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I. INTRODUCTION

MOST information about atomic energy levels has been obtained from studies of optical spectra. However, the optical selection rules limit the number of states which can be readily observed. In recent years, atomic collision techniques have been employed to extend the range of states available for observation. Experimental observations of auto-ionizing states have been carried out using electron impact methods by several groups; for a resume of their results see Smith.¹ Auto-ionizing electrons from heavy ion impacts on gases have been observed by Barker and Berry² and by Everhart's group³ and one of us (MER) has used this latter technique to obtain information about the auto-ionizing states of helium,⁴ neon,⁵ argon,⁶ and now oxygen.

The calculation of the positions and widths of auto-ionizing states has been carried out for two and three electron systems using a variety of theoretical approximations, a review of these is given in Ref. 1. One of the most successful of these approximations is the close-coupling approximation which involves expanding the over-all wave function for the system in terms of known Hartree-Fock orbitals for the target electrons and generating systems of second-order differential equations for the continuum or auto-ionizing electrons. The numerical solution of these equations yields both the positions and widths of the auto-ionizing states. The interrelationship between the phenomenon of auto-ionization and the resonant scattering of electrons by atomic systems is discussed in detail in Ref. 1; the explicit equations which describe the scattering of

electrons by singly ionized oxygen atoms, and which lead to predictions on the auto-ionized levels of atomic oxygen, have been derived by Smith *et al.*⁷ who have written a computer code⁸ to calculate, among other parameters, the eigenphases for the scattering of electrons by atomic systems with configurations $1s^22s^22p^q$, $q=0, \dots, 6$. This code has been used to compute the results given here.

A description of the experimental method and of the apparatus has been given previously⁹ and only a few brief comments will be given here. Oxygen gas at pressures varying from 0.2 to 3μ was bombarded by either protons or helium ions at 100 keV. The ejected electrons were energy analyzed by a parallel-plate electrostatic analyzer. The analysis was done at 1 eV; the electrons being accelerated or decelerated to that energy as necessary. The resolution of the analyzer was about 70 mV which was great enough to separate the energies of different electron configurations but was not sufficient to resolve the various terms and J values of a given electron configuration.

In Sec. II we discuss the selection rules for auto-ionization in a language which is convenient for relating the initial excited state of the atom (after the collision) to the final state of the residual ion as well as from the close-coupling viewpoint. In Secs. III and IV we present our results and conclusions.

II. SELECTION RULES

Since most calculations are carried out with Hamiltonians which conserve both the total orbital and spin angular momenta, L and S , we shall work in LS coupling. The fact that oxygen is a low- Z element further justifies this choice. The interrelationship between the auto-ionizing states of atomic systems and the resonant scattering of electrons is discussed in detail in Ref. 1. Here we merely remark that the auto-ionized states of atomic oxygen were calculated by considering the scattering of electrons by O^+ ions. For a given L , S and parity π , the calculation reduces to extracting the numerical solutions, denoted by $F(S_1L_1l_1)$

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¹ K. Smith, Rept. Progr. Phys. **29**, 373 (1966); see also W. Mehlhorn, Phys. Letters **21**, 155 (1966) and H. Körber and W. Mehlhorn, Z. Physik **191**, 217 (1966).

² R. B. Barker and H. W. Berry, Phys. Rev. **151**, 14 (1966).

³ Q. C. Kessel, M. P. McCaughey, and E. Everhart, Phys. Rev. Letters **16**, 1189 (1966).

⁴ M. E. Rudd, Phys. Rev. Letters **13**, 503 (1964); **15**, 580 (1965).

⁵ M. E. Rudd and D. V. Lang, in *Proceedings of the IVth International Conference on the Physics of Electronic and Atomic Collisions* (Science Bookcrafters, Hastings-on-Hudson, N. Y., 1965), p. 153.

⁶ M. E. Rudd, T. Jorgensen, Jr., and D. J. Volz, Phys. Rev. Letters **16**, 929 (1966); Phys. Rev. **151**, 28 (1966).

⁷ K. Smith, R. J. W. Henry, and P. G. Burke, Phys. Rev. **147**, 21 (1966).

