Additional resonances in electron scattering by atomic oxygen*

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(Received 17 April 1975)

Four new resonances, located at 10.73, 12.55, 14.40, and 15.65 eV, are observed in electron scattering by atomic oxygen. Two of these resonances, located at 10.73 and 15.65 eV, have been predicted theoretically to occur at 10.63 [$(^4S)3p^2\ ^6P$] and 15.75 eV [$(^2P)3p^2\ ^4D$], respectively. We attribute the two other resonances at 12.55 eV and 14.40 eV, to the configurations $(^2D)3s3p$ and $(^2P)3s3p$. With the addition of these new identifications, a total of ten resonances are now known to occur in atomic oxygen, completing the triad of resonance configurations, $3s^2$, $3s3p$, and $3p^2$, associated with each of the three lowest (^4S, ^2D, ^2P) positive ion states.

There have recently been several studies, both experimental[1-3] and theoretical,[4,5] of Feshbach resonances in atomic oxygen. These studies include the ion-atom collision studies of Edwards *et al.*[1,2] in which a fast beam of ground-state O^- collides with a gaseous target. In such a collision, the O^- ions can make a transition to a doubly excited O^{-xx} state, which may then autoionize in a radiationless transition to the ground atomic state with the ejection of an electron. By measuring the energy of the ejected electron, Edwards *et al.*[1,2] were able to locate four doubly excited states of O^-, all doublets, whose energies are listed in Table I.

Later, this author and Chupka[3] verified the location of three of these states, and found two states, of higher multiplicity, from measurements of resonances in the total cross section for scattering of electrons by atomic oxygen. The latter measurements[3] represented the first detection of resonance states whose multiplicity was different than that of the ground state of O^-.

Theoretical studies of resonances in atomic oxygen have been made by Matese *et al.*[4,5] using the method of configuration interaction. Their theoretical model is represented by a frozen O^+ core with term values $^4S^0$, $^2D^0$, and $^2P^0$, plus two electrons in excited atomic orbitals. Dominant two-particle excitations considered in their calculations include $2p^2 \rightarrow 3s^2$, $3s3p$, $3p^2$, and $4s^2$. This model has predicted the positions of several resonance states of atomic oxygen which are in excellent agreement with experimental data.

Recently, Matese[5] predicted additional resonances in atomic oxygen which had not yet been observed experimentally. This prompted us to improve our data acquisition system, mainly by signal averaging, and to search for these additional resonances. For these measurements we use the electron transmission spectrometer described in some detail previously,[3] and so a description of the apparatus will not be given here.

TABLE I. Comparison of present data with previous experimental and theoretical resonance energies and electron affinities in atomic oxygen. All energies are in eV and are referenced to the ground state of atomic oxygen.

Resonance configuration	Experimental: Present experiment	Experimental: Spence and Chupka [a]	Experimental: Edwards and Cunningham [b]	Theory: Matese [c]	Parent state configuration	Electron affinity (present)	Electron affinity theory [c]
$(^4S)3s^2;\ ^4s$	8.78	8.80		8.68	$(^4S)3s;\ ^5S$	0.366	0.456
$(^4S)3s3p;\ ^2P$			9.50	9.50	$(^4S)3s;\ ^3S$		0.008
$(^4S)3p^2;\ ^6P$	10.73			10.63	$(^4S)3p;\ ^5P$	0.010	0.018
$(^4S)3p^2;\ ^2P$	10.90	10.90	10.87	10.88	$(^4S)3p;\ ^3P$	0.089	0.107
$(^2D)3s^2;\ ^2D$	12.10	12.11	12.12	12.05	$(^2D)3s;\ ^3D$	0.441	0.484
$(^2D)3s3p$	12.55				$(^2D)3s;\ ^1D$	0.178	
$(^2D)3p^2;\ ^4F$	14.05	14.06		14.09	$(^2D)3p;\ ^3F$	0.048	0.006
$(^2P)3s^2;\ ^2P$	13.71	13.71	13.71	13.65	$(^2P)3s;\ ^3P$	0.410	0.473
$(^2P)3s3p$	14.40				$(^2P)3s;\ ^1P$	≈ 0	
$(^2P)3p^2;\ ^4D$	15.65			15.75	$(^2P)3p;\ ^4D$	0.130	0.022

[a] Reference 3.
[b] Reference 2.
[c] Reference 5.

As in our previous measurements, the partially dissociated beam of oxygen is produced by a microwave discharge. The results are shown in Figs. 1 and 2, where we have plotted the derivative of the electron current transmitted through a beam of partially dissociated oxygen (upper traces, discharge on) and through a beam of molecular oxygen (lower traces, discharge off). All other experimental parameters, including gas pressure, electron beam current, and data acquisition time are kept constant. All structures not identified by arrows are molecular resonances, which have previously been studied at higher resolution by Sanche and Schulz.[6] These molecular structures are used to calibrate our energy scale, which we believe to be accurate to 0.05 eV.

