³P^e. However, decay to the triplet states involves the least change in multiplicity and seems therefore to be more likely. Thus we consider just the two final states (1s)²2s2p ³P^o and (1s)²(2p)² ³P^e.

For the final-state energies we use the experimental values,¹⁵ as given in Table II. The small relativistic correction for the metastable-state energies has been estimated using the data compiled by Kelly and Harrison.¹⁵ The computed Auger spectrum is presented in Table III. The energies of the metastable states can easily be reconstructed from these two tables by addition of the energies of the residual ion and emitted

electron.

It is clear from Table III that the Auger spectrum is exceedingly rich. For an unambiguous interpretation of the observed spectrum, high experimental resolution must be achieved, and calculations of the lifetimes of the states against Auger emission and photon emission would be desirable. Even without such information several interesting points emerge upon comparison of the experimental^{8,12} and theoretical spectra. In the analysis which follows, the electron energy for the fluorine ions will usually be given in parentheses following the corresponding value for oxygen.

The lowest peak, which is observed near 417 eV in oxygen (530 eV in fluorine) arises from the decay of the (1s2s2p)⁴P^o(1) state of the three-electron ion. We find two peaks close to 429 eV (544 eV), but our calculated value for the lower of these peaks, which arises from a four-electron state, may be too high by about 2 eV. The most recent data¹² with a 5-MeV oxygen beam show evidence of at least two peaks in this region. Between 436 and 440 eV (553 and 558 eV) we find three peaks. This energy range corresponds to the unidentified peak A in the earlier data of Sellin *et al.*⁹ Berry¹⁶ suggested that this peak arises from the state 1s(2p)² ²P^e, and this state is indeed

TABLE III. Spectrum of Auger electrons emitted by oxygen and fluorine ions.

Electron energy (eV)		Initial state ^a	Final state	Electron energy (eV)		Initial state ^a	Final state	Electron energy (eV)		Initial state ^a	Final state
Oxygen	Fluorine			Oxygen	Fluorine			Oxygen	Fluorine		
417.3	531.3	⁴ P ^o (1)	¹ S ^e	511.5	654.2	⁴ P ^o (2)	¹ S ^e	530.8	681.7	⁴ P ^o (5)	¹ S ^e
428.3	543.6	⁵ P ^e (1)	² P ^o	511.8	654.7	⁴ F ^o (1)	¹ S ^e	531.8	682.9	⁴ D ^e (3)	¹ S ^e
429.5	545.3	⁴ P ^e (1)	¹ S ^e	512.3	655.0	² D ^o (1)	¹ S ^e	532.6	683.8	⁴ F ^o (2)	¹ S ^e
436.6	553.7	² P ^e (1)	¹ S ^e	511.9	654.9	³ S ^o (2)	² P ^o	532.8	684.3	⁵ S ^e (2)	² S ^e
438.8	556.7	⁶ S ^o (1)	³ P ^e	512.5	655.4	⁵ P ^o (3)	² P ^o	533.7	680.3	³ S ^o (3)	² S ^e
440.3	557.6	⁵ P ^e (1)	² S ^e	512.5	655.8	⁵ S ^o (1)	² S ^e	535.9	687.3	⁴ P ^o (6)	¹ S ^e
444.9	562.9	⁵ S ^o (1)	² P ^o	513.4	657.0	⁵ P ^e (2)	² S ^e	536.4	687.9	⁴ D ^e (4)	¹ S ^e
453.7	573.5	³ S ^o (1)	² P ^o	513.5	656.4	⁴ D ^o (1)	¹ S ^e	536.8	688.4	² P ^e (4)	¹ S ^e
455.1	575.9	⁶ S ^o (1)	³ P ^o	514.1	657.3	⁵ S ^o (2)	² P ^o	536.9	688.4	⁴ S ^e (4)	¹ S ^e
456.9	576.9	⁵ S ^o (1)	² S ^e	514.5	657.6	⁴ P ^o (4)	¹ S ^e	537.1	688.6	⁴ P ^e (3)	¹ S ^e
465.7	587.5	³ S ^o (1)	² S ^e	515.5	...	⁶ S ^o (2)	³ P ^o	537.3	688.8	⁴ F ^o (3)	¹ S ^e
497.2	637.3	⁵ P ^o (1)	² P ^o	515.9	...	⁶ S ^o (3)	³ P ^e	537.4	688.9	² D ^o (3)	¹ S ^e
500.2	641.4	⁴ S ^e (1)	¹ S ^e	516.8	660.3	² P ^e (3)	¹ S ^e	537.8	688.4	⁴ D ^o (2)	¹ S ^e
500.5	641.8	⁵ S ^e (2)	² P ^o	517.1	661.0	⁵ P ^e (4)	² P ^o	538.1	689.7	⁴ P ^o (7)	¹ S ^e
501.4	643.0	⁵ P ^e (2)	² P ^o	517.1	661.4	⁵ P ^o (2)	² S ^e	542.3	694.7	² P ^e (5)	¹ S ^e
502.2	...	⁶ S ^o (2)	³ P ^e	518.4	662.2	² D ^o (2)	¹ S ^e	542.5	697.7	⁴ S ^e (5)	¹ S ^e
503.9	645.8	⁴ P ^o (2)	¹ S ^e	520.8	670.3	⁵ S ^o (2)	² P ^o	542.8	697.9	⁴ P ^o (8)	¹ S ^e
505.1	647.4	⁵ P ^o (2)	² P ^o	521.5	665.8	⁵ P ^e (3)	² S ^e	543.0	695.5	² D ^o (4)	¹ S ^e
505.8	647.8	⁴ D ^e (1)	¹ S ^e	521.7	666.3	³ S ^o (3)	² P ^o	543.6	698.9	⁴ F ^o (4)	¹ S ^e
508.2	650.3	⁴ P ^o (3)	¹ S ^e	523.9	668.9	³ S ^o (2)	² S ^e	548.7	704.1	⁴ S ^e (6)	¹ S ^e
509.2	651.1	⁵ P ^o (1)	² S ^e	524.5	669.4	⁵ P ^o (3)	² S ^e	548.7	704.3	² P ^e (6)	¹ S ^e
509.5	651.8	⁵ P ^e (3)	² P ^o	526.1	671.3	⁵ S ^o (2)	² S ^e	548.7	704.3	⁴ P ^e (4)	¹ S ^e
510.0	652.4	⁴ D ^e (2)	¹ S ^e	529.1	675.0	⁵ P ^e (4)	² S ^e	548.7	704.3	² D ^o (5)	¹ S ^e
510.2	652.7	² P ^e (2)	¹ S ^e	529.2	...	⁶ S ^o (3)	³ P ^o	548.7	704.4	⁴ F ^o (5)	¹ S ^e
511.1	653.7	⁴ S ^e (2)	¹ S ^e	529.9	680.7	⁴ S ^e (3)	¹ S ^e	549.0	704.7	⁴ D ^o (3)	¹ S ^e

