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Charge transfer between O^- ions and O_2 molecules in the ground state and singlet delta excited state*

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A crossed-beam apparatus has been used to study charge transfer between O^- ions and O_2 molecules in the ground state and in the metastable, singlet delta, excited state. The energy of the incident ions ranged from 10 to 10 000 eV. The cross section for charge transfer between O^- and ground state O_2 was found to have a maximum of 7.8×10^{-16} cm^2 at about 5 keV. At the lower energies there is good agreement with the previous measurements of Snow *et al*. and Rutherford and Turner who also used crossed beam techniques. The cross section for charge transfer between O^- and metastable excited O_2 ($^1\Delta_g$) was found to be less than 1×10^{-16} cm^2 over the energy range of 100 to 5000 eV. There are no other experimental measurements for comparison.

I. INTRODUCTION

Charge transfer between O^- and O_2 molecules in the ground state, $^3\Sigma_g^-$, has been studied over the energy range of 10 to 10 000 eV using a new crossed beam apparatus. Previous studies of charge transfer between O^- and ground state O_2

$$O^- + O_2(^3\Sigma_g^-) \rightarrow O + O_2^-$$

have been carried out both at thermal energies[1,2] and in the energy range of a few eV to 3000 eV.[3-7] The present work extends the energy range of the previous measurements to 10 keV. In addition, charge transfer between O^- and metastable excited O_2 ($^1\Delta_g$)

$$O^- + O_2\,(^1\Delta_g) \rightarrow O + O_2^-$$

has been studied in the energy range of 100 to 5000 eV. Experiments involving charge transfer to molecules in a metastable excited state have not been previously reported for negative ions.

This paper is divided into three major sections. The apparatus, which has not previously been described in the literature, is discussed in Sec. II. The data and results for charge transfer to ground state O_2 are presented in Sec. III, and the data and results for charge transfer to O_2^* are presented in Sec. IV.

II. APPARATUS

This apparatus is housed in two separately pumped vacuum chambers as shown schematically in Fig. 1. The primary ion beam is produced and mass analyzed in the source chamber. After acceleration in the collision chamber it intersects the neutral beam at right angles. The secondary ions are extracted at right angles to the intersection of the primary beams and then mass analyzed and counted.

For the experiment described in this paper, the O^- ions were produced in a hot cathode arc discharge ion source[8] using N_2O gas. The arc current was typically < 0.1 A with a gas pressure of 80 μ. The O^- ion beam current at the Faraday cup was 10 to 20 nA with an energy spread of about 2 eV full width at half-maximum, as determined by retarding potential measurements (RPA, Fig. 1). The ion beam was mass analyzed with a Wien filter[8] followed by a 50 cm drift space. The resultant mass resolution was $M/\Delta M \approx 35$ at $M=16$.

The energy of the ion beam within the source chamber was held constant, usually 1500 eV. The final ion energy at the collision region was obtained by varying the potential of the entire chamber. The ion beam was accelerated or decelerated to the final energy by a series of 11 parallel plates with 0.250 in. diam holes, which provided a uniform potential gradient for changing the beam energy.

The secondary ions resulting from charge transfer in the collision region were extracted with a weak electric field. The intersection of the ion and neutral beams was at the center of a $\frac{1}{2}$ in. diam cylinder $\frac{1}{2}$ in. long. The extraction field was produced by a plane grid above the end of the cylinder. The grid potential required to saturate the secondary ion current varied from 5 to 15 V over the energy range of the experiment. The operating grid potential was always in the plateau region. After extraction the secondary ions were accelerated to 50 eV, mass analyzed by a quadrupole mass filter[8] and detected with an electron multiplier. Pulses from the multiplier were preamplified and counted with a digital sychronous computer.[8]

Figure 2 is a schematic drawing of the neutral beam source. The beam was formed by flowing gas, at a few microns pressure, through a collimated hole structure (CHS). The CHS is a stainless steel cylinder, 0.305 cm long, containing a high, uniform density of 0.005 cm diam, parallel channels.[8] In this way a relatively well-collimated neutral beam could be produced without a stage of differential pumping.[9] The neutral beam source pressure used in the present work was 10 μ, which produced a number density of O_2 of the order of 10^{11} particles/cm^3 at the collision region and allowed a pressure of about 2×10^{-7} Torr to be maintained in the collision region.

