

## Measurement of resonances in atomic oxygen by electron transmission spectroscopy\*

D. Spence and W. A. Chupka

Argonne National Laboratory, Argonne, Illinois 60439

(Received 17 January 1974)

We present the first observations of resonant states in atomic oxygen using an electron-impact technique. We verify the existence of several doublet resonant states located previously by other techniques, and observe for the first time resonant states whose multiplicity is different from that of the ground state of  $O^-$ . To one such state located at 8.80 eV we assign the configuration  $[2p^3(^4S)3s^2(^4S)]$  and to another at 14.06 eV we assign the configuration  $[2p^3(^2D)3p^2]$ .

In the decade since the discovery of resonant states (sometimes called compound states or temporary negative-ion states) in helium by Schulz,<sup>1</sup> these states have been shown to exist in all atoms and molecules. Many experimental and theoretical studies<sup>2</sup> have demonstrated the dominance of resonant structures in the cross sections for elastic and inelastic scattering of electrons at energies from near zero to a few tens of eV.

With the exception of atomic hydrogen,<sup>3-5</sup> studies of resonant states by electron scattering have been confined to stable atomic and molecular species. This is despite the probable importance of these states in processes occurring in the upper atmosphere, interstellar space, and laboratory plasmas, where highly reactive species are abundant. The reason for this dearth of information is the difficulty in producing sufficiently dense targets of free radicals to make electron scattering experiments feasible. In the present experiments we have extended electron impact studies of resonances in free radicals to include atomic oxygen—an important constituent of the upper atmosphere.

Resonant states in atomic oxygen have been the subject of previous studies, both experimental<sup>6,7</sup> and theoretical.<sup>8</sup> Earlier experimental studies involved colliding a fast beam of ground-state  $O^-$  with a gaseous target. In such a collision the  $O^-$  ions can make a transition to a doubly excited  $O^{--}$  state, which then autoionizes in a radiationless transition to the ground atomic state with the ejection of an electron. By measurement of the energy of the ejected electron, Edwards *et al.*<sup>6,7</sup> were able to obtain the energies of some resonant states in atomic oxygen.

In those experiments, the collision dynamics were such that charge-exchange or spin-dependent interactions were unlikely.<sup>6,7</sup> Consequently, as the ground-state term of  $O^-$  is  $^2P^\circ$ , only doublet excited states of  $O^-$  were located by this technique. In an electron scattering experiment, where selection rules are different, we can observe states

of different multiplicity. A configuration-interaction study of autodetaching states of  $O^-$  has been made by Matese *et al.*<sup>8</sup> Their theoretical model is represented by a fixed  $O^+$  core with term values  $^4S^\circ$ ,  $^2D^\circ$ , and  $^2P^\circ$ , with configuration mixing of states with two electrons in excited atomic orbitals. This model has predicted the positions of some resonant states of atomic oxygen which are in impressive agreement with experimental data.

The present electron scattering experiments provide the first direct confirmation of the results of the ion-atom collision experiments, and, in addition, locate resonant states of oxygen which were not accessible in previous experiments.

The apparatus used in the present experiments is a transmission electron spectrometer similar to that described by Sanche and Burrow,<sup>5</sup> and only a brief description will be given here. A high-resolution electron beam in an axial magnetic field is selected by a trochoidal monochromator,<sup>9</sup> and accelerated into a region containing the target-gas beam. Electrons which have had their velocity vector reoriented in a collision with the gas target are prevented from leaving the collision region by a retarding potential. Electrons which have made no collisions are transmitted to an electron collector and detected. In the present experiments we modulate the electron energy with a sine wave of small amplitude ( $\approx 20$  meV) and measure the derivative of the transmitted current with a lock-in amplifier. This modulation technique, introduced by Sanche and Schulz,<sup>10</sup> enhances resonant structure in the total cross section. The partially dissociated target beam of oxygen is produced by a microwave discharge in a quartz tube. This discharge extends to a slit at the end of the tube where the gas effuses out into a collision region which is pumped at high speed. To achieve high target-gas densities, the electron beam intersects the gas jet 0.3 cm from the slit. Dissociation of the gas beam was found to be considerably increased by the addition of a small amount (of

the order of 0.1–0.5%) of water to the discharge. Nitrogen in similar quantities was also found to be an efficient catalyst for dissociating oxygen, but only about half as effective as water. A typical spectrum of the derivative of the electron current transmitted through a partially dissociated beam of oxygen is shown in Fig. 1. Several resonances, indicated by arrows, are clearly visible in the upper trace. The lower traces are independent scans with increased gain and electronic time constant, and, therefore, show the smaller resonances more clearly. The observed widths of all the resonances in Fig. 1 are purely instrumental. The positions of the atomic resonances are tabulated in Table I, together with previous experimental<sup>6,7</sup> and theoretical<sup>8</sup> values. On extinguishing the discharge, all the features of Fig. 1 indicated by arrows disappear while all other structures due to molecular oxygen resonances remain.