^a The number of electrons in the initial state can be determined from the multiplicity of the final state in column 4; three-, four-, and five-electron states lead to singlet, doublet, and triplet final states, respectively.

responsible for one of the lines that we find. In the more recent data¹² there is also evidence for multiple structure within this peak. We find a single peak at 445 eV (563 eV), which can be seen in some of the recent data.¹² The broad structure, which was called peak *B* by Sellin *et al.*, remains somewhat puzzling. In fluorine we find three peaks, between 553 and 558 eV, which lie within the span of the observed broad peak. The corresponding lines in oxygen lie between 453 and 457 eV. Although there is some structure observed in this region, there is a peak close to 449 eV in the recent 2-MeV oxygen data that we cannot explain.

Above a single peak at 466 eV (587 eV) there is a large gap of 30 eV in oxygen and 50 eV in fluorine. There should be a few lines in this region from the decay of states with no *K* electrons such as $(2p)^2\ ^3P^e$. In the regions 500–570 eV in oxygen and 640–735 eV in fluorine, there are a very large number of states, many of which can be assigned to Rydberg series. The three-electron states of the form $1s\ 2s\ nl$ appear in groups near 504, 532, and 543 eV (646, 682, and 692 eV), whereas the states $1s\ 2p\ nl$ form clusters near 511, 537, and 548 eV (654, 688, and 704 eV). The positions of these Rydberg states are in reasonable agreement with the predictions of Berry.¹⁶

The observed oxygen spectra for the 2-MeV beam shows one or more strong peaks near 500 eV which are much weaker in the 5- and 6-MeV data. We find several lines arising from states with three, four, or five electrons and a careful analysis of this energy dependence would be useful. There is a gap in the three-electron spectra between 518 and 530 eV (662 and 681 eV), but there are many four-electron states which appear in this region. The observed spectrum for the 5-MeV oxygen beam shows a strong peak near 522 eV, which is not seen at 2 MeV. We find several lines arising from four-electron states near this energy, but further study of the energy dependence is required before this assignment can be made with confidence.

We terminated our calculations of spectra from three-electron states at 550 eV (705 eV) and from

four- and five-electron states around 535 eV (685 eV). However, the density of spectral lines will be exceedingly dense up to the series limits around 565 eV (725 eV).

IV. X-RAY ENERGIES

Some of the three-electron states studied in this paper have been observed through x-ray emission in two types of experiment. Gabriel and Jordan⁴ detected the radiative decay of the states $(1s)(2p)^2\ ^2P^e$ and $^4P^e$ in a θ -pinch plasma. A group from Kansas State University^{17, 18} has observed x rays from the $(1s)(2s)(2p)^4\ P^o$ state bombarding a carbon foil with 15-MeV fluorine ions. The theoretical and experimental values for the x-ray energies are in good agreement, as can be seen from Table IV.

In their analysis of the peak that they observed at 724.8 eV, Kauffman *et al.*¹⁸ suggest three possible initial states for the transition $1s\ 2s\ 2p\ ^2P^o$, $1s(2p)^2\ ^2D^e$, and $1s(2p)^2\ ^2P^e$. The fluorescence yield from the third of these states should be considerably greater than that of the other two, since the $^2P^e$ state is metastable against Auger emission. Thus we associate this state with the observed line in Table IV.