⁸ K. Smith, R. J. W. Henry, and P. G. Burke, Phys. Rev. **157**, 51 (1967).

⁹ M. E. Rudd, Rev. Sci. Instr. **37**, 971 (1966); M. E. Rudd, C. A. Sautter, and C. L. Bailey, Phys. Rev. **151**, 20 (1966).

of coupled second-order ordinary differential equations. The quantum number l_1 denotes the orbital angular momentum of the scattered electron relative to the ion in the state S_1L_1 . The energy associated with the scattered electron, when the core is in the $4S$ state, is denoted by k_1^2 ; if k_1^2 is positive, then the scattered electron is in a continuum orbital, while if k_1^2 is negative the electron is said to be in a bound orbital. When the ionic core is excited to the $2D$ or $2P$ state, then the energy of the outer electron is denoted by k_2^2 or k_3^2 , respectively. We have remarked above that for a given $LS\pi$, there may be several F 's coupled together; if at least one of these F 's is bound and at least one F is a continuum, then we have the condition for auto-ionization. The number of such F 's which can be coupled together for a given $LS\pi$ is obtained quite simply from the number of different ion states taken into account, denoted by L_1S_1 , the rules of vector addition of angular momenta and the conservation of parity.

In Fano's notation¹⁰ let ψ denote those independent particle model states of the ion plus electron in which

TABLE I. For a given set of the conserved quantum numbers $LS\pi$, we list the coupled, discrete, independent particle model states ϕ which can auto-ionize into the nearby continua ψ . The final column denotes the rows of Table XIV of Smith *et al.*^a which gives the positions of these auto-ionized levels.

L	S	π	ψ	ϕ	Smith <i>et al.</i> ^a	
0	1	-1	$F(4Ss)$	$F(2Dd)$	1	
1	1	+1	$F(4S\phi)$	$\left\{ \begin{array}{l} F(2D\phi) \\ F(2Df) \\ F(2P\phi) \end{array} \right.$		
			$(k_2^2 > 0)$	$\left. \begin{array}{l} F(2D\phi) \\ F(2Df) \end{array} \right\}$	$F(2P\phi)$	
1	1	-1	$F(2Dd)$	$\left\{ \begin{array}{l} F(2Ps) \\ F(2Pd) \end{array} \right.$	4 and 5	
1	0	+1	$\left. \begin{array}{l} F(2D\phi) \\ F(2Df) \end{array} \right\}$	$F(2P\phi)$		
1	0	-1	$F(2Dd)$	$\left\{ \begin{array}{l} F(2Ps) \\ F(2Pd) \end{array} \right.$		
2	1	-1	$F(4Sd)$	$\left\{ \begin{array}{l} F(2Ds) \\ F(2Dd) \\ F(2Dg) \\ F(2Pd) \end{array} \right.$	2, 3, and 6	
			$(k_2^2 > 0)$	$\left. \begin{array}{l} F(2Ds) \\ F(2Dd) \\ F(2Dg) \end{array} \right\}$	$F(2Pd)$	6
2	1	+1	$\left. \begin{array}{l} F(2D\phi) \\ F(2Df) \end{array} \right\}$	$\left\{ \begin{array}{l} F(2P\phi) \\ F(2Pf) \end{array} \right.$		
2	0	-1	$\left. \begin{array}{l} F(2Ds) \\ F(2Dd) \\ F(2Dg) \end{array} \right\}$	$F(2Pd)$		
2	0	+1	$\left. \begin{array}{l} F(2D\phi) \\ F(2Df) \end{array} \right\}$	$\left\{ \begin{array}{l} F(2P\phi) \\ F(2Pf) \end{array} \right.$		

^a Reference 8.