The neutral beam was chopped at 560 Hz by a toothed wheel mounted on a shaft extending through a Ferrometic rotary feedthrough mounted in the vacuum wall.[8] This feedthrough employs a low vapor pressure magnetic fluid trapped by intense magnetic fields in small annular gaps for a vacuum seal. An identical chopper

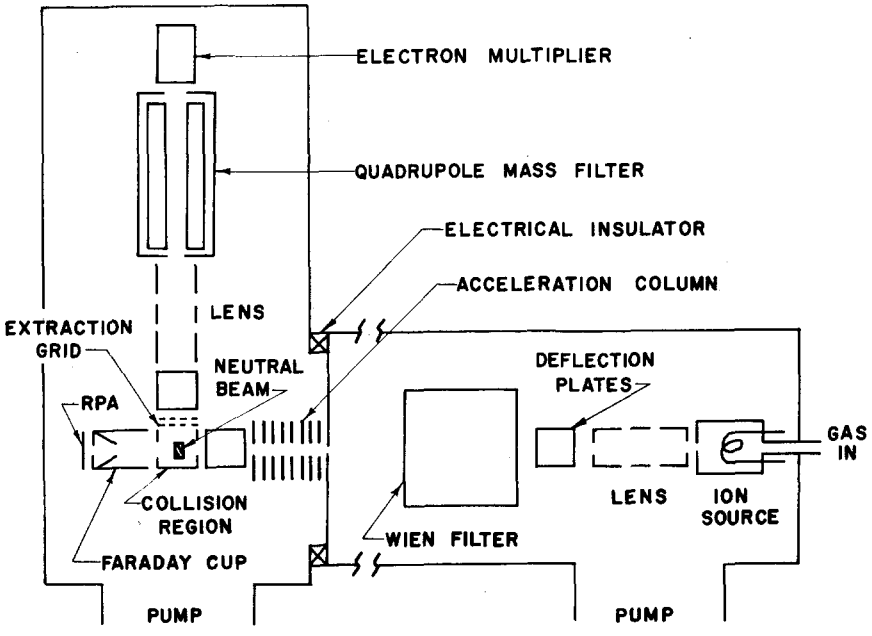

FIG. 1. Experimental apparatus. In this schematic cross sectional view the primary ion beam intersects the neutral beam (cross hatched) which is normal to the page. Secondary ions are extracted, mass analyzed, and counted in the vertical column.

wheel, mounted on the same shaft outside the vacuum, was used to generate a reference square wave for the synchronous detection system.

The metastable O_2^* was produced in a microwave discharge in a section of Pyrex tubing preceding the collimated hole structure. A small orifice in the end of the Pyrex tube permitted a pressure of a few Torr to be maintained in the discharge region while the pressure behind the CHS remained at 10 μ.

This method of producing $O_2(^1\Delta_g)$ was possible because of its unusually long lifetime and stability against collisional deactivation.[10] A radiative lifetime of 45 min was reported by Badger *et al.*[11] Reported values of γ (the fraction of collisions with the vessel walls that lead to deactivation) range from 1.5 to 2.9×10^{-5} for glass walls[12,13] and from 7×10^{-6} to 1.3×10^{-5} for stainless steel walls.[14]

The metastable $O_2(^1\Delta_g)$ traveled through approximately 40 cm of stainless steel tubing before entering the collision region. This distance was sufficient to permit the quenching of $O_2(^1\Sigma_g)$ and the recombination of O atoms, thus insuring that only ground state and singlet delta excited state O_2 molecules were present in the neutral beam at the collision region.

The relative density of the neutral beam at the collision region was monitored by measuring the pressure in the reservoir before the CHS, which was held at constant temperature. The pressure was independent of the microwave discharge to within the 0.5% accuracy of the capacitance manometer.

The fraction of excited molecules in the neutral beam was estimated indirectly since no direct measurements were available. The estimation procedure is described in Sec. IV.

III. GROUND STATE O_2

The results of the measurement of the charge transfer cross section for O^- to ground state O_2 are shown in Fig. 3. The solid curves show the data of Rutherford and Turner (RT); Bailey and Mahadevan[4] (BM); Roche and Goodyear[5] (RG); Snow, Rundel, and Geballe[6] (SRG); and Dimov and Roslyakov[7] (DR). The dots are the present results. The scatter in the data is indicated by the error bars which represent the standard deviations of the means. The present data have been normalized to the value $\sigma = 1.4\times10^{-16}\text{cm}^2$ at 300 eV reported by Rutherford and Turner. This point was chosen because it is in the energy range in which Rutherford and Turner expect their results to be the most reliable. In addition, the independent results of Bailey and Mahadevan at 300 eV lie within the ± 30% uncertainty quoted by Rutherford and Turner.

