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Two Autodetaching States of O^-†

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Two autodetaching states of O^- have been found by observing the electron energy spectrum of O^- ions excited in collisions with a He target at keV beam energies. The energies of the states have been measured as 10.112 and 12.115 ± 0.010 eV. The H^- ^1S, ^3P, and ^1D autodetaching states below the $n=2$ hydrogen level are excited in O^- on H_2 collisions, and the Ar^- autodetaching states below the first excited argon level are formed in O^- on Ar collisions. No structure in the electron energy spectrum was seen for collisions of O^- on O_2 or Ne.

INTRODUCTION

Doubly excited states of negative ions (two electrons in excited levels) are known to exist for various elements, [1] and usually decay by radiationless transitions. One of the excited electrons falls to a lower level, giving its energy to the other excited electron which is ejected, forming a neutral atom and free electron. The autodetached electron has a kinetic energy equal to the difference of the energy levels of the doubly excited negative-ion state and the final state of the neutral atom. These autodetached electrons are known to produce peaks, [2] superimposed on a continuum, in the electron energy spectrum produced in negative-ion–neutral-gas collisions. The smoothly decreasing background of the spectrum is produced by stripping and ionization of both the incident ions and target particles.

The electron energy spectra of the halogen negative ions have been studied by Bydin, [3] using a retarding potential method and, for I^-, an electrostatic analyzer. The I^- spectrum showed a large peak between 6 and 7 eV, which is attributed to an autodetaching I^- state.

We have found and measured the energy of two large peaks in the electron energy spectrum formed from collisions of O^- ions with He atoms. These are believed to arise from the excitation of two autodetaching states of O^-. We also find that known autodetaching states of H^- and Ar^- are formed in collisions of O^- ions with H_2 and Ar, respectively.

EXPERIMENTAL PROCEDURE

The O^- ions were formed in a duoplasmatron ion source [4] using helium in the source to form the plasma. The atomic oxygen forming the ion beam is believed to come from the oxide coating of the source filament. Various gases were tried in the source, with the helium plasma producing the most intense O^- beam. No OH^- component of the beam was detected.

The ions were accelerated (1–5 keV), momentum analyzed, and focused into a collision chamber containing a target gas. The target-gas pressures, as read by a Bayard-Alpert ionization gauge, ranged from 3×10^{-4} Torr for helium to 2×10^{-3} Torr for argon. The electrons leaving the collision region were energy analyzed by an electrostatic-cylindrical-mirror analyzer [5] and detected with a channel electron multiplier. The resolution of the electron energy analyzer was about $\frac{1}{2}\%$. The collision chamber and analyzer were coated with gold black to reduce reflection of electrons. The analyzer could be moved continuously to various positions to observe the electrons ejected from 9° to 80° from the beam direction. The angle could be set to ± 1°. The earth's magnetic field and stray fields from the analyzing magnet and ion source were reduced by a set of three perpendicular pairs of Helmholtz coils.

The detector pulses could be recorded using three different methods. Figure 1 shows the method by which a point-by-point plot of electron count-rate versus electron energy could be made. The detector pulses were discriminated and counted by a scaler while the electron analyzer voltages remained constant. The ion beam was collected in a Faraday cup and integrated until a set voltage was recorded on a capacitor and the scaler stopped.

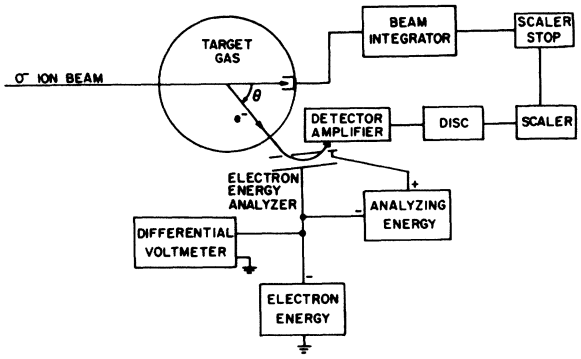

FIG. 1. Schematic diagram of the experimental apparatus used in obtaining a point-by-point plot of the electron energy spectra.

The voltage on the back plate of the analyzer was changed and the process repeated. This voltage was measured to 1 mV. The analyzing voltage between front and back analyzer plates remained at 20 V for all data recorded.

Another procedure was to connect the discriminator output to a count-rate meter whose output was read by a signal averager. The voltage on the back analzyer plate was continuously swept over a 4-V region by the ramp voltage of the signal averager, which switched the averager from channel to channel. In this way, the electron energy spectrum was recorded by the signal averager. The beam current was read by an electrometer and did not change significantly in the time required to make one sweep through the 4-V region. Normally, the beam current showed only small drifts during a day's running.

The third method uses an X-Y recorder, and has been described in detail elsewhere.[6] The electron count rate was divided by the beam current using an analog divider, and the quotient recorded on the Y axis of the recorder. The X axis read the output of a voltage sweep circuit which was connected to the back analzyer plate.