¹⁰ U. Fano, Phys. Rev. 126, 1866 (1961).

the electron is in a continuum state, while ϕ denotes the independent particle model states in which the excited electron is in a bound orbital. In Table I we present the close-coupling assignments for the F 's for the various combinations of ϕ and ψ which lead to auto-ionization within the framework of the theoretical approximations introduced in Ref. 7. The angular momentum of the auto-ionizing electron is given immediately by the quantum number l (s, p, d, f, \dots) of the ψ column, while the number of auto-ionizing series is given by the number of F 's in the ϕ column for a particular choice of $LS\pi$. On this latter point it must be emphasized that while the ϕ column gives the number of distinct series, it does not say how each series is constructed from the various F 's. In other words, the mixture of $F(2Ds)$, $F(2Dd)$, $F(2Dg)$, and $F(2Pd)$ for $L=2, S=1, \pi=-1, k_2^2 < 0$ required for the four series which auto-ionize via $F(4Sd)$ are unknown.

In Fig. 1 we have drawn a schematic of the energy levels of the oxygen atom based on the independent-particle model. The shaded areas denote the various continua ψ , while the broken horizontal lines denote possible ϕ states. The various possibilities for ϕ auto-ionizing into ψ are denoted by the horizontal lines with arrows on them.

For some purposes it will be convenient to restate some of the selection rules in a form which relates the initial excited states of the atom (after the collision) to the final state of the remaining ion rather than the ion plus ejected electron. For LS coupling the parity and L value rules can be combined to yield the following:

- (1) If neither of the states is an S state, then the auto-ionizing transition is not forbidden.
- (2) If one of the states is an S state, then (a) if the parities of the configurations are the same, then the other state must be an S, D, G, \dots state; (b) if the parities of the configurations are opposite, then the other state must be a P, F, H, \dots state. Since an auto-ionizing electron is ejected carrying its spin of $\frac{1}{2}$, the spin rule can be restated as follows:

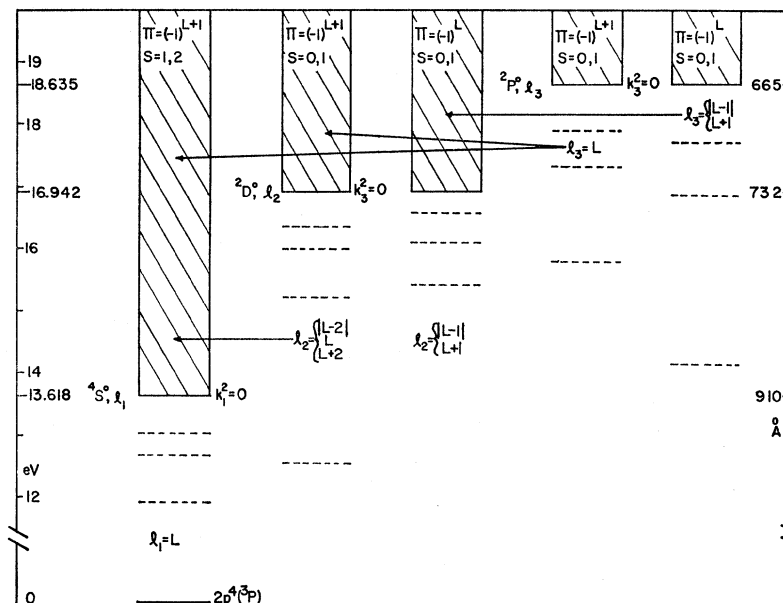
The multiplicities $(2S+1)$ of the initial state and of the final state of the ion must differ by unity.

In addition to these selection rules, the excitation process used to obtain the experimental results reported here is subject to additional rules which are, however, less restrictive than for photon excitation.¹¹ Because of the possibility of electron exchange between target and projectile, the following rules hold for excitation of neutral states:

- (1) For atoms subject to LS coupling, the multiplicity

¹¹ R. E. Huffman, J. C. Larrabee, and Y. Tanaka, J. Chem. Phys. 46, 2213 (1967).

FIG. 1. Schematic diagram of the single-particle energy levels and continua for an atomic system whose ground-state configuration is $1s^2 2s^2 2p^4 (^3P)$. Shaded areas represent the continua, dashed horizontal lines represent excited states. The connection among the various columns for auto-ionization is explained in the text.



can change at most by a number equal to twice the number of electrons in the projectile.

