Multiply Excited States in the Two- and Three-Electron Oxygen Ion*

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High-resolution measurements of x-ray decay from excited states in highly stripped oxygen ions have yielded many transitions not attributable to the Lyman series in hydrogenic oxygen or to the analogous heliumlike oxygen series. These additional transitions are explained by considering the "screening" effects associated with adding a $2s$, $2p$, or $3p$ "spectator" electron to configurations governing the single-electron decays in excited heliumlike and lithiumlike oxygen. By comparing Hartree-Fock calculations for term energies, many of the observed transitions can be assigned to the doubly excited configurations $2pnp$ and $1smsnp$ in the heliumlike and lithiumlike sequencies, respectively.

I. INTRODUCTION

Experimental studies of photon and electron decays from excited states in highly stripped ions have been a popular subject in recent years.[1] Spectroscopic measurements on these systems are of prime importance in confirming theoretical atomic-structure calculations as well as in determining the collision mechanisms governing excited-state populations. One of the developments in this field has been the measurement and description of those transitions[2] in heliumlike and lithiumlike ions which clearly do not stem from singly excited atomic states. These transitions have been attributed to decays of doubly (or multiply) excited levels. In fact, using the beam-foil technique, Berry *et al.*[3] successfully made lifetime measurements on doubly excited states in neutral helium.

Measurements of these doubly (multiply) excited configurations are not restricted to radiative transitions or even to the use of beam-foil techniques. For instance, measurements of electron decay from multiply excited metastable autoionization states in OVI and FVII by Sellin *et al.*[4] demonstrated the importance of spin-orbit and spin-spin interactions in determining the transition probabilities for excited states (in simple ions) which are metastable against autoionization by the Coulomb interaction. Other methods for observing doubly excited doublet and quartet levels in lithiumlike ions have also been reported in papers on measurements of plasma discharges[5] and on observations of the solar corona[6] (where the levels have high excitation energies of about 500 keV). Holøien[7] has suggested that many doubly excited configurations will be observed for the He-like and Li-like isoelectronic sequences. However, there are no reported measurements of x-ray decays from multiply excited states in systems such as OVI and OVII. The purpose of this experiment, then, was to measure the radiative decay from a highly stripped beam of oxygen ions in the relatively soft x-ray region 14.0–24.5 Å. This region includes the entire Lyman-series spectra for hydrogenlike and heliumlike oxygen. For this wavelength region the resolution was sufficient to clearly separate singlet and triplet heliumlike doubly excited states and doublet and quartet lithiumlike doubly excited states. Sellin *et al.*[8] have reported x-ray measurements in oxygen in this wavelength region; however, their experimental apparatus had insufficient energy resolution and efficiency to permit observation of most of the presently reported transitions.

II. EXPERIMENTAL PROCEDURE

Using the beam-foil excitation technique the x rays from an energetic oxygen-ion beam were measured at a lab angle of 90° using a curved-crystal vacuum spectrometer. The spectrometer was equipped with a rubidium-acid-plate (RAP) analyzing crystal and a gas-flow proportional counter (operated at 2 kV, with 10% methane, 90% argon gas flowing at a rate of 0.5 l/hr.) utilizing a 2.0-μ Mackrofol[9] entrance window. The Bragg angle of the analyzing crystal and the position of the proportional counter were varied simultaneously using a stepping motor, controlled by a PDP-7 computer. Data were taken at each detector-crystal position for the same amount of integrated oxygen-ion beam current. The resulting data, for $\lambda = 14.0$–24.5 Å, were stored in histogram form, using a 36 684-channel grid of computer memory.

The oxygen-ion beam was provided by the University of Texas tandem Van de Graaff accelerator. Measurements were made at incident O^{n+} ion energies from 5.3 to 32.3 MeV (n depends on the maximum yield for a charge state given by MeV/amu curves by Marion and Young[10]). Thin carbon foils, typically about 10 μg/cm^2, were used to excite the ion beam near the primary entrance slit to the

