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A Study of Na-O_2 Collisions Using Merging Beams*

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A merging beams technique was used to study two-body collisions of Na and O_2. In particular, some processes which resulted in positive ions, and negative ions or electrons were investigated. These processes were endothermic and included charge transfer, ionization, and rearrangement. Interaction energies W were varied from threshold, i.e., several electron volts up to 25 eV. In the center-of-mass system and for processes resulting in Na^+ formation, scattering of Na^+ was predominantly at angles less than 90° from the well-defined direction of the reactant Na. For the reaction $Na+O_2 \rightarrow Na^+ + O_2^-$, a very narrow lab energy distribution of Na^+ was observed for which scattering of Na^+ in the center-of-mass system was confined to just a few degrees about the Na direction. For this distribution it was also observed that at least 92% of the excess translational energy of the reactants (i.e., interaction energy minus the endothermicity) was converted into translational energy of the products. Therefore, 8% or less went into internal energy of the products. The cross section for $Na+O_2 \rightarrow Na^+ + O_2^-$ leading to the formation of Na^+ in this narrow energy distribution is called Q_a. At or near threshold (i.e., 4.71 eV), Q_a rises from zero and reaches a maximum at about 8 eV. From absolute measurements, $Q_a \approx 0.05$ Å^2 at $W=10$ eV. The existence of NaO^+, first reported by Rol and Entemann, was confirmed in the study of collisions of Na and O_2 leading to rearrangement.

INTRODUCTION

The merging beams technique has been used in past experiments to investigate two-body collisions in which one or both reactants were ions. In the present paper, studies of five processes in each of which both reactants were neutrals will be discussed. These reactions were

$Na+O_2 \rightarrow Na^+ + O_2^-$ (charge transfer) (a)
$Na+O_2 \rightarrow Na^+ + O_2 + e$ (ionization) (b)
$Na+O_2 \rightarrow Na^+ + O + O^-$ (dissociative charge transfer) (c)
$Na+O_2 \rightarrow NaO^+ + O^-$ (rearrangement) (d)
$Na+O_2 \rightarrow NaO^+ + O + e$ (rearrangement). (e)

For ground-state reactants and products all of the above reactions are endothermic. The heat of the reaction ΔH is positive for an endothermic process. ΔH for (a), (b), and (c) is 4.71, 5.14, and 8.78 eV, respectively, assuming the electron affinity of O_2 is 0.43 eV[1] and O is 1.48 eV.[2] The magnitude of ΔH is unknown for reactions (d) and (e).

CHARGE TRANSFER AND IONIZATION EXPERIMENTS

Apparatus

To study reactions (a), (b), and (c), a retarding potential curve of product ions was obtained for each of several interaction energies W. These curves yielded information on the lab energy distribution of the product ions and cross sections for the processes. To investigate (a) alone, attempts were made to detect O_2^-. Although some measurements were made on O_2^-, in general the signal-to-noise ratio was too small (for unkown reasons) to extract good data. Most of our information for (a) and all of it for (b) and (c) were obtained by observing Na^+, and further discussion will be confined to experiments involving detection of this ion.

The apparatus used for these measurements was very much like that employed in the study of $H_2^+ + H_2 \rightarrow H_3^+ + H$ and described previously.[3] Figure 1 is a schematic of the apparatus. An Na^+ beam from source 1 was obtained by emission from a heated glass made from Na_2O, SiO_2, and Al_2O_3. The energy spread (i.e., full width at half maximum) of particles in the Na^+ beam was 1.5 eV or less. The Na^+ beam was then merged in the merging magnet with an O_2 beam. The O_2 beam was obtained by passing O_2^+ at 4000 eV from source 2, which was a low-pressure, oscillating electron bombardment source, through a charge transfer cell containing O_2. An electric field between the condenser plates that follow the cell was used to remove O_2^+ which did not undergo charge transfer. The energy spread of the O_2^+ was 1.5 eV or less. The energy of Na^+ was adjusted to give the desired W.