(2) For atoms not subject to LS coupling, or for atoms formed from the dissociation of molecules, there is no restriction on the change of spin, except that the total spin must be conserved.

Using the selection rules just stated, the allowed transitions were deduced and are listed in Table II. The singlet states listed in the first column can be excited even by protons because the excited oxygen atoms are formed by dissociation of molecules. Singlet states do not appear in the second column because the multiplicity would have to change by more than unity in going to the quartet final state. This would violate the spin rule. Alternatively, Table II can be constructed from Table I by taking the ψ column, which yields the 4S and 2D columns of Table II, and collecting together on successive lines of Table II those sets of $LS\pi$ which contribute to each l . The letter n is merely a numerical index used to characterize the members of a Rydberg series; while the orbital angular momentum l of the auto-ionizing electron is primed, or double primed, if the core is 2D or 2P , respectively.¹²

III. THEORETICAL RESULTS

In all computations in collision theory, approximations of one kind or another must be made. In the close-coupling approximations, which form the basis for the present theoretical results, all configurations which involve a change of the target ion configuration $1s^2 2s^2 2p^3$ to some excited configuration have been

neglected. Consequently, the entries in the column of Table I are the lowest members of the configurations which can mix together to form the ϕ state. It is the hope, which can be justified by comparison with experiment, that the terms in the ϕ column give the dominant contribution to the ϕ state. Smith and Morgan¹³ have developed a theory which does include excited state configurations and so it will be possible to compute higher F contributions to the ϕ state.

For $LS\pi=0, 1, -1$, we have a single discrete state mixing with a single continuum, which is the classic case treated by Fano.¹⁰ This combination should give rise to a single Rydberg series which has a series limit lying 16.942 eV above the ground state of oxygen. As indicated in the last column of Table I, this series was obtained by Smith *et al.*⁸ and was identified with a series observed by Huffman *et al.*¹¹ in ultraviolet absorption. This series was also observed in the experiments reported here—see Table III where we compare the

TABLE II. Allowed auto-ionizing transitions in the usual spectroscopic notation of prime indicating the 2D core and double prime the 2P core. The observations of the heavy ion bombardment experiment reported here cannot distinguish total L and total S .

States which make transitions to the (2D) final state	States which make transitions to the (4S) final state
$^2P ns'' (1,^3P)$	$^2D ns' (^3D)$
$^2P n p'' (1,^3P, 1,^3D)$	$^2D n p' (^3P, ^3F)$
$^2P n d'' (1,^3P, 1,^3D, 1,^3F)$	$^2P n p'' (^3P)$
	$^2D n d' (^3S, ^3D, ^3G)$
	$^2P n d'' (^3D)$

¹² C. Moore, *Atomic Energy Levels*, Natl. Bur. Std. (U. S.) Circ. No. 467 (U. S. Government Printing Office, Washington, D. C., 1949), Vol. 1.

¹³ K. Smith and L. A. Morgan, *Phys. Rev.* **165**, 110 (1968).

different observations as well as listing the principal quantum numbers of the series.

For $LS\pi=1, 1, +1$, we have a mixture of three discrete states decaying into a single continuum below the 2D limit. Consequently, there will be three auto-ionizing series, two having 2D as a series limit (we have computed only three members) and the final series having 2P as its series limit. In other words, the pair of series terminating on 2D can be expected to be a mixture of 2Dp and 2Df while the final series will be predominantly 2Pp . These series were inaccessible to Huffman and were not calculated by Smith *et al.*⁸ In Table III we present our experimental and theoretical results for these series. While the identification for both n and μ (the quantum defect) is clear for the $np''({}^3P)$ series, there are not enough members to distinguish the two mixed series. In Table III we also list the pair of levels given by Moore¹²: see column CM. The energies we have given in Table III are all relative to the ground state of atomic oxygen; in other words, when a ϕ state can decay into both 4S and 2D continua then the auto-ionizing electrons should separate into two energy groups (16.942–13.618) eV apart.