The present results are in good agreement with the results of SRG below about 1500 eV but are higher than their results at energies above 1500 eV. The general variation of the cross section above 100 eV is in good qualitative agreement with predictions of the two state approximation of Rapp and Francis,[15] although the velocity at

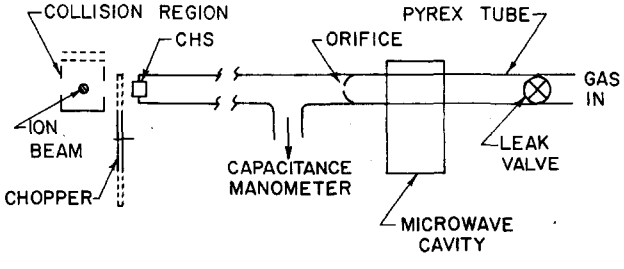

FIG. 2. Neutral beam source. The target beam is formed by a collimated hole structure (see text) and modulated by a toothed wheel before intersecting the ion beam in the collision region. The microwave cavity (2450 MHz) produced the discharge used for the experiments with metastable $O_2(^1\Delta_g)$.

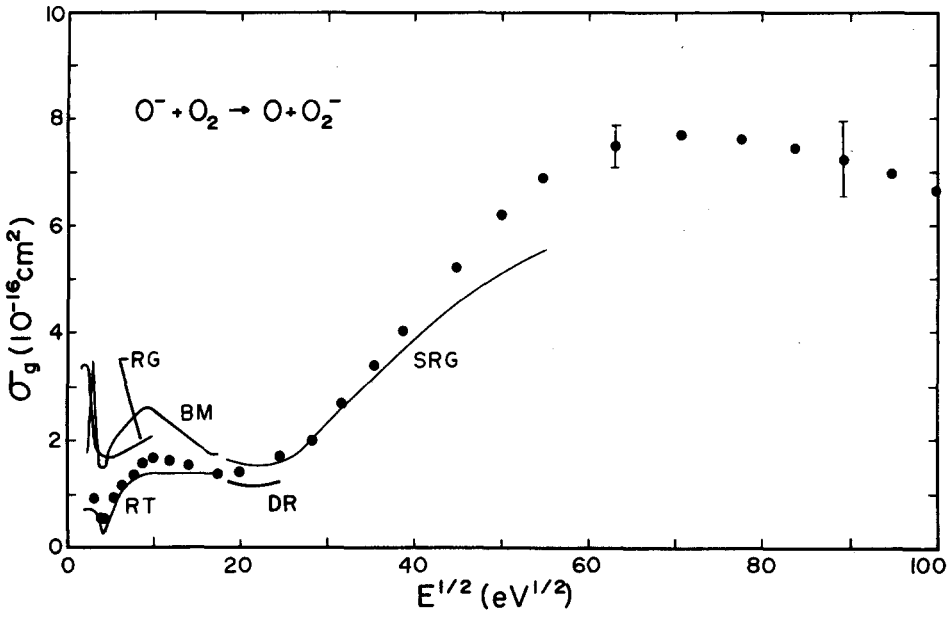

FIG. 3. Cross section for charge transfer to ground state O_2. Solid circles are the data from the present experiment. Solid lines are measurements reported by Roche and Goodyear (RG),[5] Bailey and Mahadaven (BM),[4] Rutherford and Turner (RT),[3] Dimov and Roslyakov (DR),[7] and Snow, Rundel, and Geballe (SRG).[6]

which the maximum occurs is about a factor of 1.4 greater than that predicted. This could be explained by assuming that the parameter "a" in the adiabatic criterion is 10 Å rather than 7 Å.[16] Larger values of "a" may be characteristic of negative ion charge transfer.[17]

The low energy portion of the present measurement is in good agreement with the results of Rutherford and Turner. The discrepancies between the results of RT and the results of BM and RG have been discussed by the previous investigators.[4,5] Both the results of Rutherford and Turner and the present results assume a constant collection efficiency at all energies. However, at the lowest energies the possibility of large angle scattering and ion-atom interchange increases. Both of these effects could contribute to an increase in the range of the initial momenta of the reaction products thus decreasing the collection efficiency and leading to a resultant cross section that is too low.

On the other hand, in both of the other experiments, (BM, RG) the total product ion current was measured without mass discrimination. Only the electrons were removed from the reaction products. Thus any reaction channels other than charge transfer that result in slow negative ion products will result in measured cross sections that are too high. Rutherford and Turner suggested dissociative charge transfer as a possible competing reaction. Roche and Goodyear conceded that this reaction may be more important at these energies than would be expected on the basis of a simple adiabatic analysis. No O^- product ions were observed in the present experiment at primary ion energies near 300 eV. It seems possible that the O^- product ion might have some kinetic energy, in which case the collection efficiency would be greatly reduced.