The two structures indicated by arrows at 10.73 and 10.90 eV are energetically coincident with two of the four *molecular*[6] resonances (clearly visible on the lower trace) which occur between about 10.50 and 11.0 eV. However, all other molecular structures (including those at 10.48 eV and 10.61 eV) in the upper trace of Fig. 1 are of equal magnitude to those of the lower trace. Hence, we confidently attribute the large increase in the structures at 10.73 and 10.90 eV to atomic oxygen resonances. Because of poor signal/noise ratios in our earlier experiments,[3] we had previously identified only one atomic resonance between 10.5 and 11.0 eV.

The remaining three new resonances are shown in Fig. 2, and are located at 12.55, 14.40, and 15.65 eV. The band of molecular resonances[6] (band a) are of similar intensity in both the upper and lower traces, making the identification of atomic structures a simple procedure. Other than the structure at 15.65 eV, all atomic resonances in Figs. 1 and 2 reflect the intrinsic energy spread of the incident electron beam (about 0.075 eV). As the structure at 15.65 eV is very different in shape from all the other structures, we have performed certain checks to verify that it is not instrumental. One check is the absence of this structure in the transmission spectra for pure O_2 in the lower trace of Fig. 2.

In experiments employing magnetically confined electron beams, such as used here, artifact structures with a spectral shape similar to the structure at 15.65 eV can arise from the spiraling electron beam colliding with slit edges at certain energies. This is especially true in our type of spectrometer where we apply a weak retarding field to the electron beam after passing through the collision region in order to enhance resonant structures. The energy location of such artifact structures is dependent upon the strength of the confining magnetic field. Though all the spectra

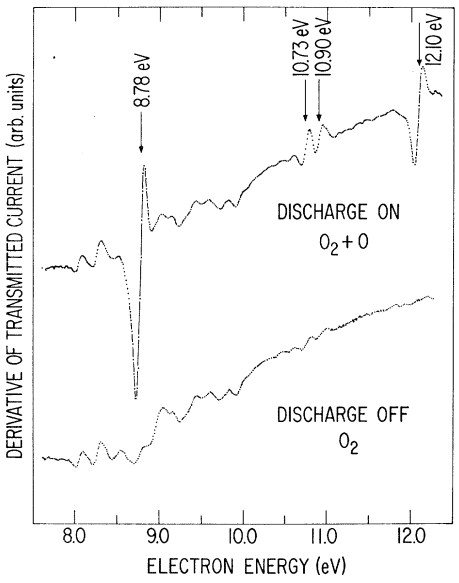

FIG. 1. Derivative of the electron current transmitted through beams of partially dissociated oxygen (upper trace) and pure O_2 (lower trace) between 7.5 eV and 12.5 eV. The locations of atomic oxygen resonances are indicated by the vertical arrows. One new resonance, that at 10.73 eV, is shown in this figure.

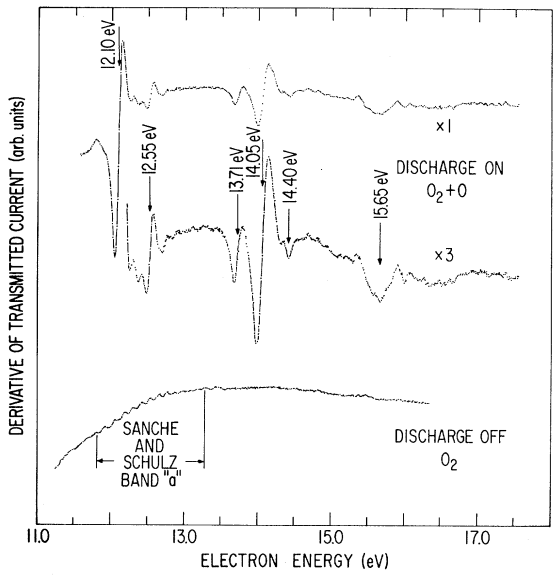

FIG. 2. Derivative of the electron current transmitted through beams of partially dissociated oxygen (upper trace) and pure O_2 (lower trace) between 11.5 and 18.0 eV. The location of atomic oxygen resonances is indicated by the vertical arrows. Three new resonances, those at 12.55, 14.40, and 15.65 eV, are clearly visible.

of Figs. 1 and 2 were taken with confining fields of about 150 G, we obtain identical spectra with magnetic fields of 100 and 200 G. We are confident, therefore, that the 15.65 eV structure is, in fact, an atomic oxygen resonance and not an experimental artifact.

Curiously, a fairly strong resonance feature observed at 9.5 eV in the ion-atom collision experiments of Edwards *et al.*[2] was not observed in our previous electron-scattering experiments. Despite the greatly improved signal/noise ratio in our present experiments, a superposition of the upper and lower traces of Fig. 1 gives no hint of an atomic resonance at 9.5 eV. Though different selection rules must apply to ion-atom and electron scattering experiments, it is not clear to us at present why the 9.5-eV resonance, with configuration $(^4S)3s3p$; ^2P, should be so highly forbidden in electron scattering experiments.