According to Eq. (6) of Ref. 1, the positions of the members of a Rydberg series are given in eV by

$$E_n = E_\infty - 13.6/(n-\mu)^2, \quad (1)$$

where E_∞ is the series limit. Curves were drawn of μ versus $E_\infty - E_n$ for various integers n . The values for n and μ given in Table III of this paper were obtained by plotting a series on a parallel abscissa scale and moving it upwards until members of the series coincided with the μ versus $E_\infty - E_n$ curves in a sequential pattern.

For $LS\pi=1, 1, -1$, we have a mixture of two discrete states decaying into a single continuum. In Table I we note the fact that these series have been obtained by Smith *et al.* and in Table III we compare these theoretical results with the uv observations of Huffman *et al.* and the heavy ion bombardment experiments reported here. Although we have identified the series as either ns'' or nd'' , we note that such assignments are approximate and each series is in fact a mixture of s and d .

For $LS\pi=2, 1, -1$, auto-ionizing states of oxygen may be detected by photon absorption and so Table III gives the results of Huffman *et al.* and Smith *et al.* For this set of quantum numbers there will be four series: one easily being identified as ϕ being $F({}^2Pd)$ while the remaining three series will be some linear combination of $F({}^2Ds)$, $F({}^2Dd)$, and $F({}^2Dg)$. The series ng' has yet to be found. In Table III we present the heavy ion results with square brackets; this is because the experiment cannot distinguish the L and S . That is to say, in Table II we show that the nd'' series could appear in ${}^1, {}^3P$, ${}^1, {}^3D$, and ${}^1, {}^3F$; the D and F entries would have square brackets in Table III.

The final triplet series given in Table III, $LS\pi=2$,

TABLE III.† Positions of the auto-ionizing levels of atomic oxygen between the ground-state terms. These levels are given in terms of eV relative to the ${}^3P^o$ term of the configuration $1s^2 2s^2 2p^4$. In the last column each series is identified in two ways: by the usual spectroscopic notation and by the S_1L_1l notation explained in the text.

$LS\pi$	CM ^a	Huffman ^b	Smith ^c	Present work		μ	n	ϕ
				Expt.	Theory			
Triplets								
0, 1, -1		15.415	15.428	15.41			3	$nd'({}^3S)$
		16.085	16.090	16.10			4	
		16.394	16.397	16.41			5	2Dd
		16.561	16.563	16.58			6	
1, 1, +1				15.77	15.768		3	$np''({}^3P)$,
				17.31	17.305		4	
					17.849		5	2Pp
					18.121		6	
					18.278	0.83	7	
		14.046		14.16			3	$np''({}^3P)$,
		15.595		15.62			4	
			16.22	16.121		5	${}^2Dp + {}^2Df$	
				16.312		6		
				16.507		7		
1, 1, -1		17.686	17.702	17.73			5	$ns''({}^3P)$,
		18.041	18.049	18.02			6	
		18.229	18.234				7	${}^2Ps + {}^2Pd$
		17.103					3	$nd''({}^3P)$,
		17.774	17.779	17.80			4	
		18.085	18.087	18.09			5	${}^2Ps + {}^2Pd$
		18.254	18.255	18.28			6	
	18.355	...	18.36			7		
2, 1, -1		17.104			3	$nd''({}^3D)$,
		17.774	17.780	[17.80]			4	
		18.085	18.088	[18.09]			5	2Pd
		18.254	18.255	[18.28]			6	
		15.179	15.229	15.15			4	$ns''({}^3D)$
		15.992	16.011	15.95			5	
		16.349	16.357	...			6	
		15.406	15.422				3	$nd''({}^3D)$
		16.080	16.087				4	
		16.392	16.395				5	
The 3rd series ng' has been neither observed nor calculated.								
2, 1, +1				[17.31]	17.332		4	$np''({}^3D)$,
					17.882		5	
					18.140		6	broad
					18.287	0.84	7	${}^2Pp + {}^2Pf$
					17.787		4	
					18.086		5	$nf''({}^3D)$,
					18.252		6	narrow
				18.374	0.01	7	${}^2Pp + {}^2Pf$	
Singlyts								
1, 0, +1				[17.31]	17.338		4	$np''({}^1P)$
					17.880		5	
					18.142		6	2Pp
					18.286		7	
					18.376	0.79	8	
1, 0, -1				[17.73]	17.720		5	$ns''({}^1P)$,
				[18.02]	18.057		6	
					18.238		7	${}^2Ps + {}^2Pd$
					18.344		8	
					18.415		9	
					18.460		10	
					18.494	1.19	11	
				[17.80]	17.785		4	$nd''({}^1P)$
				[18.09]	18.090		5	
				[18.28]	18.256		6	${}^2Ps + {}^2Pd$
			[18.36]	18.357		7		
				18.422		8		
				18.468		9		
				18.499	0.03	10		
2, 0, -1				[17.80]	17.781		4	$nd''({}^1D)$
				[18.09]	18.086		5	
				[18.28]	18.253		6	2Pd
				[18.36]	18.355	0.02	7	
2, 0, +1					17.387		4	$np''({}^1D)$,
					17.904		5	
					18.135		6	${}^2Pp + {}^2Pf$
					18.285		7	
					18.366	0.71	8	
The 2nd series nf'' has not been observed.								