After leaving the merging magnet, the superimposed beams passed through a collimating aperture and then a charge transfer cell containing Na vapor. The temperature of this cell was adjusted so that the vapor pressure of Na was optimum for

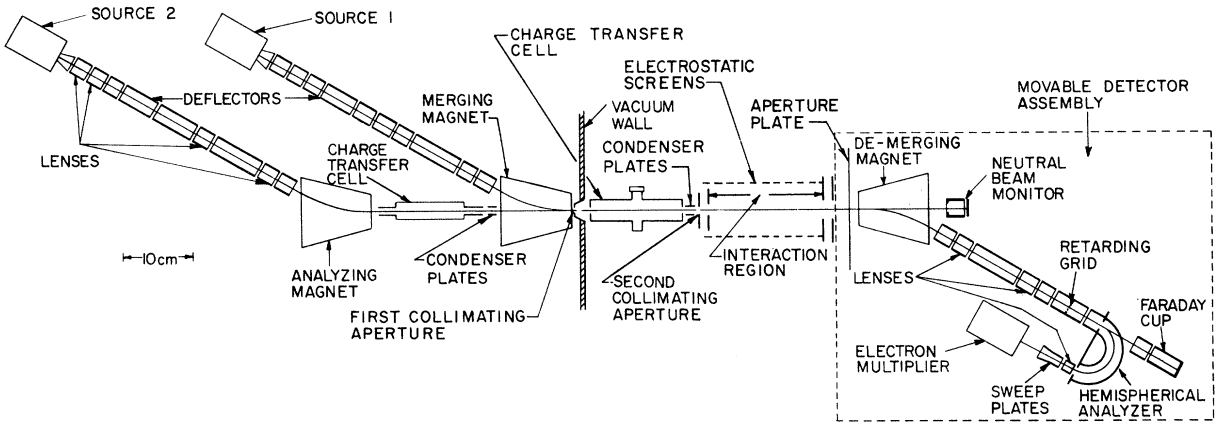

FIG. 1. Schematic of apparatus for studying Na-O_2 collisions. Apertures are not to the scale shown.

neutralization of the Na^+ beam. Under these conditions the O_2 beam suffered about 35% attenuation.

The Na vapor had negligible effect on the energy distribution of particles in the O_2 beam. This conclusion was reached by measuring the energy distribution of O_2^- particles in a beam formed by interaction of the O_2 beam with background gas. The energy distribution of O_2^- was the same for the Na cell at room temperature and at the optimum temperature for neutralization of Na^+.

The merged beams then passed through an electric field between a set of condenser plates. Charged particles were eliminated by this field. After passage through a second collimating hole, the resultant neutral beams entered the interaction region. This region was surrounded by a device used in previous ion-molecule experiments[3,4] to establish the desired energy difference between the primary beams and to accelerate product ions when they left the region. In the present experiment the device was used in conjunction with the retarding grid in the detector assembly to allow product ions formed inside the interaction region to reach the detector but to prevent those formed outside from doing so. This was accomplished by applying an appropriate potential P to the device in order to accelerate ions formed inside the region. The potential of the retarding grid R allowed transmission of these ions, but prohibited the passage of slower product ions formed outside the region.

Since de-excitation of excited states of Na to the ground state can occur by direct, optically allowed transitions or by cascading, we assume that the Na beam in the interaction region consisted of only particles in the ground state. The general conclusions of this paper, however, are independent of this assumption. In this region the O_2 beam presumably contained some excited particles.

After leaving the interaction region, the reactants and products passed through a 0.874-cm diam hole in the aperture plate. Na^+ was separated from the reactants by the demerging magnet. Other undesired particles were prevented from reaching the detector (a Bendix multiplier) by passing Na^+ through the retarding grid and a hemispherical electrostatic energy analyzer tuned for the passage of these ions. The output of the multiplier was fed into a Cary 31 electrometer and then displayed on a strip chart recorder. The experiment was conducted using dc techniques.

