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ELECTRON TRANSFER FROM O^- TO THE $3p$ LEVEL OF Na^+ IN 0- TO 7-eV COLLISIONS

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We have determined the cross section for the process $Na^+ + O^- \rightarrow Na(3p) + O$ as a function of relative kinetic energy in the range 0.06-7 eV. The measurements were achieved by monitoring the intensity of the Na-D doublet at 5890 Å emitted from the collision region of a merged-ion-beam device. The cross section is extremely large, 10^{-12} - 10^{-11} cm², and shows at least one sharp peak, at 2.75 eV.

I. Introduction.—The merged-beam technique is exceptionally useful for the study of collisions of ions because the relative energy range from thermal to a few hundred electron volts is made accessible with very high energy resolution. It is usually not possible to study interaction energies in this range with conventional crossed-beam devices since space-charge spreading of the ion beams at low energy results in severe intensity loss. The merged-beams technique overcomes this difficulty by producing and focusing ion beams at high energy (~2-3 keV) in the laboratory frame and then allowing the two beams to merge collinearly so that their relative energy is low. A more detailed discussion of the theory of merged beams can be found elsewhere.^{1,2}

To date, merged beams have been used to study charge transfer and charge rearrangement in ion-neutral reactions,^{3,4} charge transfer and rearrangement in neutral-neutral collisions,⁵ and mutual neutralization in ion-ion collisions.^{6,7} The experiment described below, however, is apparently the first to combine the high collision energy resolution of the merged beam technique with the high photon energy resolution of spectroscopy. We have found that it is possible with this arrangement to measure the individual cross section as a function of energy for those specific charge-transfer channels which result in optically allowed transitions. It is our hope that detailed information of this nature will shed light on the mechanism by which charge transfer be-

tween positive and negative ions takes place.

II. Experimental.—A top view schematic layout of the apparatus is shown in Fig. 1. The positive ions are produced by heating a mixture of Al_2O_3 , SiO_2 , and Na_2CO_3 on a tungsten mesh. The Na^+ ions emerge from the source aperture, are focused by an einzel lens into a nearly parallel beam, and injected into a uniform magnetic field. In the field the beam is deflected 180° and collected by a Faraday cup.

The negative ion source is a duoplasmatron similar to the one described by Aberth and Peterson.⁸ Negative ions, in this case O^- , are formed in a low-pressure gas discharge and drawn out of

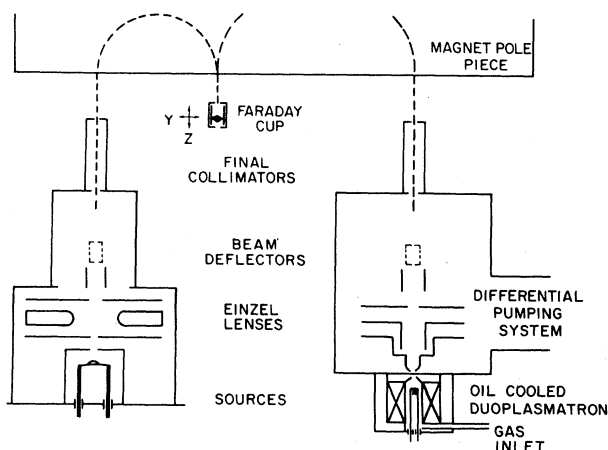


FIG. 1. Top view schematic diagram of merged-beam apparatus.

a hole in the anode. The O^- ions are then focused, deflected, and collected in a manner similar to the positive ion beam. The laboratory energies of the beams as well as the lateral and angular positions of the sources can be adjusted independently so as to merge the two ion beams with the desired relative energy.

The Faraday cup, as is shown in Fig. 1, is free to move parallel and perpendicular to the axis of the merging beams in the horizontal plane. These two motions allow us to line up the beams in a convenient merging region and to determine the small residual transverse velocity components in the beam paths. The Faraday cup also gives us beam profiles necessary for determining the degree of overlap of the two beams in the interaction region.

Photons emitted in the interaction region are detected through viewing parts either above the merging area or on the side of the vacuum chamber level with the merging area. The light is focused through an interference filter onto the cathode of a photomultiplier. Pulses from the photomultiplier pass through a pulse-shaping and discriminating network and are then counted.

In a given experimental run the following factors are taken into account: The angular divergence of each beam and the angle between the two beams in the interaction region, the detailed shape of the two beams in the interaction region and the extent to which they overlap, and the photon noise associated with each beam separately as well as the electronic dark noise which is present even with both beams turned off. A procedure based on a double-modulated pulsing scheme due to Harrison⁹ is used to distinguish signal from noise. If we use (+, -), (+, 0)(0, -), and (0, 0) to denote the signals with both beams on, with positives on and negatives off, and so forth, then one computes the net signal S as (+, -) + (0, 0) - (+, 0) - (0, -). The residual count represents signal arising only from the interaction of both beams. These data plus the beam angular and overlap information are used to calculate the total cross section for the process under study.