ENERGY CALIBRATION

The electrons ejected from the moving O^- ions are shifted in energy. The unshifted electron energy is given by[7]

$$E_e = E_{obs} + (m/M)E_B - 2[(m/M)E_{obs}E_B]^{1/2}\cos\theta, \quad (1)$$

where E_{obs} is the measured shifted energy, E_B is the ion beam energy, m/M is the ratio of the electron mass to the beam-particle mass, and θ is the angle of observation measured from the beam direction. The peaks in the electron spectrum that were produced by the beam particles shifted their energy as θ or E_B was changed. The true beam energy was checked using a retarding-potential method, and found to be 14 V higher in energy than the set accelerating potential because of the voltage drop across the plasma. The 14-V differential remained constant over all accelerating potentials. The unshifted electron energies were calculated with 14 V added to the nominal beam energy. The energy spread in the beam was approximately 30 V.

The instrumental electron energy scale was affected to the extent of a few hundred millivolts by contact potentials, Helmholtz-coil current settings, ion-beam intensities, and target-gas pressures. Therefore, in order to determine absolute energies, it was necessary to calibrate the scale against a known transition which would produce a peak in the spectrum. We were able to use two different known transitions to measure the energies of the O^- transitions.

In collisions of O^- ions with H_2 molecules, H^- resonances below the $n=2$ hydrogen level were produced, presumably in a charge-exchange process. Figure 2 shows the peaks arising in the electron energy spectrum of collisions of O^- on H_2. The smaller peak was used for calibrating the scale, since the first peak is believed to consist of two unresolved transitions. The transition used for calibration arises from the $(^1D)H^{-**}$ state with an energy of 10.13 ± 0.015 eV, as measured by an electron scattering experiment.[8] The stronger transition is believed to consist of the ^1S and ^3P states[9] at 9.56 and 9.71 eV, respectively, since the energy separation of the two peaks in Fig. 2 is 0.50 eV instead of 0.57 or 0.42 eV, which would be the separation if the first peak were either all ^1S or all ^3P.

The other known transition used as a calibration was the Ar^- resonance measured in an electron scattering experiment.[1] Figure 3 shows the electron energy spectrum produced by collisions of O^- on Ar. The large peak is produced by the autodetaching Ar^- configuration $3p^5(^2P)4s^2(^2P)$ lying below the first excited argon level. The ^2P splitting appearing in Fig. 3 is 0.173 eV, in agreement with Kuyatt *et al.*[1] The resonance energy of the lower-lying

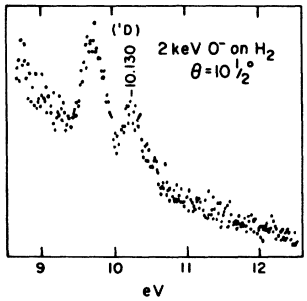

FIG. 2. Electron energy spectrum produced by collisions of 2-keV O^- ions on H_2. The peaks are due to H^- autodetaching states below the $n=2$ hydrogen level.

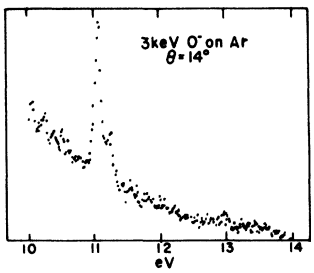

FIG. 3. Electron energy spectrum produced by collisions of 3-keV O^- on Ar. The peaks are due to the Ar^- autodetaching states below the first excited argon level.

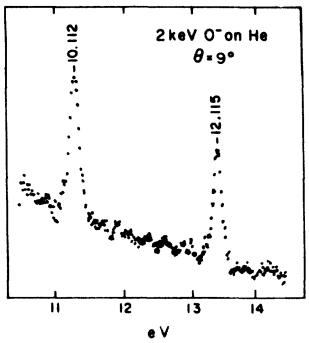

FIG. 4. Electron energy spectrum produced by collisions of 2-keV O^- on He. The unshifted electron energies are given above the peaks.

Ar^- transition was set at 11.079 eV, which is the center of the observed asymmetric resonance in the electron scattering experiment. The maximum and minimum of the resonance lie 15 mV either side of its center; therefore the true resonance energy must lie within ± 0.015 eV of this value.

O^- STATES

Figure 4 shows the electron energy spectrum obtained from collisions of O^- on He. The two large peaks in the spectrum were produced by electrons ejected by the moving beam particles, since changing the beam energy or the angle of observation shifted the electron energy according to Eq. (1). The widths of the peaks, about 120 mV, are instrumental. This width implies the lifetimes of the states are longer than the collision times involved; thus the O^- ion is not decaying from an (O^-He) molecular configuration. If the decay occurred in the collision time, the peaks would be from 0.5 to 1 eV wide.