Kinematics

Kinematics for reaction (a) are shown by the Newton diagram of Fig. 2. In this case the magnitude of the lab velocity of Na, $|\vec{v}_1|$, is less than that of O_2, $|\vec{v}_2|$.

General expressions for the magnitude of the c.m. velocity of Na before the collision $|\vec{V}_1|$ and that of Na^+ after the collision $|\vec{V}_3|$ are given by Eqs. (1) and (2):

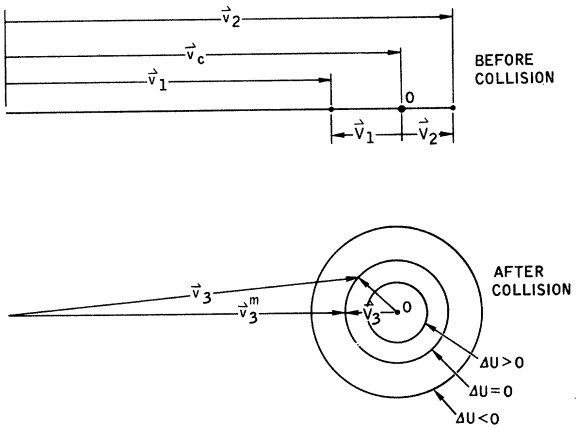

FIG. 2. Newton diagram for $Na + O_2 \rightarrow Na^+ + O_2^-$. Subscripts 1, 2, 3, and c refer to Na, O_2, Na^+, and the c.m., respectively. ($\vec{v}$) laboratory velocity; ($\vec{V}$) velocity in c.m. system; (ΔU) internal energy of products minus that of reactants; ($\vec{v}_3^m$) minimum lab velocity of Na^+ for $\Delta U = 0$.

$$|\vec{V}_1| = (2\mu W)^{1/2}/m_1, \quad (1)$$

$$|\vec{V}_3| = [2\mu(W - \Delta U - \Delta H)]^{1/2}/m_1, \quad (2)$$

where μ is the reduced mass before and after the collision, m_1 is the mass of sodium, and ΔU is the internal energy of the products minus that of the reactants. If W' is defined as the relative KE in the center-of-mass system after the collision, then

$$W' = W - \Delta U - \Delta H. \quad (3)$$

For the "after collision" case, three circles are shown for the loci of the tip of the c.m. velocity of Na^+. Therefore, points on a given circle indicate different angular scattering of Na^+. Each circle represents one of the three possible cases for the conversion of c.m. energy from internal to translational modes and vice versa. For $\Delta U > 0$, translational energy of the reactants is converted into internal energy of O_2^-. Sufficient energy to excite Na^+ was never available. $\Delta U = 0$ if all of the internal energy of O_2 is converted into internal energy of O_2^- or if all of the reactants and products are in the ground state. When $\Delta U < 0$, there is a conversion of internal energy of O_2 into translational energy of the products.

For the case of $\Delta U = 0$, two directions are shown for the c.m. velocity of Na^+. When the direction is the same as that of the c.m. velocity of Na before the collision, we define the c.m. scattering angle to be zero. Note that the minimum lab velocity of Na^+, $\vec{v}_3 m$, exists for this condition. The minimum lab velocity of Na^+ for $\Delta U = 0$ is less than that for $\Delta U > 0$ and greater than that for $\Delta U < 0$.

In some previous experiments,[4,5] stripped primary neutrals were a source of noise. The maximum energy that these neutrals had was the primary beam energy minus the ionization energy of the particles. In the present experiment the maximum speed of stripped Na was very close to the lab speed of Na. If stripped neutrals were not to have been a source of noise in the study of the $\Delta U = 0$ case (which was important because it included the case when all of the reactants and products were in the ground state), then $|\vec{v}_1|$ had to be less than $|\vec{v}_3|$, where $\vec{v}_3$ is the lab velocity of Na^+. Figure 2 and Eqs. (1–2) show that this was the case since $|\vec{v}_1| < |\vec{v}_2|$ and $|\vec{V}_3| < |\vec{V}_1|$. Experiments for which $|\vec{v}_1| > |\vec{v}_2|$ could not be conducted because of the noise introduced by stripped Na.