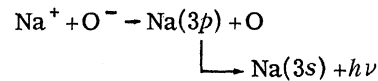
In view of the results which follow, some comments about the experiments are in order. The beam profiles were measured independently, both along their axes and transversely, with a resolution of about $\frac{1}{10}$ the beam widths. The profiles of the merged beams were also measured in the same way; the resulting currents were the algebraic sums of the independent beam currents, indicating that beam-beam interactions were neg-

ligible. Calculations of the expected beam-beam interactions likewise indicated that the effects would be negligible.

The beam profile measurements were used for calculation of the overlap factors in the evaluation of the cross sections. The geometry of the region subtended by the optical system was determined by scanning through this region with a near-point source and recording the photon counts at the detector.

The only effects we have seen from background pressure is a photon background in the positive beam (at the Na- D line, particularly) that increases with background pressure. Our operating pressures were generally $(1-2) \times 10^{-8}$ Torr.

III. Results and discussion.—The cross section as a function of relative energy for the process



is shown in Fig. 2. The size of the cross section

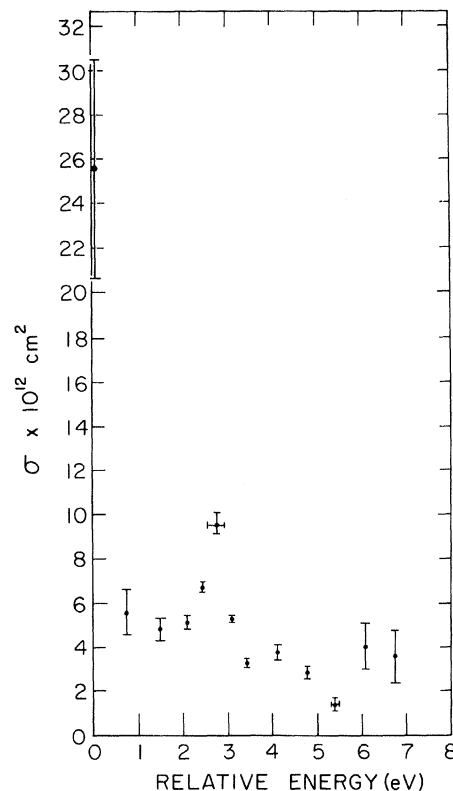


FIG. 2. Cross section versus relative energy for charge transfer from O^- into $\text{Na}(3p)$. Vertical error bars are based on beam overlap and beam divergence uncertainties. When statistical uncertainties are included, the errors corresponding to 90% confidence limits are approximately 1 scale unit high ($\pm 1.0 \times 10^{-12} \text{ cm}^2$).

is remarkably large. For example at a relative velocity of 9×10^5 cm/sec the cross section is about 15 times larger than the H^+, H^- neutralization cross section⁷ and about 30 times larger than that calculated from the data of Aberth et al.⁶ for the N^+, O^- mutual neutralization. Mahan and Person¹⁰ have also reported very large bimolecular rate coefficients for charge neutralization. Cross sections calculated from their data are on the order of 10^{-12} cm², but the relative energy of their ionic species was in the thermal range so that direct comparison with our results cannot be made.

The expression used for calculating cross sections from experimental quantities has been given in a number of different forms by various authors.^{1,7,11-13} Here we have followed Dunn's¹ treatment in which he writes the formula for the total cross section as

$$\sigma = \frac{Sc}{I} \left\{ \frac{2E_A E_B}{(M_A + M_B)T'} \right\}^{1/2}.$$

In this expression E_A and E_B are the laboratory energies of the two beams, T' is their relative energy, M_A and M_B are the ionic masses in energy units, c is the velocity of light, S is the number of signal events per second, and I is a form factor given by

$$I = \int_v \Gamma_A(x, y, z) \Gamma_B(x, y, z) dx dy dz.$$

The particle fluxes in the two beams, Γ_A and Γ_B , are functions of position within the interaction region detected by the photomultiplier. With our scanning Faraday cup we have determined the variation of Γ_A and Γ_B in both the y and z directions. The y variation reflects the penetration of the broader positive beam by the narrower negative beam. The z or axial variation, reflecting the beam divergence, is small; the overlap variation along the z axis is a few tenths of a percent per cm. We have also found that the beam shape varies somewhat among experimental runs and requires careful determination. In our estimation, the determination of the form factor is the most important single source of uncertainty in our measured cross sections. Each point on the cross-section curve (Fig. 2) represents an average of at least ten runs. The ordinate error bars show the range of uncertainty in the form factor at each relative energy setting. The abscissa error bars reflect the uncertainty in the relative energy due to the small but finite angle between the beams in the interaction region.