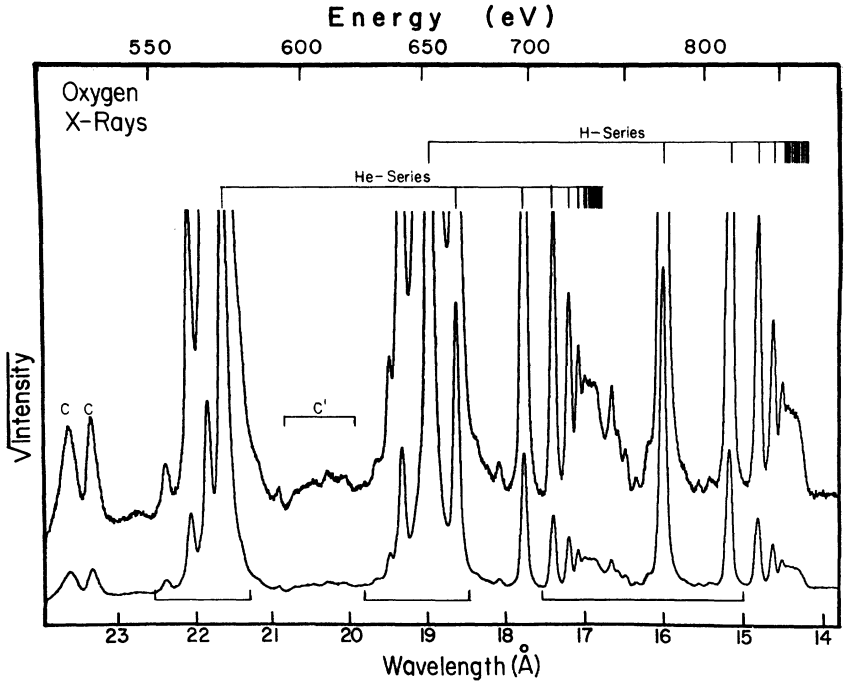

FIG. 1. Spectrum shows the entire wavelength region scanned in this experiment. The data are plotted as the square root of the measured intensity vs wavelength to facilitate identification of peaks above background. This spectrum was taken with detector viewing the back side of a carbon exciter foil.

x-ray spectrometer. Gold foils were also tried, but the signal-to-noise ratio for the resulting data was slightly less than with carbon. This effect is due to the wavelength overlap of Au M x rays with the spectral region of interest. The resolution of the x-ray spectrometer was about $\Delta E/E = 0.3\%$ full width at half-maximum for this experiment. Calibration of the spectrometer was accomplished using known wavelengths[11] for the Lyman series lines in both H-like and He-like oxygen.

III. RESULTS AND DISCUSSION

Figure 1 shows the entire wavelength region studied in this experiment. The brackets beneath several portions of this spectrum denote regions shown with greater detail in Figs. 2–4. Relative intensities between transitions should not be extracted from this figure since it is the sum of spectra taken at 17, 20, 27, and 32 MeV. The relative line intensities in each spectrum will vary in the same fashion as the yield of the associated charge state. The transitions marked C in Fig. 1 are the $K\alpha_{1,2}$ and SK for normal oxygen. They appear in the sum spectrum of this figure because all the data were accumulated with the counter viewing the target. This contamination is from target-associated oxygen x rays which were produced by the oxygen beam fluorescing trace amounts of oxygen-containing compounds present in the carbon target. The complex emission band marked C′ is also attributed to target-oxygen x rays. Good support for claiming both C and C′ to be contaminants was obtained by noting their disappearance after viewing the beam only slightly (less than 1 mm) downstream from the stripper foil. All other reported transitions were still observed at this distance.

Table I lists transition energies for the He-like series and the H-like series which were shown in the spectrum of Fig. 1. The spectrometer was calibrated using these transition energies, with suitable corrections included for the transverse doppler shift. In addition, the experimental line energies were found to agree with the theoretical values of Edlen[11] even when the calibration lines were restricted to the $K\alpha$(He), $K\alpha$(H), and $K\alpha_{1,2}$ transitions. The values for the series limit of transitions for both one-electron and two-electron oxygen were measured directly from the experimental data. However, no rigorous fitting routine was used to extract these values. Consequently, the assigned series-limit wavelengths are only accurate to ±0.01 Å.