Newton diagrams similar to Fig. 2 can be drawn for reactions (b) and (c). The diameter of a circle is proportional to $\sqrt{W'}$. For a given ΔU the circle diameters are different for reactions (a), (b), and (c) because the ΔH are different. The diameter for reaction (a) is the largest.

Kinematic considerations of reaction (b) show that Eq. (2) gives the magnitude of the c.m. velocity of Na^+ if the KE of the electron in the center-of-mass system is considered as a contribution to the internal energy of the products of the reaction. With this interpretation, Eq. (3) gives the relative KE in the center-of-mass system of the products Na^+ and O_2.

For reaction (c) and a given ΔU, Eq. (2) gives only the maximum $|\vec{V}_3|$, which occurs when the velocities (magnitude and direction) of O and O^- are the same. Equation (3) then gives the relative KE in the center-of-mass system for Na^+ and the O, O^- complex.

Method

As mentioned previously, the experiment primarily consisted of measuring retarding potential curves of Na^+. To do this, settings of components in the detector assembly were adjusted for optimum transmission of Na^+ in the expected energy band. These settings were the current through the demerging magnet, the voltages on the pole faces of this magnet,[5] and the voltages on the lenses and hemispherical analyzer. The settings were obtained by optimizing the detector output for a small current of Na^+ from source 1 at a given energy within the expected band. When this was done, the charge transfer cell containing Na was at room temperature and the condenser plates after this cell were grounded. At the given energy, the response of the detector as a function of each of the settings was a flat-topped curve. Therefore, for given settings, an entire band of energies (whose width could be determined) could be detected. Signals from two or more adjacent bands or from a specific portion of a band could be obtained by properly adding or substracting signals obtained at different values of R. It should be noted that the retarding grid only retards normal components of the Na^+ velocity.

The desired Na^+ signal, or current I_3, was the detector output with both primary beams on, minus the sum of the outputs due to each beam separately. The output from a single beam was similar to ion noise, which has been described previously.[5] Extraneous signals caused by one primary beam modulating (attenuating or enhancing) the noise associated with the other primary beam were investigated by making $P = 0$. This had the effect of eliminating the real signal without altering the noise significantly. For this case, the detector output with both beams on, minus the sum of the outputs for each beam by itself, was negligible indicating the absence of any significant modulation.

An absolute cross section could be obtained by a technique discussed previously.[5] This technique included measuring the profiles of each primary beam in the interaction region, the gain of the detector assembly, and determining the secondary electron emission coefficient of the neutral beam

monitor for both Na and O_2. Typical primary beam currents in the interaction region were 0.5 μA for both Na and O_2.

RESULTS AND DISCUSSION

Figure 3 shows I_3 as a function of R for $W = 12$ eV. (For this case, the lab energy of Na was $E_1 = 2408$ eV.) The solid curve (except the kink at 2995 V, which will be discussed later) is drawn on the basis of statistical evidence for the existence of inflections. It can be shown that smooth curves confined to 80% confidence limits associated with the points for each R (or to the average when there is more than one point for a given R) have an inflection in or very near to the plateau having the lowest R values. This will be called the first plateau. Curves confined to 60% confidence limits have an inflection in the region of both plateaus (i.e., the first and second plateaus). Standard deviations for the points were obtained through consideration of 147 data points taken over the entire observed ranges of W and R.[6] These inflections suggest the existence of discrete energy distributions of Na^+. The data are not sufficiently good to deduce fine details of these distributions. The inflections together with the data points and confidence limits only give some indication of energy limits and integrals of the distributions. The solid curve of Fig. 3, which consists of straight lines, is used to represent this information. The curve is visually drawn consistent with the data