We have confidence that the peak at about 2.75

eV is real since this point is an average of 30 runs taken over a period of about two weeks. Results for the Na($4p \rightarrow 3s$) line at 3303 Å show no maximum in this energy range, indicating that the maximum is not an artifact of the apparatus. Moreover our measurements show that the cross section for the process generating Na($4p$) lies between 10^{-13} and 10^{-14} cm² in the range 0.5-7 eV. This corresponds closely to what one expects for a direct electron transfer when the outer maximum of the $2p$ orbital of O^- overlaps that of the $4p$ orbital of Na. In other words the cross section for production of Na($4p$) is in no way anomalously large. This observation, together with careful measurements to evaluate and eliminate experimental artifacts, persuade us to believe that the cross section leading to production of Na($3p$) is anomalously large, and that this cross section shows a rather sharp peak at about 2.75 eV. Whether there is further structure at 4.12 and 6.08 eV remains to be confirmed.

One may speculate on the mechanism by which such a large cross section could arise. Simple geometric arguments would require the active electron to move from one atom to the other when the nuclei are over 100 Å apart. It is our current working hypothesis that the mechanism is either actually a cascade process, involving transfer into the $3d$ level of Na, followed by a radiative transition to the $3p$, or a transition into a polarized $3p$ orbital containing a large admixture of $3d$. The reason this particular level is attractive is the fact that the levels Na($3d$) + O^- and Na⁺ + O^- are nearly degenerate; the Coulomb curve of the ions crosses this particular atomic dissociation energy (which is essentially the same as the energy of the two neutral atoms) at 278 Å. Consequently the colliding ions spend a large fraction of the duration of their collision with the two states approximately degenerate, and the electron subject to the Coulomb field of the alkali. Without expanding further on this mechanism, we should mention that experiments are now in preparation to search for the spectral line of Na at 8200 Å, due to the $3d - 3p$ transition.

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OBSERVATION OF OPTICAL NUTATION IN AN ACTIVE MEDIUM*

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An intense optical pulse at $10.6\ \mu\text{m}$, of rise time that is short compared with the inverse bandwidth of an active CO_2 medium in which it is amplified, has been observed experimentally to attain a sharpened leading edge and attenuated lagging edge. This is an effect attendant upon optical nutation in the CO_2 medium. Computer solutions are presented for comparison.

The response of an amplifying or attenuating medium to intense pulses of length comparable with, or shorter than, T_2 (the phase-coherence time) can exhibit nonlinear inertial effects such as nutation and self-induced transparency. Although nutation effects are known at low frequencies in nuclear magnetic resonance, they have only been reported in the optical region for the attenuating case, using SF_6 as the medium.^{1,2} In SF_6 , the exact absorbing transitions are not known and so the results cannot be fitted to theory.

In this paper, we report the first observation of the optical nutation effect in an amplifying medium. The transitions are known and experimental results agree well with theory. The experiments were done in a CO_2 - N_2 laser amplifier fed with a pulsed signal from a CO_2 - N_2 -He oscillator at $10.6\text{-}\mu\text{m}$ wavelength. A combination of high gain, high power, and large T_2 makes this medium uniquely suitable for demonstrating the effect. On the other hand, a number of factors tend to smooth out the nutation.

(a) Each of the multiply degenerate vibrational-rotational transitions of the CO_2 molecule has its

own dipole moment. In the case of the $P(20)$ CO_2 transition, the pulse interacts with 20 different dipole moments in the amplifier. The rate of population reversal is proportional to the product of the dipole moment and the electric field.

(b) Rotational relaxation also affects the interaction, particularly at high operating pressures.

(c) The nonuniform intensity of the beam introduces further complexity. These factors have not proved severe enough in practice to prevent the observation of nutation. The smoothing effects prevent repetitive ringing, yet still allow population reversal leading to attenuation of the lagging edge of the pulse. A realistic theory is obtained by taking account of degeneracy. Experimentally, the population-reversal effect is achieved by operating the amplifier at low pressure to reduce rotational relaxation.

Observation of the nonlinear effect in an amplifier of reasonably short length requires an intense pulse with a very sharp leading edge. Such a pulse with a rise time of 5 nsec and a peak power on the order of 1 kW was generated by a laser oscillator with electro-optic Q switching and cavity dumping.³ As a result of optical inho-