PARTIALLY AUTOIONIZING STATES OF ATOMIC OXYGEN

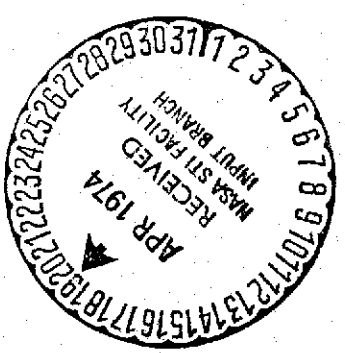
JAMES A. R. SAMSON and V. E. PETROSKY

Behlen Laboratory of Physics

University of Nebraska, Lincoln, Neb. 68508

ABSTRACT

The Rydberg states $3d'\ ^3P^o_{2,1,0}$ and $3s''\ ^3P^o_{2,1,0}$ and the inter-shell transition $2s2p^5\ ^3P^o_{2,1,0}$, which are forbidden to autoionize on the basis of LS coupling, have been observed in emission spectroscopy and in autoionization spectra produced in the photoelectron spectrum of atomic oxygen.



Previously unidentified structure has been observed in the photoelectron spectrum of atomic oxygen when it is produced by the 584 Å HeI line from an undispersed discharge in helium. This structure was also observed in the work of Jonathan et al.[1]

In the present work it is shown that the structure is caused by impurity OI resonance lines from the light source. These resonance lines populate Rydberg states lying above the first ionization potential of atomic oxygen. The states responsible for the structure are the Rydberg levels $3d'\ ^3P^o_{2,1,0}$ and $3s''\ ^3P^o_{2,1,0}$ and the inter-shell transition $2s2p^5\ ^3P^o_{2,1,0}$. The states subsequently de-excite via the two competing paths of emission and autoionization. When autoionization takes place an electron is ejected with an energy equal to the difference between the energy of the state and the ionization potential of the continuum interacting with the state (in this case the ^4S continuum). The interesting point is that these states are forbidden to autoionize on the basis of LS coupling. However, in the present work the states are observed both in emission spectroscopy and in photoelectron spectroscopy.

The emission spectrum of atomic oxygen was taken over the wavelength range 770-920 Å by adding a trace of O_2 (about ½%) into a helium glow discharge. The radiation was dispersed

with a ½ m Seya monochromater operating with a 1 Å band pass. The detector was a photomultiplier sensitized to vacuum uv radiation with a coating of sodium salicylate. The resulting spectrum is shown in Fig. 1. The top spectrum was run with the He + O_2 mixture whereas the bottom spectrum was taken with helium purified by passing through a zeolite trap cooled with liquid nitrogen. With pure helium in the discharge no emission lines were observed in the wavelength range of interest. When a trace of O_2 was added to the discharge radiation was observed from the autoionization-forbidden states with wavelengths 791.98 Å, 811.08 Å, and 877.89 Å. Actually, each state emits six lines covering about a 2 Å spread.[2] The wavelengths quoted above correspond to the $J' = 2 \rightarrow J'' = 2$ transitions. In Fig. 1 the $3s'' \ ^3P^o$ multiplet (877.89 Å) is partially resolved. If more than a few percent of O_2 was added to the helium discharge the lines were quenched. No radiation was observed from states which were fully allowed to autoionize on the basis of the selection rules, namely $\Delta S = 0$, $\Delta J = 0$, $\Delta L = 0$, and no change in parity. Many other oxygen lines are produced at longer wavelengths (e.g. the 1304 Å OI triplet).

The helium lamp was used undispersed (with and without the trace of O_2) as an ionizing source to produce the photoelectron spectrum of atomic oxygen. The lamp is still essentially a monochromatic source of 584 Å radiation even with the trace of O_2 because the intensity of the 791.98 Å OI line ($2s2p^5 \ ^3P \rightarrow 2s^2 2p^4 \ ^3P$) is about 200 less than the 584 Å line

under optimum conditions for the OI lines. Thus, no appreciable contribution to the PE spectrum would be expected.