Another process that can have a large cross section at low energies is the elastic scattering of the primary beam. Roche and Goodyear have concluded that a significant part of the discrepancy in these cross sections below 25 eV is due to this process, which will cause their measurement to be too high.

IV. EXCITED STATE O_2

Charge transfer to metastable excited O_2 ($^1\Delta_g$) was studied by measuring the change in the O_2^- signal when the microwave discharge, which produced the metastable O_2, was turned on. The normalized signal S observed with the discharge on, is given by

$$S = (1-f)S_g + fS_e \ , \tag{1}$$

where f is the fraction of molecules in the neutral beam that are in the $^1\Delta_g$ state and S_g and S_e are the normalized signals which would result if only ground state molecules or excited state molecules, respectively, were present in the neutral beam. The cross section for charge transfer to excited state $O_2(^1\Delta_g)$ is given by

$$\sigma_e = \sigma_g(S_e/S_g) = \sigma_g - \sigma_g f^{-1}(1 - S/S_g) \ , \tag{2}$$

where σ_g is the cross section for charge transfer to ground state O_2. Both σ_g and S/S_g are measured quantities but f cannot be measured directly with the present apparatus. However, it is possible to set bounds on f indirectly.

A minimum can be obtained using the present data. Since it was found that $S_g > S$ over this energy range, it is clear that $S_g > S_e$. If at some point $S_e = 0$, we would have from Eq. (1) that

$$f = 1 - S/S_g \ . \tag{3}$$

On the other hand, if $S_e \neq 0$, then

$$f = S_g - S)/(S_g - S_e) > 1 - S/S_g \ . \tag{4}$$

Therefore, the quantity $1 - S/S_g$, which can be obtained from the present data, represents the minimum value that f can have, and will be nearly equal to f when $S_e \ll S_g$.

The measured change of $1 - S/S_g$ with energy approaches a constant value of 0.035 near 5000 eV. Therefore the lower bound of f was taken as 0.035.

This general behavior of the data is consistent with theoretical considerations. The energy defect for charge transfer to the excited state is small (0.05 eV), therefore, according to the theory of Rapp and Francis,[15] σ_e is expected to be small at high energies. Since the ground state cross section σ_g is maximum near 5000 eV it is expected that the condition $S_e \ll S_g$ will best be fulfilled near 5000 eV. This expectation is in qualitative agreement with the present results indicating that the lower limit determined for f may be close to its actual value.

The results of previous measurements[10] of the $O_2(^1\Delta_g)$ concentration in microwave discharge excited oxygen indicate that near the discharge f is approximately 0.1. This value is an upper bound for f in our experiment. However, since the metastables have passed through approximately 40 cm of stainless steel tubing before they reach the collision region, it is assumed that f is probably much smaller than 0.1.

Atomic oxygen or ozone formed in the discharge could dilute the beam yielding a value of f larger than that due to $O_2(^1\Delta_g)$ alone. However, since both O and O_3 charge transfer readily with O^-, their presence could easily be detected. Neither O^- nor O_3^- was observed.

The experimental values for the cross section for charge transfer of O^- with $O_2(^1\Delta_g)$ are shown in Fig. 4. Cross section values are calculated from Eq. (2) using a value of $f = 0.035$, so that the graph represents the minimum value of the cross section. The error bars shown for representative points are the root mean square deviations from the means of the experimental data. The large error bars are consistent with the statistical errors involved in a measurement which depends on the difference between two large numbers. It should be pointed out that the value of σ_e at the lowest energies is relatively insensitive to f. For example, even if the true value of f was as large as 0.07 the value of σ_e at 100 eV would still lie within the error bars shown in Fig. 4.