Table II lists the energy and wavelength assignments for the remainder of the transitions observed in this experiment. Assignment of photon energies to particular atomic transitions was accomplished using nonrelativistic Hartree-Fock (HF)[12] calculations for the various configuration eigenenergies. Comparisons were also made with more sophisticated calculations done by Drake and Dalgarno,[13] Doyle *et al.*,[14] and Holøien and Geltman.[15] Tentative assignments for initial-state and final-state electron configurations and terms were then made, for the most part, on the basis of these

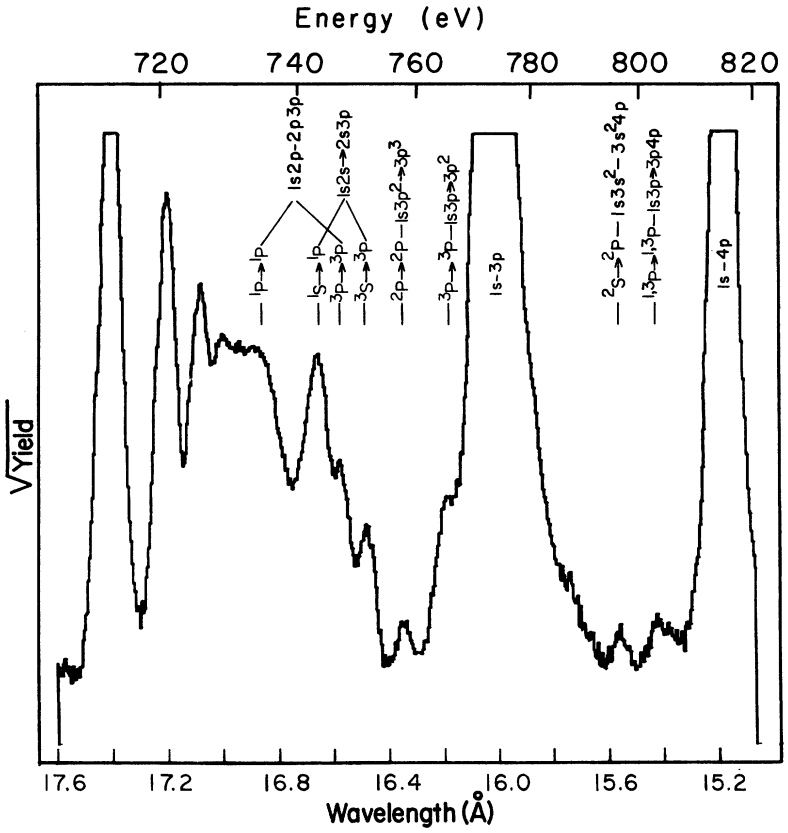

FIG. 2. Spectrum of transitions is shown at higher energies than the series limit of heliumlike oxygen. Suggested configuration and term assignments are listed above each designated peak.

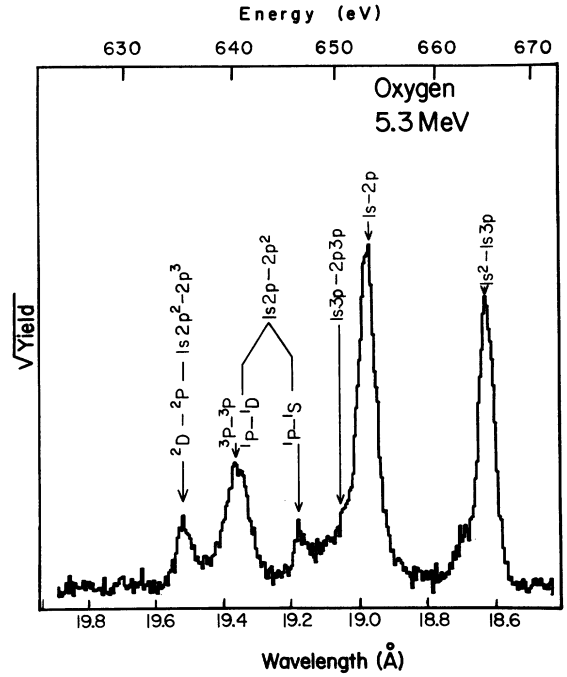

FIG. 3. Spectrum of transitions is shown for energies below the hydrogenic-oxygen Lyman α transition. Suggested configuration and term assignments are listed above each designated peak. The energy of the incident oxygen-ion beam was 5.3 MeV.