Atomic oxygen was produced by flowing O_2 through a microwave discharge. The main products emerging from the discharge were $O(^3P)$, $O_2(X^3\Sigma_g)$, and $O_2(^1\Delta_g)$. These products have been identified in previous photoionization studies.[3-6] The experimental arrangement for flowing the atomic oxygen into the cylindrical mirror analyzer is shown in Fig. 2. The stream of atomic oxygen was directed to intersect the photon beam and the electron trajectory leading into the analyzing region. The original energy of the photoelectrons was modified as they passed through a retarding/accelerating lens, L. This allows the electrons to be analyzed at a fixed voltage. A pass energy of 2 eV was used which gave a constant energy resolution of 30 meV. The analyzer is described in more detail elsewhere.[7] Photoelectrons will be produced from each product in the gas stream. Figure 3 shows the photoelectron energy spectrum from 0 to 5 eV. Figure 3(a) was taken with pure He in the light source while Fig. 3(b) was taken with a trace of O_2 added to the light source. Both spectra show identical peaks caused by the direct photoionization of the discharged products by the HeI 584 Å line.[7] However, Fig. 3(b) shows the additional peaks produced by the OI resonance transitions at 877.89 Å (3s'), 811.08 Å (3d'), and 791.98 Å ($2p^5$). Although the emission lines are about 200 times less intense than the 584 Å line they produce comparable photoelectron signals. Thus, the photoionization cross section of atomic oxygen at these lines is roughly 200

times greater than at 584 Å. Figure 4 shows, schematically, a term diagram of the above transitions autoionizing into the ^4S continuum. The predicted energies of the ejected photoelectrons are shown in the diagram. These energies correspond to the autoionizing structure in the photoelectron spectrum.

Further confirmation of the identity of the structure comes from the photoionization - mass spectrometry studies of Dehmer et al.[8] By the use of the Hopfied continuum they studied the photoionization of atomic oxygen as a function of wavelength over the range 912 to 660 Å. They observed autoionizing structure at all the allowed transitions including the LS forbidden states discussed here.

Thus, it is firmly established that the 3d' $^3P^o$, 3s" $^3P^o$, and $2s2p^5$ $^3P^o$ states partially auto-ionize and that emission processes compete with autoionization. It is just this combination that produces the spurious peaks in the 584 Å undispersed photoelectron spectrum of atomic oxygen when a small air leak exists in the light source.