The electron energy scale for the O^- transitions was set by mixing helium with the target gases H_2 and Ar. Figures 5 and 6 show the spectra obtained using the mixed gases. With the helium-hydrogen mixture, the energy scale was shifted to place the $(^1D)H^-$ state transition at 10.130 eV and the shifted O^- transition was measured. The unshifted electron energy was calculated from Eq. (1). With the helium-argon mixture the strong Ar^- transition was set at 11.079 eV and the same procedure as above was followed. Five determinations of the lowest-lying O^- transition were measured, each having a different target, beam energy, or angle of observation. The unshifted electron energy of the first peak produced by the O^- on He collisions was found to be 10.112 eV, with a mean deviation of ± 0.010 eV.

Knowing the first transition energy, the second peak in the O^--He spectrum (Fig. 4) was measured with respect to the first. The unshifted energy of the separation of the two peaks was found from eight determinations, each having a different beam energy or angle of observation. The peak separation is 2.003 eV, with a mean deviation of ± 0.007 eV. This places the second unshifted transition at 12.115 eV.

The ground-state O^- ion has a $2p^5(^2P)$ configuration. If the autodetaching states have two electrons in excited states, then the available configurations are $2P^3(^4S, {}^2D, {}^2P)nln'l'(^2L)$. This assumes that the autodetaching-state configuration will be a doublet, since a charge-exchange or spin-dependent interaction would be necessary to change the multiplicity. If both electrons excited in the collision enter the 3s orbital, then the lowest doublet configuration available would be the $2p^3(^2D)3s^2(^2D)$. The transition at 12.115 eV could occur from this level lying below the $2p^3(^2D)3s$ oxygen state[10] at 12.539 eV, autodetaching to the oxygen $2p^4(^3P)$ ground state plus a free electron. The transition at 10.112 eV should be associated with the $2p^3(^4S)$ core and could have a $2p^3(^4S)3p^2(^2P)$ configuration. This state would lie 0.628 eV below the oxygen $2p^3(^4S)3p$ state at 10.740 eV. The lower transition energy is more than the lowest $2p^3(^4S)3s$ oxygen state at 9.146 eV. Of course, there are many possible configurations available in the energy regions of the observed transitions, and the O^- autodetaching states could arise from the configuration interaction of these

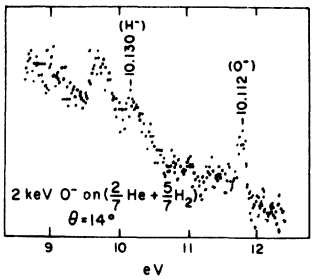

FIG. 5. Electron energy spectrum produced by collisions of 2-keV O^- on a target-gas mixture of He and H_2. The peak due to H^- production does not shift with a change in collision energy, whereas the peak from O^- does.

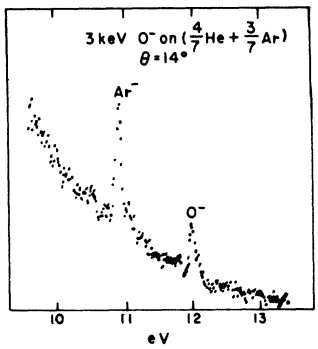

FIG. 6. Electron energy spectrum produced by collisions of 3-keV O^- on a target-gas mixture of He and Ar. The peak due to Ar^- production does not shift with a change in collision energy, whereas the peak from O^- does.

levels.

A different interpretation of these two peaks in the electron spectrum would be to assume that the extra electron of the O^- ion is stripped in the collision and the neutral oxygen atom is excited into an autoionizing level. The lowest-lying configuration which would autoionize producing ejected electrons of the proper energy would be the inner-shell excited configurations $2s2p^4(^4P)nl$. An estimate[11] of the energies of the two lowest-lying members of this Rydberg series (3s and 3p) can be made by using the expression

$$E = E_\infty - 13.6/(n-\mu)^2 , \qquad (2)$$

where E_∞ is the series limit, n is the principal quantum number, and μ is the quantum defect. An approximate value for the quantum defect can be obtained by calculating the quantum defect from the known $2s^2 2p^4 3s$ and $3p$ levels of fluorine and using this in Eq. (2). The series limit for the oxygen series is given in Ref. 10. The calculated transition energies are 10.15 eV for the 3s level and 11.81 eV for the 3p. Good agreement is obtained for one but not the other. Other objections to identifying these transitions as autoionizing oxygen states are the following: (i) Other members of the series should also be excited, along with other series, but they are not seen; (ii) in the collisions of O^- with H_2 and Ar, it appears that the extra electron is lost by the O^- through charge transfer along with stripping, and no peak that could be attributed to neutral oxygen is seen, (iii) autoionizing levels of argon of comparable energy[7] were not excited in the O^- on Ar collisions.

OTHER INVESTIGATIONS

Collisions of O^- on O_2 and Ne were also investigated. O_2 was used as a target molecule to see if it would capture the extra electron (as did H_2) and produce autodetaching O^- states at rest in the lab frame. No structure was seen from either the O_2 target or O^- beam. The electron resonances seen in electron-neon scattering[1] were not produced in collisions of O^- on Ne, as were the argon resonances with an argon target.

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