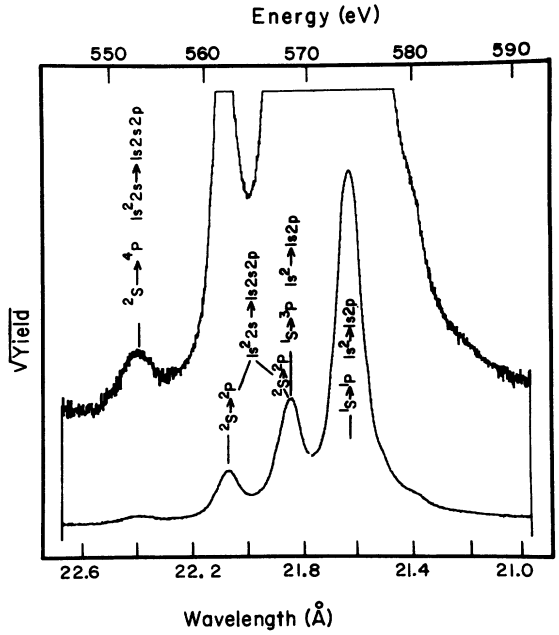

FIG. 4. Spectrum shows transitions from the Li-like doubly excited states. The ^2S-^2P ($1s^2 2s$-$1s2s2p$) transitions have two terms owing to the different parentages in the $1s2s2p$ configuration.

TABLE I. Transition energies for the He-like and H-like series.

Energy (eV)	Wavelength[a] (Å)(±0.005)	Ion	Configuration and state
524.9[b]	23.620	II	$K_\alpha(CO_2)$
531.2	23.341	III	$SK(CO_2)$
	Heliumlike series		
568.6	21.804	VII	$1s^2(^1S)$-$1s2p(^3P)$
573.9	21.602	VII	$1s^2(^1S)$-$1s2p(^1P)$
665.5	18.627	VII	$1s^2(^1S)$-$1s3p(^1P)$
697.6	17.768	VII	$1s^2(^1S)$-$1s4p(^1P)$
712.5	17.396	VII	$1s^2(^1S)$-$1s5p(^1P)$
720.7	17.200	VII	$1s^2(^1S)$-$1s6p(^1P)$
725.9	17.080	VII	$1s^2(^1S)$-$1s7p(^1P)$
734.9	16.87	VII	Series limit
	Hydrogenlike Lyman series		
653.60	18.969	VIII	$1s$-$2p$
774.4	16.006	VIII	$1s$-$3p$
816.5	15.176	VIII	$1s$-$4p$
836.1	14.821	VIII	$1s$-$5p$
846.8	14.634	VIII	$1s$-$6p$
853.2	14.524	VIII	$1s$-$7p$
871.4	14.22	VIII	Series limit

[a] Calibrated using values given from Ref. 11.
[b] Target x ray—also used as calibration points.

energy comparisons.

One of the difficulties encountered when assigning a particular transition in He-like oxygen has been whether to choose a $2snp$ or a $2pnp$ doubly excited configuration. Berry *et al.*[3] were confronted with this same problem in their measurements on He I. For He-like doubly excited terms, the $2snp$ series should autoionize more readily than radiatively decay. This is supported by calculations[16,17] of radiative deexcitation probabilities for several autoionizing ^1P and ^3P states from the $2snp$ configuration. Support for the large radiative-decay probabilities from the $2pnp\ ^{1,3}P$ doubly excited terms in the He I isoelectronic sequence is obtained from Wu's calculations.[18] Therefore, in this experiment, for consistency, all transitions relating to He-like doubly excited states were first assigned to $2pnp\ ^{1,3}P$ terms. Any remaining transitions that could not be fit by a $2pnp$ configuration were then assigned to any $2snp\ ^{1,3}P$ terms which matched in energy. There is only one example of this and it will be discussed later in the paper.

A similar problem is encountered in the lithium-like $1snsmp$ and $1snpmp$ series. Here the autoionizing probability of the $1snsmp\ ^4P^0$ states and the $1snpmp\ ^4P^e$ are similar.[7] Calculated energy separations[15] of the $^4P^0$ and $^4P^e$ states in these Li-like oxygen configurations are too small to permit

TABLE II. Transitions from multiply excited states.