ACKNOWLEDGEMENT

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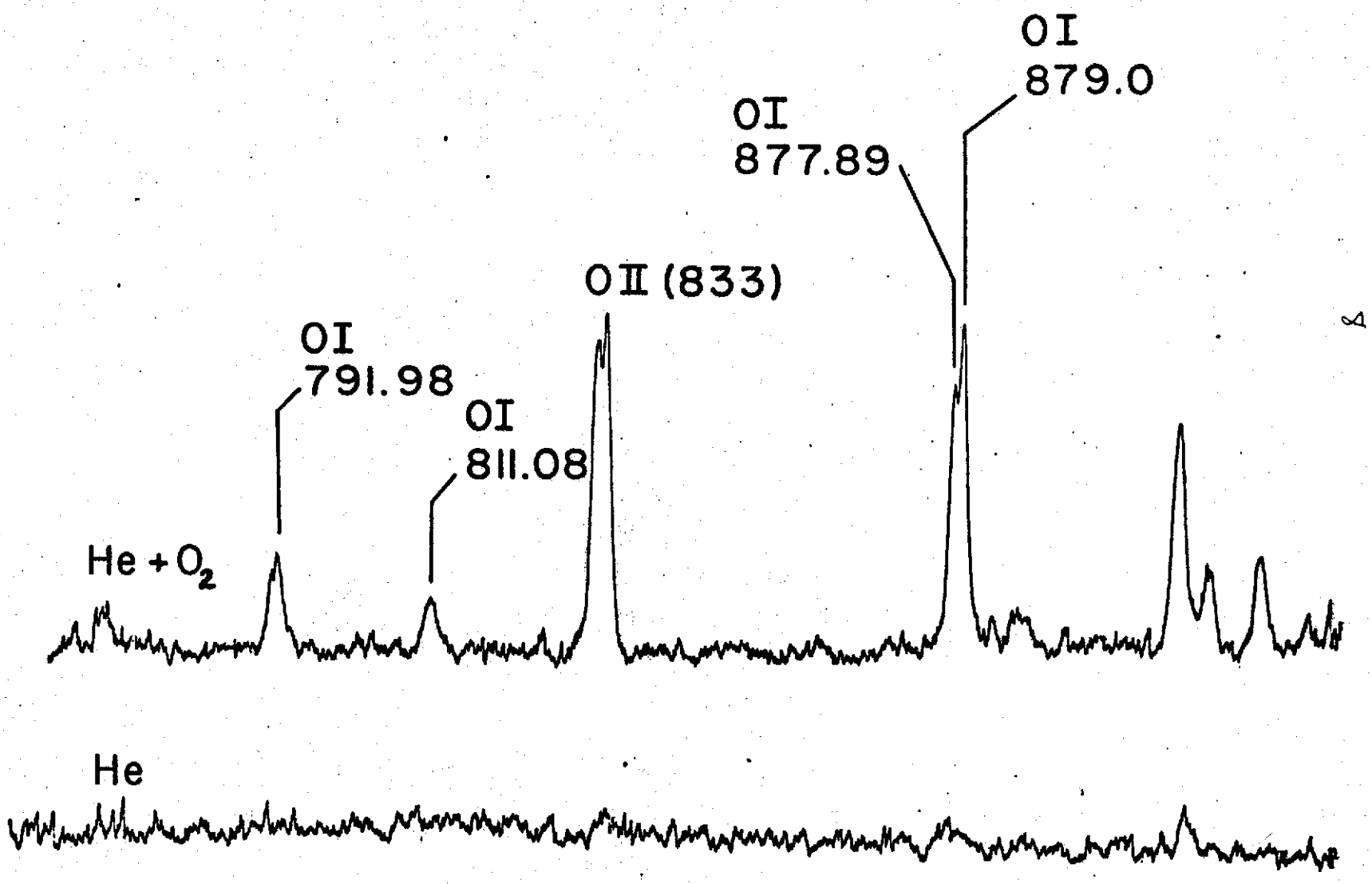