A weak atomic structure located at 10.10 eV in our previous experiments, due to a transition from the excited $O(^1D)$ state to the $2s2p^6(^2S)$ *singly* excited O^- state, (and also observed by Edwards *et al.*)[2] is not observed in our present experiments. The reason for this is that in our previous experiments the microwave discharge extended to the entrance slit to our collision region, whereas in the present experiments, we have moved the discharge region a distance of about one foot away from the collision region. We find this has little effect on the degree of dissociation we can achieve in the beam, but undoubtedly the $O(^1D)$ produced in the discharge is quenched, to some extent, by wall collisions on the way to the collision region.

The energies of atomic oxygen resonances obtained in the present experiment are compared in Table I with all previous experimental and theoretical values. The agreement between experimental values is extremely good, 0.03 eV discrepancy at worst, and the agreement with theory is within the theoretically estimated error[5] of 0.10 eV in all cases. Also listed in Table I are the parent state configurations and the experimental and theoretical values of the electron affinities of these states. The agreement between experiment and theory is quite good, being always well within the combined experimental (0.05 eV) and theoretical error. The disagreement is greatest, as expected,[5] where the value of electron affinity is large.

Not included in Table I are the three theoretically predicted resonance states in which the excited electrons have principal quantum number 4. Though on some scans we have observed a weak structure at 11.63 eV, the predicted location of the $(^4S)4s^2$; ^4S state, this feature was not always reproducible.

The resonances observed in the present experiment, plus the resonance at 9.5 eV observed by Edwards *et al.*,[2] together with their neutral parent states and positive ion grandparent states are plotted in Fig. 3. All these states, with the exception of the $(^2D)3s3p$ and $(^2P)3s3p$ states, have been predicted theoretically.[5] Figure 3 illustrates clearly that the electron affinity of parent states is largest when the orbital angular momentum of both excited electrons is zero, and is smallest when the angular momenta of the two excited

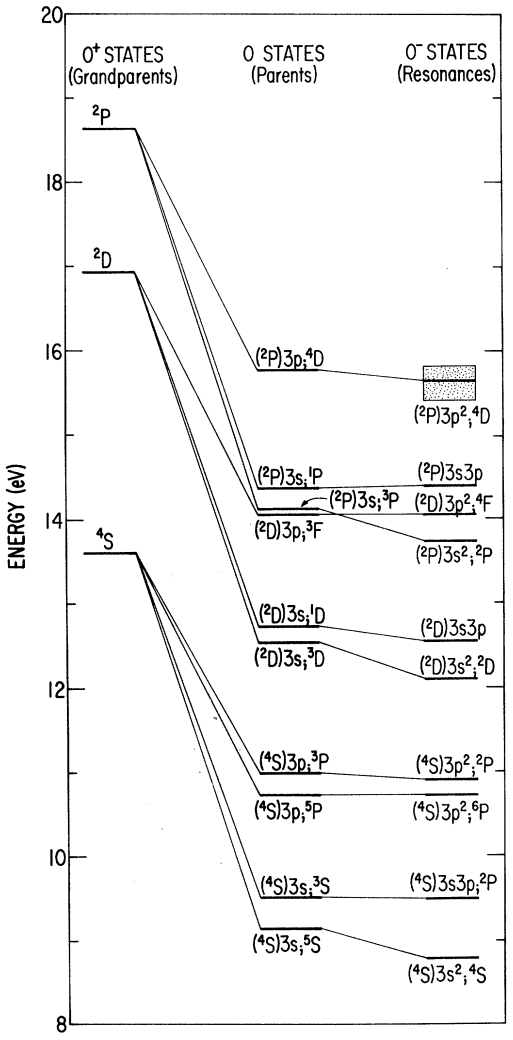

FIG. 3. Energy level diagram of O^- states, together with their respective parent (O) states and grandparent (O^+) states. A triad of resonance configurations, $3s^2$, $3s3p$, and $3p^2$, is associated with each of the ^4S, ^2D, and ^2P positive ion grandparent states.

electrons differs. The exception to this rule is the $(^2D)3s3p$ state, where the electron affinity of the parent $(^2D)3s;^1D$ state has the unusually large value of 0.178 eV.

The present data complete the triad of resonance configurations, $3s^2$, $3s3p$, and $3p^2$, associated with each of the three lowest $(^4S, ^2D, ^2P)$ positive ion states, which we had previously predicted to occur in atomic oxygen[3] from considerations of resonance systematics.

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*Work performed under the auspices of the U. S. ERDA.

[1]A. K. Edwards, J. S. Risley, and R. Geballe, Phys. Rev. A 3, 583 (1971).

[2]A. K. Edwards and D. C. Cunningham, Phys. Rev. A 8, 168 (1973).

[3]D. Spence and W. A. Chupka, Phys. Rev. A 10, 71 (1974).

[4]J. J. Matese, S. P. Rountree, and R. J. W. Henry, Phys. Rev. A 7, 846 (1973).

[5]J. J. Matese, Phys. Rev. A 10, 454 (1974).

[6]L. Sanche and G. J. Schulz, Phys. Rev. A 6, 69 (1972).