^a Reference 12.

^b Reference 11.

^c Reference 8.

1, +1, are seen from Table I to be a pair of discrete states auto-ionizing into a pair of continua giving rise to two series, one having a noticeably larger width than the other, hence the designations "broad" and "narrow" in the ϕ column of Table III.

As far as the singlet series are concerned, which are not accessible in the uv experiment, we can see at a glance at Fig. 1 that auto-ionization can only occur from ϕ states with a 2P core into ψ states with a 2D core, the maximum energy carried by the auto-ionizing electron being (18.635–16.942) eV; in other words all series limits will be 18.635 eV above the ground state of oxygen. For $LS\pi=1, 0, +1$, we have a single discrete state $F(^2P\phi)$ decaying into a pair of degenerate continua. As remarked above, the heavy ion experiment cannot distinguish the spin states and so we have enclosed this observation in square brackets. All the calculated quantum defects and principal quantum number assignments for the singlet states were obtained by the method described earlier.

For $LS\pi=1, 0, -1$, we have a coupled pair of discrete states decaying into a single continuum giving rise to a pair of series converging on the 2P threshold. In Table III we have identified these states as ns'' and nd'' states on the basis of the quantum defects for the two series. For $LS\pi=2, 0, -1$, there is a single auto-ionizing series terminating at the 2P threshold. The ϕ state, being a pure $F(^2Pd)$, decays into a mixture of three degenerate continua.

The final singlet state which we have computed is the $LS\pi=2, 0, +1$ given in Table III. Here we have a pair of discrete states decaying into a pair of degenerate continua and which must result in two series of auto-ionizing levels; only one of these series, the np' identified by its quantum defect, has been located.

IV. EXPERIMENTAL RESULTS

Figure 2 shows several overlapping runs on the oxygen spectrum. Some were made detecting electrons at 160° from H^+-O_2 impacts and in other runs electrons were observed at 10° from He^+-O_2 collisions. No differences were noticeable in the spectra taken under these two conditions and therefore the energies and intensities given in this paper are averages over many runs taken under both conditions. Portions of six Rydberg series appear, two of which were previously unobserved.

Not all of the allowed transitions listed in Table II were observed. The np'' and nd'' states have two continua (2D and 4S) available into which they can auto-ionize, but our observations indicate that the np'' states make transitions only into the 4S continuum and the nd'' states go only into the 2D continuum. It thus appears that some additional selection rules are operating.

The energy scale was calibrated by taking the transition from the $3d'$ state to have an energy of 1.79 eV. The measured energies have an absolute uncertainty of 40 meV.

TABLE IV. Energies and intensities of observed transitions.