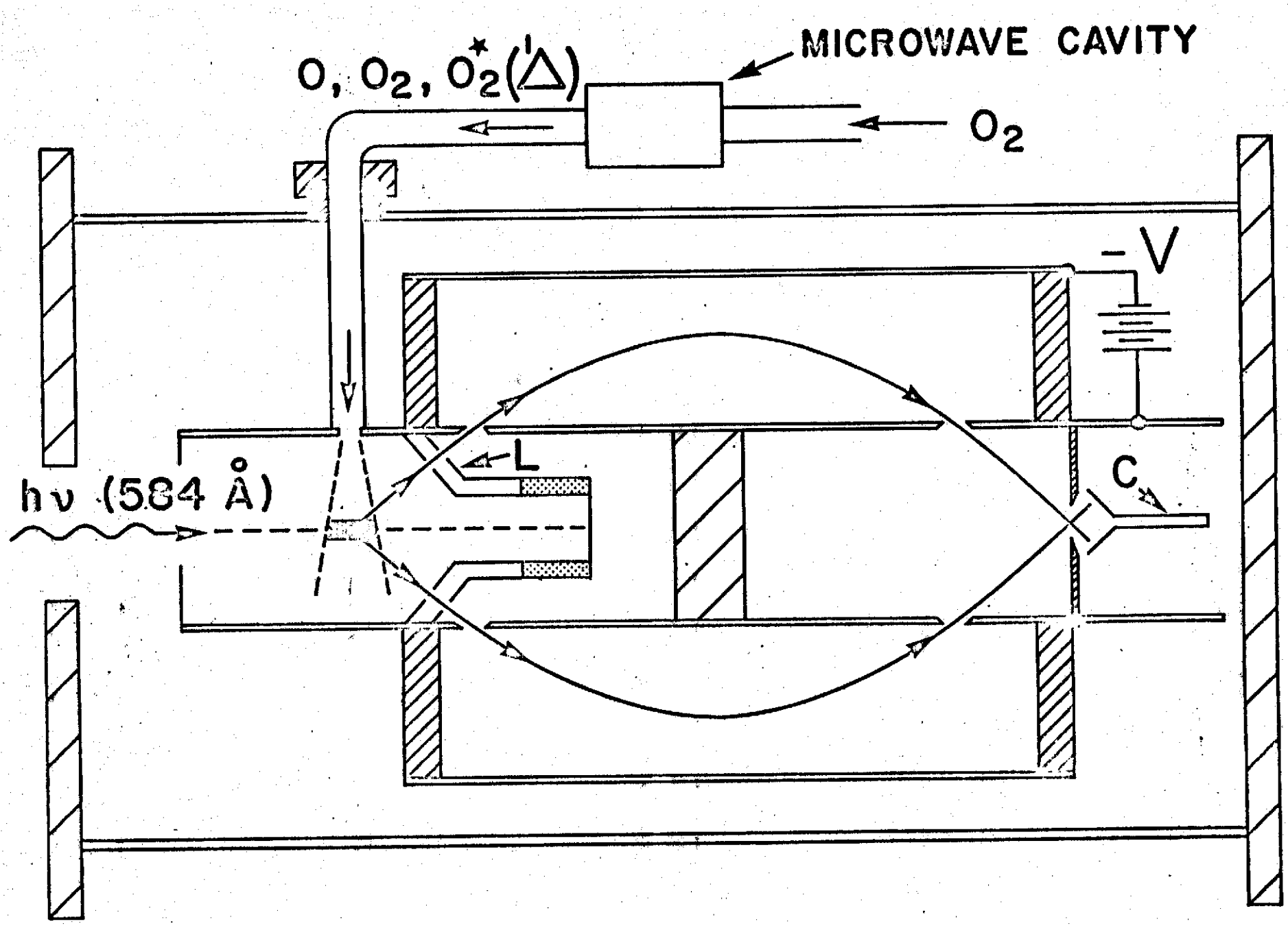
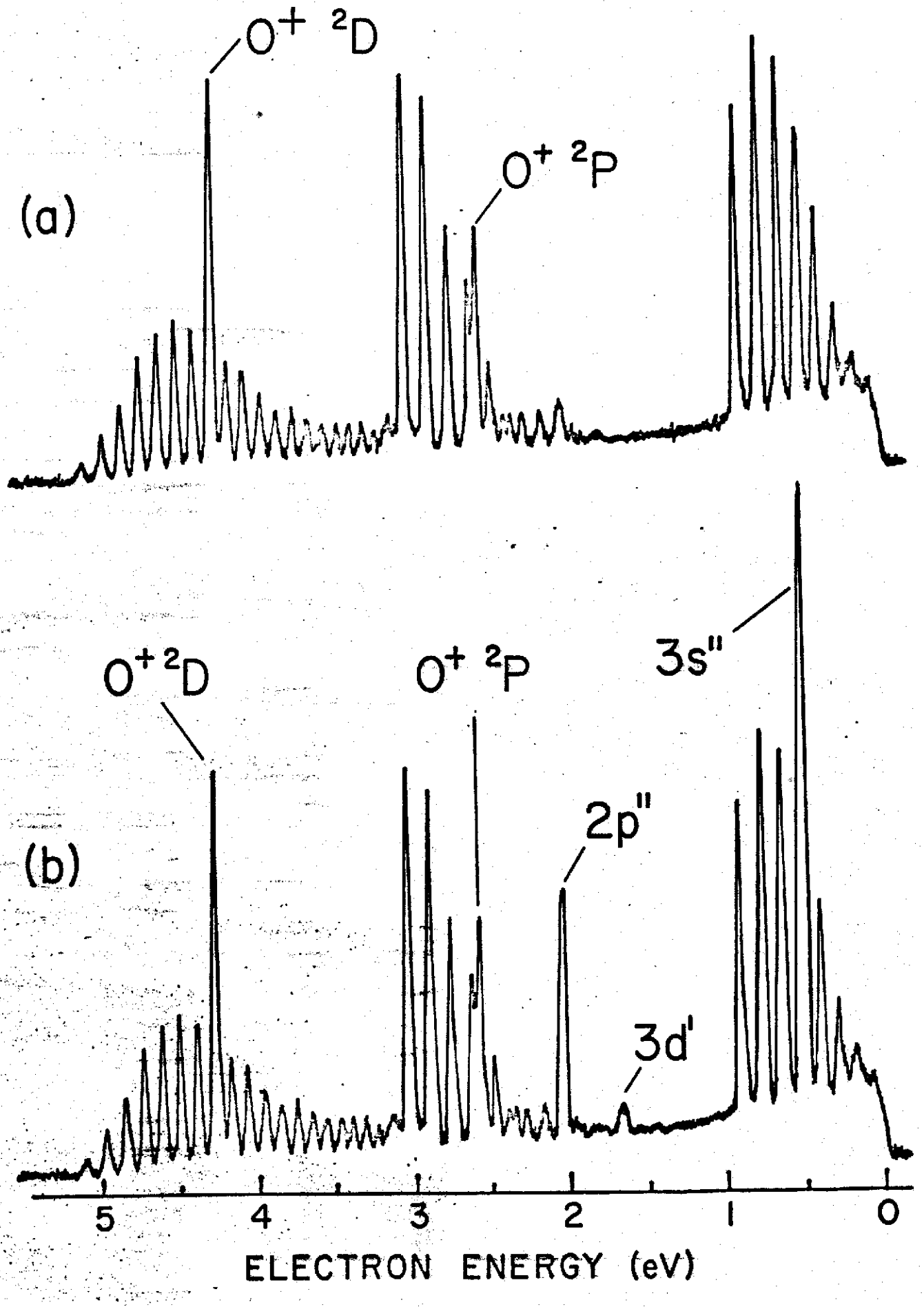
FIGURES