Kauffman *et al.*¹⁸ also observed strong lines at 800.6 and 813.2 eV in fluorine. If a relativistic correction is made to the calculations of Doyle *et al.*¹⁹ one finds a value of 813.5 eV for $1s2p\ ^3P^o - (2p)^2\ ^3P^e$ transition in F^{7+} . The lower of these lines probably arises from the transition $1s(2p)^2\ ^4P^e - (2p)^3\ ^4S^o$ in F^{6+} . We have calculated the position of this line and obtain a value of 800.8 eV.

V. CONCLUSIONS

We have shown that the Auger spectra of highly ionized atoms can be exceedingly rich, and have found that most of the peaks observed in the oxygen and fluorine spectra could be associated with more than one Auger transition. The major uncertainty in the interpretation of this data lies in the region near 450 eV in oxygen, that is near the peak called *B* by Sellin *et al.*^{9, 12}

TABLE IV. Experimental and theoretical values for x-ray energies.

Transition	Energy (eV)					
	Oxygen		Fluorine			
	Expt.	Theory	Expt.	Theory	Expt.	Theory
$1s(2p)^2\ ^2P^e - (1s)^2\ 2p\ ^2P^o$	562.3 ^a	...	562.7 ^b	724.2 ^a	724.8 ^c	724.8 ^b
$1s(2p)^2\ ^4P^e - (1s)^2\ 2p\ ^2P^o$	555.2 ^a	555.5 ^d	555.7 ^b	716.3 ^d
$1s\ 2s\ 2p\ ^4P^o - (1s)^2\ 2s^2\ S^e$...	554.3 ^d	555.4 ^b	...	715.1 ^c	715.1 ^d

^a Ref. 1. ^b This calculation. ^c Ref. 18. ^d Ref. 13.

For a more detailed analysis of these spectra, calculations should be performed of the rates of decay of the ionic states, both through Auger and x-ray emission. A detailed study, with high resolution, of the relative peak intensities as a function of beam energy and detector position would be valuable. For example, as the beam energy is increased, say from 2 to 10 MeV, the relative population of more highly ionized states should be enhanced. If the detector is moved so that the time of flight between the target and detector remains constant, then the relative importance of different charge states in each peak could be assessed. The

peaks near 428, 500, and 522 eV in oxygen would be particularly suited for this type of analysis.

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¹A. H. Gabriel and C. Jordan, *Nature (Lond.)* **221**, 947 (1969).

²B. C. Fawcett, A. H. Gabriel, and T. M. Paget, *J. Phys. B* **4**, 986 (1971).

³A. H. Gabriel and T. M. Paget, *J. Phys. B* **5**, 673 (1972).

⁴A. H. Gabriel, *Mon. Not. R. Astron. Soc.* **160**, 99 (1972).

⁵G. Fritz, R. W. Kreplin, J. F. Meekins, A. E. Unzicker, and H. Fried, *Astrophys. J. Lett.* **148**, L133 (1967).

⁶H. R. Rugge and A. B. C. Walker, *Space Res.* **8**, 439 (1968).

⁷B. B. Jones, F. F. Freeman, and R. Wilson, *Nature (Lond.)* **219**, 252 (1968).

⁸N. J. Peacock, R. J. Speer, and M. G. Hobby, *J. Phys. B* **2**, 798 (1969).

⁹I. A. Sellin, D. J. Pegg, M. Brown, W. W. Smith, and B. Donnally, *Phys. Rev. Lett.* **27**, 1108 (1971).

¹⁰I. A. Sellin, D. J. Pegg, P. M. Griffin, and W. W. Smith, *Phys. Rev. Lett.* **28**, 1229 (1972).

¹¹D. J. Pegg, I. A. Sellin, P. M. Griffin, and W. W. Smith,

Phys. Rev. Lett. **28**, 1615 (1972).

¹²D. J. Pegg, I. A. Sellin, R. Peterson, J. R. Mowat, W. W. Smith, M. D. Brown, and J. R. MacDonald, following paper, *Phys. Rev. A* **8**, 1350 (1973).

¹³E. Holstén and S. Geltman, *Phys. Rev.* **153**, 81 (1967).

¹⁴See, e.g., B. Donnally, W. W. Smith, D. J. Pegg, M. Brown, and I. A. Sellin, *Phys. Rev. A* **4**, 122 (1971), and references therein.

¹⁵R. L. Kelly and D. E. Harrison, *At. Data* **3**, 177 (1971)

¹⁶H. G. Berry, *Phys. Rev. A* **6**, 514 (1972).

¹⁷P. Richard, R. L. Kauffman, F. F. Hopkins, C. W. Woods, and K. A. Jamison, *Phys. Rev. Lett.* **30**, 888 (1973).

¹⁸R. L. Kauffman, C. W. Woods, F. F. Hopkins, D. O. Elliott, K. A. Jamison, and P. Richard (unpublished).

¹⁹H. Doyle, M. Oppenheimer, and G. W. F. Drake, *Phys. Rev. A* **5**, 26 (1972).