Measured	Wavelength(Å) Present calculation	Previous calculation[a]	Measured energy(eV)	Configuration
22.370	22.42	b	554.2	$1s^22s(^2S)$-$1s2s2p(^4P)$
22.038	22.04	b	562.6	$1s^22s(^2S)$-$1s2s2p(^2P)$
21.358			580.5	
~21.18			585.4	
20.925			592.5	
20.1–20.7			599–617	Hypersatellite band from oxygen in target
19.650	19.66		630.4	$1s2p^2$-$2p^3(^2P$-$^2P)$
19.549	19.51		634.21	$1s2p^2$-$2p^3(^2D,^2S$-$^2P)$
19.383	19.37	19.35	639.64	$1s2p$-$2p^2(^3P$-$^3P,^1P$-$^1P)$
19.205	19.19		645.57	$1s2p$-$2p^2(^1P$-$^1S)$
19.069	19.07	19.03	650.17	$1s3p$-$2p3p$
18.385			674.3	
18.092	18.07		685.3	$1s^23s$-$1s3s4p$
16.770	16.79	16.78	739.3	$1s2p(^1P)$-$2p3p(^1P)$
16.650	16.63		744.4	$1s2s(^1S)$-$2s2p(^1P)$
16.581	16.57	16.60	747.7	$1s2p(^3P)$-$2p3p(^3P)$
16.478	16.47		752.4	$1s2s(^3S)$-$2s2p(^3P)$
16.350	16.36		758.0	$1s3p^2$-$3p^3$
16.186	16.18		766.0	$1s3p(^3P)$-$3p^2(^3P)$
15.750	15.74		(787.2)	$1s2s(^3S)$-$2s4p(^3P)$
15.572	15.57		796.2	$1s3s^2(^2S)$-$3s^24p(^2p)$
15.439	15.43		803.0	$1s3p(^{1,3}P)$-$3p4p(^{1,3}P)$

[a] Reference 14; also Ref. 13.
[b] Initial-state eigenenergies calculated in Ref. 15.

their respective decay lines to be resolved by our experimental apparatus. As a result, our assignments in Table II of the $1s^22s$-$1s2s2p$ transitions are tentative, and we do not exclude the possibility of $1s^22p$-$1s2p^2$ assignments to these transitions.

In this experiment our attention was first focused on explaining the origin of the radiative transitions observed just above the He-like series limit,[19] as shown in Fig. 2. These transitions were assigned, as well as two weaker ones at even higher energies, by the excellent agreement of their spectral positions with calculated transition energies based on the $2s3p$, $2p3p$, $3p^2$, $3p^3$, $3p4p$, and $3s^24p$ doubly excited and triply excited configurations. Where possible, our calculated line energies are compared with other published calculations. These comparisons are given in Table II where the wavelengths of the $1s2p$-$2p3p(^{1,3}P)$ terms are seen to agree fairly well with the calculations by Drake and Dalgarno[13] and Doyle *et al.*[14]

The strong transitions occurring at 16.63 and 16.47 Å in Fig. 2 could not be attributed to the decay of any $2pnp$ doubly excited configuration; however, the line energies are in excellent agreement with the calculated transition energies from the $(1s2s$-$2s3p)$ decays of the $^{1,3}P(2s3p)$ states. Berry *et al.*[3] also made these term assignments in their work on He I. The transitions assigned to $1s3p \rightarrow 3p^2$ and $1s3p \rightarrow 3p4p$ configurations support the speculation by Holøien[7] that these configurations should be strong. Finally, the association of transitions with the triply excited configurations $1s3p^2$-$3p^3$ and $1s3p^2$-$3p^24p$ must be considered as tentative until more sophisticated calculations are available.

Other doubly excited configurations have been identified with transitions in the wavelength region shown in Fig. 3. Here the magnitude of the hydrogenic oxygen $K\alpha$(H) transition is suppressed relative to the transitions from doubly excited states. This was done by taking the spectral data at the lower oxygen-ion energy of 5.3 MeV. At this energy the satellite transitions on the high-wavelength side of the $K\alpha$(H) transition can be seen most clearly. Here also the $1s2p$-$2p^2(^3P, ^1D, ^1S)$ terms are clearly observed. In this decay of the ^3P state, the predicted line energy is very close to that for the transition we have assigned $1s2p(^1P)$-$2p^2(^1S)$. However, since the ^3P term of the $2p3p$ configuration is expected to be fairly weak (which implies that the ^1P term would be even weaker), we have favored the $2p^2(^1S)$ assignment.