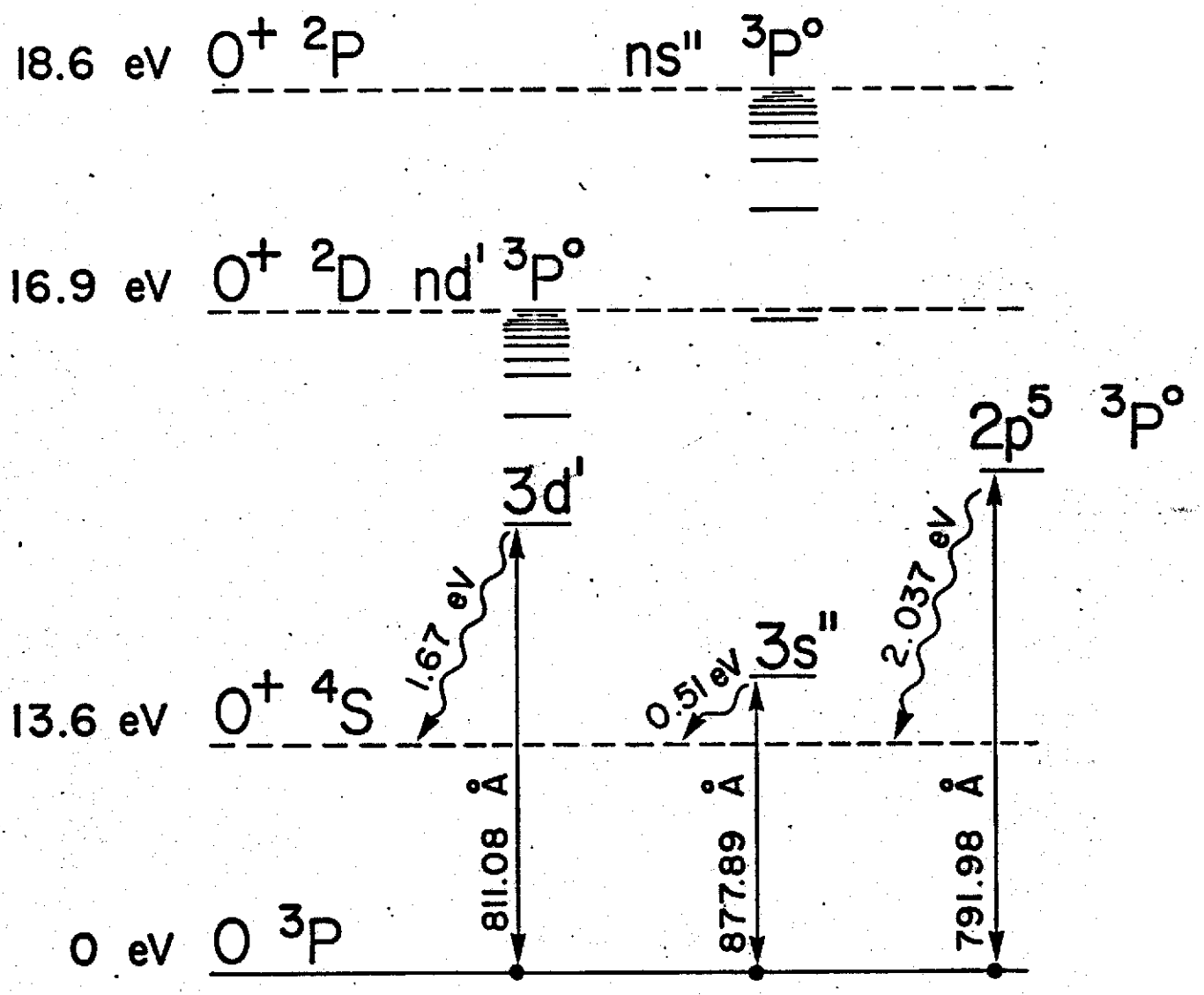
1. Emission spectrum of atomic oxygen from a helium dc glow discharge with a trace of O_2 added (~ ½% O_2). The OI emission lines are produced from partially autoionizing states. The bottom trace illustrates that no observable emission could be seen from the light source in this wavelength region when no O_2 was present.
2. Cylindrical mirror electron energy analyzer. L is the retarding/accelerating lens and C is the channeltron detector. The microwave discharge for the production of atomic oxygen is shown in relation to the analyzer.
3. (a) Photoelectron spectrum of the discharged products produced by a microwave discharge in O_2. Pure helium was used in the light source.