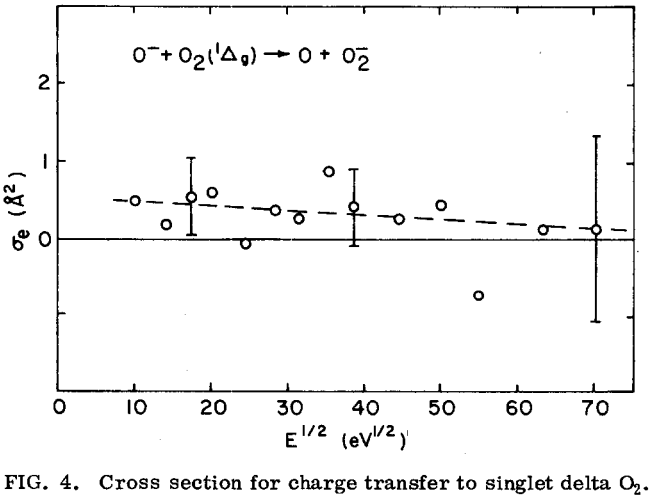

FIG. 4. Cross section for charge transfer to singlet delta O_2. Error bars represent rms deviation of the experimental points.

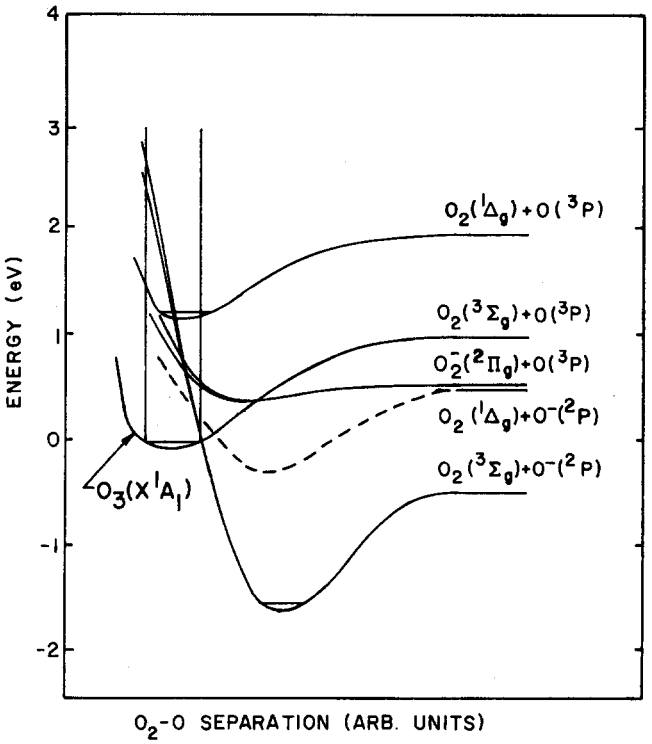

FIG. 5. Schematic diagram of the potential energy curves for the ground state of O_3+e and O_3^- states. The solid curves are from Mauer and Schultz.[18] The dashed curve is a possible curve involving the singlet delta state of O_2.

Fig. 4.

The data shown in Fig. 4 indicate that σ_e is relatively small over the entire range from 100 eV to 5 keV. Since the energy defect is only 0.05 eV one might expect a quasiresonant behavior and a considerably larger cross section at the lowest energies. No selection rules are violated in the transfer of an electron from the ground state $O^-(^2P)$ ion to the singlet delta state of O_2 whose electron configuration is $KK(\sigma 2s)^2(\sigma^*2s)^2(\sigma 2p)^2(\pi 2p)^4 \times (\pi^* 2p)^2$ to yield the ground state of $O_2^-(^2\pi)$ whose electron configuration is $KK(\sigma 2s)^2(\sigma^*2s)^2(\sigma 2p)^2(\pi 2p)^4(\pi^* 2p)^3$.

One possible explanation for the small size of the measured cross section is that strongly competing channels, such as collisional detachment and collisional deactivation, are present. This argument can be illustrated using the potential energy diagram shown in Fig. 5. These hypothetical curves published by Mauer and Schultz[18] represent the potential energy of O_3+e and O_3^- as a function of the internuclear separation of the O atom from the static O_2 molecule. The dashed curve is a schematic potential for the $O_2(^1\Delta_g)+O^-(^2P)$ system, which has been added by the authors. The curve has been drawn diverging rapidly from the $O_2^-(^2\pi_g)+O(^3P)$ curve with no possibility of crossing, as suggested by the small value of the experimental cross section. It can be seen that for almost any well depth, the curve will cross both the $O_2(^3\Sigma_g)+O^-(^2P)$ and the $O_2(^3\Sigma_g)+O(^3P)$ curves before crossing the $O_2^-(^2\pi)+O(^3P)$ curve. A transition to the $O_2(^3\Sigma_g)+O^-(^2P)$ curve will result in collisional deactivation and a transition to the $O_2(^3\Sigma_g)+O(^3P)$ curve results in detachment. Thus both of these processes appear likely as compared with charge transfer, which results from a transition to

the $O_2^-(^2\pi_g)+O(^3P)$ curve.

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