The tentative assignment in Fig. 3 of the ^2D-$^2P(1s2p^2$-$2p^3)$ transition to the lowest-energy spectral peak may not be complete, since there is some weak evidence that two unresolved transitions may both contribute to it. The second transition that may contribute is the intercombination line between ^3P-^1S terms in the $1s2p$-$2p^2$ configuration. We have preferred the ^2D-^2P assignment in this spectrum since the observed peak is still quite strong at this low energy (5.3 MeV), where Marion and Young[10] predict that O VI is about three times more likely than O VII. However, at higher incident-ion energies there may be some contribution from the ^3P-^1S intercombination line. This speculation was given some support in a recent experiment done by the authors at a higher beam energy. There, this transition was observed to decay with a greater mean life than any of its near neighbors ($\tau \sim 0.05$ nsec). This small amount of metastability favors the assignment of some metastable ^3P-$^1S(1s2p$-$2p^2)$ over a pure ^2D-$^2P(1s2p^2$-$2p^3)$ assignment.

A transition at 19.650 Å (630.4 eV) is observed in Fig. 1 on the high-wavelength shoulder of the ^2D-^2P transition (labeled in Fig. 3). This transition can be seen in Fig. 1 as a weak satellite peak, three peaks to the left of the $K\alpha$(H). This observed transition is tentatively assigned to the ^2P-^2P component of the $1s2p^2$-$2p^3$ configuration. Although the $(1s^22s$-$1s2s3p)$ decay transition of the $^4P^o$ state is calculated to lie at 636.4 eV, it is not expected to contribute to this peak. This is because the $(1s^22s$-$1s2s3p)$ decay transition of the ^2P state is expected to be much stronger (than the decay of ^4P), and it is not seen at its predicted line energy of 646 eV. Since no such transition is observed, the $1s2s3p$ configuration has been ruled out.

The final region emphasized in this experiment is shown in Fig. 4. This figure shows the fairly well-studied[4,8] heliumlike $^{1,3}P$ transitions and lithiumlike $^{2,4}P$ transitions. In a recent measurement by Moore *et al.*[20] the mean lifetime of the $^4P^o(1s2s2p)$ lithiumlike state was measured to be 3.48 nsec. The reported[8] lifetime of the ^1S-^3P heliumlike intercombination line was also confirmed by their measurement. There is evidence for satellite transitions on the low-wavelength side of He-like ^1S-^1P transition but no assignments have been made. As shown in Table II, these transitions occur at 21.358 Å and at about 21.18 Å.

Two other transitions at 18.385 and 18.092 Å were observed in this experiment. The transition at 18.092 Å was tentatively assigned to the $1s^23s$-$1s3s4p(^2P)$ configuration; however, no unique assignment for the 18.385-Å transition could be determined.

Measurement of the mean transition probabilities for most of these multiply excited states should certainly be considered. From a practical standpoint, however, this may be difficult. For instance, the time required to accumulate the data shown in Fig. 1 was 72 h of continuous scanning.

In addition, cascading effects in the H-like and He-like Lyman series make their intensities very strong even at considerable distances downstream from the exciter foil.[21] Thus the signal above background would not improve at appreciable distances from the exciter foil. As a result, lifetime measurements appear difficult for these doubly excited states when using a beam-foil method.

In summary, transitions from many doubly excited states in He-like and Li-like oxygen have been assigned from a comparison between measured and calculated line energies. Where ambiguities occurred in these assignments, they have been noted and discussed. With these transitions assigned, the way is now open for studies of these unusual states. Further, some candidates for triply excited states are presented, but no definite configuration assignments have been made. It is worth special emphasis to note that the short-wavelength region studies here (including the H-like and He-like Lyman transitions) are relatively uncluttered with overlapping transitions. This is because of the simplicity of the electron decays in this region, since the active (nonspectator) electron must jump directly to the 1*s* final configuration.

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