   (b) Photoelectron spectrum of the discharged products as in Fig. 3(a) but with a trace of O_2 added to the helium discharge. The autoionizing states are clearly observed at 0.51, 1.67, and 2.037 eV.
4. Simplified term energy diagram of atomic oxygen illustrating the Rydberg levels nd' $^3P^o$ and ns" $^3P^o$ and the $2s2p^5$ $^3P^o$ level. The resonance wavelengths corresponding to the lowest level of each state is given in Angstrom units. Autoionizing transitions into the ^4S continuum are indicated along with the predicted energy of the ejected electron.


OI
879.0
OI
877.89
OII (833)
OI
791.98
OI
811.08
He + O_2
He


MICROWAVE CAVITY
O, O2, O2*(1Δ)
O2
-V
L
C
hν (584 Å)


O+ 2D
O+ 2P
(a)
O+ 2D
O+ 2P
3s''
2p''
3d'
(b)
5
4
3
2
1
0
ELECTRON ENERGY (eV)


18.6 eV
O+ 2P
ns'' 3P°
16.9 eV
O+ 2D nd' 3P°
3d'
2p5 3P°
1.67 eV
2.037 eV
0.51 eV
3s''
13.6 eV
O+ 4S
811.08 Å
877.89 Å
791.98 Å
0 eV
O 3P