Initial state	Final state	Electron energies (eV)	Relative intensities ^a	n^{*b}
$4s'$	$2p^3(^4S)$	1.53	2	
$5s'$		2.33	0.8	
$3p'$	$2p^3(^4S)$	0.54	6	2.21
$4p'$		2.00	3	3.21
$5p'$		2.60	0.8	4.3
$3d'$	$2p^3(^4S)$	1.79	10	
$4d'$		2.48	4	
$5d'$		2.79	2	
$6d'$		2.96	1	
$5s''$	$2p^3(^2D)$	0.79	2	
$6s''$		1.08	0.5	
$3p''$	$2p^3(^4S)$	2.15	1.8	2.18
$4p''$		3.69	0.4	3.2
$4d''$	$2p^3(^2D)$	0.86	2	
$5d''$		1.15	1.4	
$6d''$		1.34	0.9	
$7d''$		1.43	0.7	

^a The intensities have only a rough significance.
^b Effective quantum numbers of the new levels.

The two new series are the $np''(^3P)$ and the $np'(^3P, ^3F)$. The energies and intensities of these lines along with the others observed are given in Table IV.

A peak with an energy of 1.68 eV and an intensity of 3 remains unidentified. This line falls approximately at the series limit of the ns'' and nd'' series which decay into the 2D continuum, but the shape and intensity of

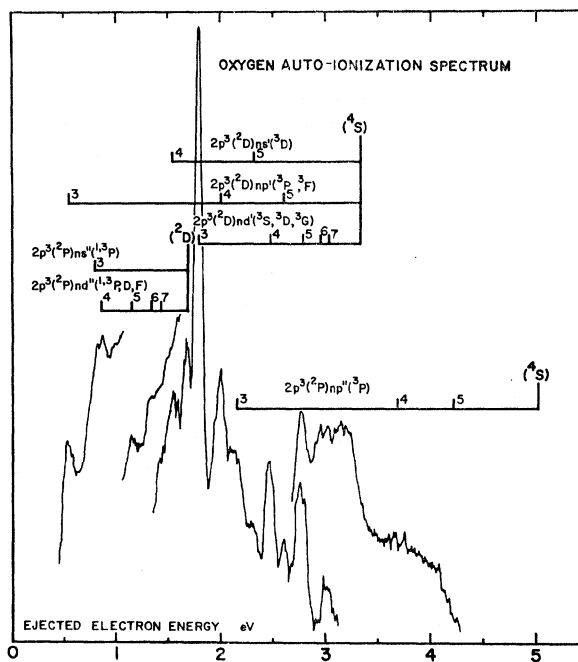


FIG. 2. Energy spectrum of electrons from oxygen gas bombarded by 100-keV H^+ or He^+ ions. Six series are seen; four representing auto-ionizing transitions into the 4S continuum and two into the 2D continuum. Resolution 70 meV.

the peak indicate that it is a separate line and not a series limit. It also falls at the energy expected for the transition of the $3d'(^3P)$ state into the $4S$ continuum. This transition is forbidden in LS coupling, but the presence of this peak (which was well verified in many runs) probably indicates a breakdown of LS coupling. This is not surprising since Codling *et al.*¹⁴ have observed such a breakdown in neon.

The only other feature of the spectrum observed between 0.5 and 18 eV is the hump just above 4 eV. This could represent the series limit for the transitions from the $ns\sigma^3\Sigma_u^-$ and $nd\pi^3\Pi_u$ molecular states into the $^2\Sigma_g^-$ continuum. Codling and Madden¹⁵ have observed

these excited states in the absorption spectrum in the 500–600 Å region and by their broadened, asymmetric nature deduce that they are auto-ionizing. These levels converge on the $c^4\Sigma_u^-$ state of O_2^+ which is 4.26 eV above the $^2\Sigma_g^-$ limit. This energy is consistent with our interpretation of the hump as this series limit. However, none of the individual lines from this series of transitions could be observed. Evidently most of the auto-ionization observed in this experiment occurs after dissociation of the oxygen molecule.

That the lines reported here are from atomic oxygen is further verified by the fact that we observe the same line spectrum using carbon dioxide as a target gas.

¹⁴ K. Codling, R. P. Madden, and D. C. Ederer, *Phys. Rev.* **155**, 26 (1967).

¹⁵ K. Codling and R. P. Madden, *J. Chem. Phys.* **42**, 3935 (1965).

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