The molecular oxygen resonances have been extensively studied by Sanche and Schulz,<sup>10</sup> using better energy resolution than in the present experiments, and we use these to calibrate our energy scale which we consider to be accurate to

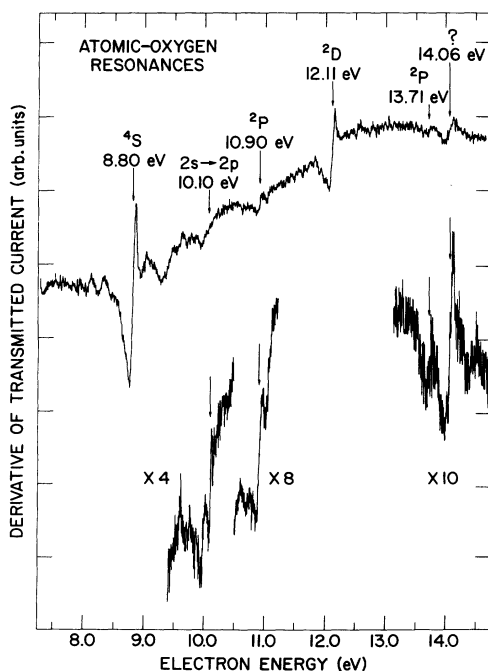


FIG. 1. Derivative of the electron current transmitted through a beam of partially dissociated oxygen versus electron energy. The locations of the  $O^-$  resonances are indicated by the vertical arrows. The lower plots are independent scans that because of increased gain show more clearly the smaller resonances. All other structures on the plots are due to resonances in  $e-O_2$  scattering.

0.050 eV.

The resonances indicated by arrows in Fig. 1 are interpreted as doubly excited states of  $O^-$ , with the exception of the resonance at 10.10 eV. This resonance, which is very weak in our experiments, is a dominant transition in the ion-molecular experiments, indicating that a doublet state of  $O^-$  is involved. However, calculations<sup>8</sup> indicate no doublet excited states in the region of 10.10 eV. Edwards and Cunningham<sup>7</sup> argue on grounds of energetics and selection rules for  $LS$  coupling, that this feature is due to a  $2s2p^6(^2S)$  singly excited  $O^-$  state at 12.08 eV, autoionizing into the  $^1D$  atomic state at 1.97 eV. In our experiments, a small amount of  $O(^1D)$  undoubtedly exists in the beam and we interpret the feature at 10.10 eV as a transition from  $O(^1D)$  to the  $2s2p^6(^2S)$   $O^-$  singly excited state. From energetics, we agree with Edwards and Cunningham<sup>7</sup> that this feature is not due to a transition from  $O(^1D)$  to the  $(^2D)2s^2(^2D)$   $O^-$  doubly excited state at 12.11 eV. If strict  $LS$  coupling applies, we should not observe the  $2s2p^6(^2S)$  state in a transition from the ground ( $^3P$ ) atomic state, and indeed do not. This interpretation is consistent with recent calculations<sup>11</sup> of the photodetachment cross section of  $O^-$ , which places the  $2s2p^6(^2S)$  state at 12.62 eV above the oxygen-atom ground state.

Of the six other resonances tabulated in Table I, four (all doublets) have been observed in ion-molecule experiments.<sup>7</sup> We will not comment further on these except to point out the very good agreement between our experiments and previous experimental and theoretical values for the resonance energies. We do not observe the  $(^4S)3s3p(^2P)$  state located at 9.5 eV. This may be due to the obscuring effects of molecular structure in this

TABLE I. Resonant states of atomic oxygen.

Present work (eV)	Edwards and Cunningham (expt) <sup>a</sup> (eV)	Matese <i>et al.</i> (theoret) <sup>b</sup> (eV)	Configuration
8.80		8.73	$(^4S)3s^2(^4S)$
	9.50	9.50	$(^4S)3s3p(^2P)$
10.10	10.11		$(2s2p^6)(^2S)$ <sup>c</sup>
10.90	10.87	10.87	$(^4S)3p^2(^2P)$
12.11	12.12	12.05	$(^2D)3s^2(^2D)$
13.71	13.71	13.65	$(^2P)3s^2(^2P)$
14.06			$(^2D)3p^2$

<sup>a</sup> Reference 7.

<sup>b</sup> References 8 and 12.

<sup>c</sup> As explained in the text, to obtain the energy of this state above the  $^3P$  ground atomic state, one should add 1.97 eV to the tabulated value.

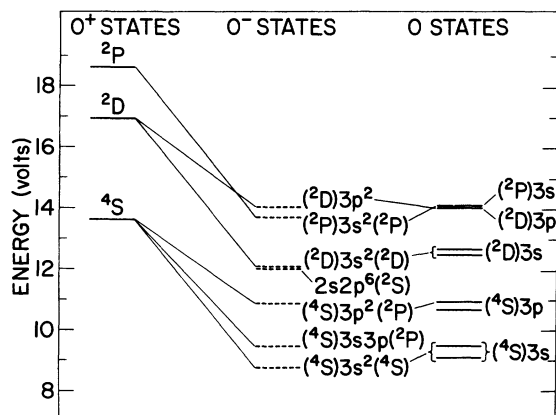


FIG. 2. Energy level diagram of  $O^-$  states and their respective parent (O) and grandparent ( $O^+$ ) states.

energy region in our experiments.

The strongest feature in our experiments is the resonance located at 8.80 eV. The only possible configuration for this  $O^-$  state is  $(^4S)3s^2(^4S)$ , and, being a quartet, this state has not been observed in ion-molecule experiments. Recent theoretical calculations by Matese and Henry,<sup>12</sup> yield a value of 8.73 eV for the lowest quartet state of  $O^-$ , in very good agreement with our experimental value.

In Fig. 2 we show an energy level diagram of all the observed resonant states in atomic oxygen, together with their parent excited atom states and grandparent positive ion states. By analogies with the binding energies of  $3s^2$ ,  $3s3p$ , and  $3p^2$  electron configurations to the  $^4S$  positive ion core, we attribute a configuration  $(^2D)3p^2$  to the resonant

state we locate at 14.06 eV. We are unable to specify unambiguously the term value for this state, as the addition of a pair of  $3p$  electrons to the  $^2D$  ion core can give rise to several doublet or quartet states. One may make arguments in favor of a quartet state because of nonobservation of this state in ion-molecule experiments.<sup>7</sup> However, this may be due to lack of intensity. In this aspect, we await further theoretical guidance.

In the present experiments we observe no resonances with configuration  $(O^+ \text{ core})3s3p$ , although one such state,  $(^4S)3s3p(^2P)$ , is observed using the ion-neutral collision technique. This may be because of different selection rules governing transitions in the two different types of experiments. From Fig. 2 one may expect an additional resonant state associated with the  $^2D$  ion core to occur at about 12.70 eV [ $(^2D)3s3p$ ]. However, Henry<sup>12</sup> has suggested that this and higher states with configuration  $(O^+ \text{ core})3s3p$  may not be bound. Similarly, additional resonances may occur at 15.1 eV [ $(^2P)3s3p$ ] and 15.8 eV [ $(^2P)3p^2$ ] associated with the  $^2P$  ion core. The latter resonances, even if they are bound, may be unobservable in our experiments because of the general trend to smaller structures with increasing electron energy. One should note from Fig. 2 the binding energies of a pair of  $3s$  electrons to the positive-ion cores is of the order of 4.8 eV. This binding energy is significantly larger than the value  $4.1 \pm 0.1$  eV, which has been observed for a pair of  $s$  electrons in more than a dozen previously studied systems.<sup>2</sup>

The authors are grateful to P. D. Burrow and R. J. W. Henry for helpful discussions in the course of this work.

\*Work performed under the auspices of the U. S. Atomic Energy Commission.

<sup>1</sup>G. J. Schulz, Phys. Rev. Lett. **10**, 104 (1963).

<sup>2</sup>G. J. Schulz, Rev. Mod. Phys. **45**, 378 (1973).

<sup>3</sup>G. J. Schulz, Phys. Rev. Lett. **13**, 583 (1964).

<sup>4</sup>J. W. McGowan, E. M. Clarke, and E. K. Corley, Phys. Rev. Lett. **15**, 917 (1965).

<sup>5</sup>L. Sanche and P. D. Burrow, Phys. Rev. Lett. **29**, 1639 (1972).

<sup>6</sup>A. K. Edwards, J. S. Risley, and R. Geballe, Phys. Rev. A **3**, 583 (1971).

<sup>7</sup>A. K. Edwards and D. C. Cunningham, Phys. Rev. A **8**, 168 (1973).

<sup>8</sup>J. J. Matese, S. P. Rountree, and R. J. W. Henry, Phys. Rev. A **7**, 846 (1973).

<sup>9</sup>A. Stamatovic and G. J. Schulz, Rev. Sci. Instrum. **41**, 423 (1970).

<sup>10</sup>L. Sanche and G. J. Schulz, Phys. Rev. A **6**, 69 (1972), and papers cited therein.

<sup>11</sup>A. L. Chase and H. P. Kelly, Phys. Rev. A **6**, 2150 (1972).

<sup>12</sup>R. J. W. Henry (private communication).