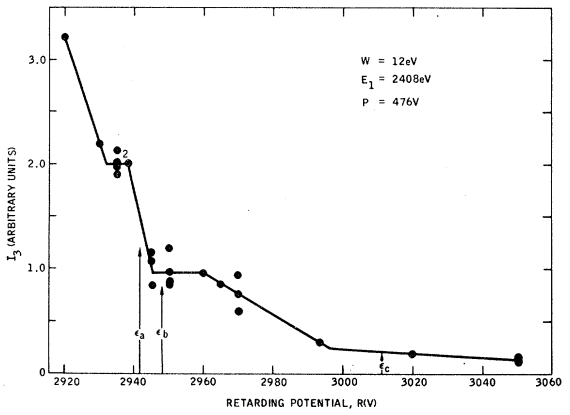

FIG. 3. Na^+ current (I_3) versus R for Na-O_2 collisions at $W = 12$ eV. (E_1) lab energy of Na; (P) potential of interaction region; (ϵ_a) minimum lab energy of Na^+ from reaction $Na + O_2 \rightarrow Na^+ + O_2^-$ for $\Delta U = 0$; (ϵ_b) minimum lab energy of Na^+ from reaction $Na + O_2 \rightarrow Na^+ + O_2 + e$ for $\Delta U = 0$; (ϵ_c) minimum lab energy of Na^+ from reaction $Na + O_2 \rightarrow Na^+ + O + O^-$ for $\Delta U = 0$. Each dot represents a value obtained for a single measurement; the dot accompanied by the number 2 means that two measurements resulted in the same quantity. The basis for drawing the solid curve is described in the text.

and with plateaus located in the regions of the inflections. The I_3 of the plateaus represent the integrals of the distributions. The actual energy limits of a particular distribution may be somewhat different from those indicated by the curve, but an analysis of the data shows that the latter limits contain most of that distribution. This fact together with the constraints imposed by the I_3 of the plateaus mean that only minor changes at the plateaus (e.g., rounding off corners) would be allowed to achieve consistency between actual energy limits and those indicated by the curve. Such changes would permit the attainment of this consistency.

At R values less than 2995 V, there is evidence of two Na^+ distributions. One of these distributions is between the two plateaus and is rather narrow. Tails of this distribution may extend beyond the right and left termini of the first and second plateaus, respectively, but from an analysis of the data including the inflections, we estimate that at least 80% of the distribution lies between these termini. The other distribution is broader and appears to extend from about 2963 V to at least 2995 V. It is plausible to expect to see evidence of Na^+ from reactions (a), (b), and (c) for the W above threshold. If Na^+ scattering in the c.m. system is confined to a given angle and ΔU has a single value, such evidence could be manifested in the existence of three sharp energy distributions of Na^+ for each W. (A small range of scattering angles and ΔU will broaden the distributions.)

To determine if two of these reactions could account for the two distributions discussed above, we will calculate Na^+ energies for a reasonable choice of scattering angle and ΔU. We will then compare these energies with those observed in the distributions.

Consider first the choice of scattering angle. At $W = 12$ eV, Na^+ formed in the interaction region at the velocity of the c.m. $\vec{v}_C$ would just be retarded by $R = 3151$ V. In Fig. 3 it is noted that I_3 is very small at $R = 3050$ V; significant signals were only observed for $R < 3151$ V. Therefore, scattering of Na^+ in the center-of-mass system after the collision was predominantly confined to angles less than 90°. For our calculations we choose a c.m. scattering angle of 0°, which is consistent with the data. Collection of essentially all scattered Na^+ was verified by the observation that the I_3 of the first plateau were the same for holes in the aperture plate of two different sizes (i.e., diameters of 0.874 cm and 1.27 cm). Furthermore, the flat-topped response curves (discussed earlier) of the detector for settings of components in the detector assembly indicated that large angle scattering would be detected efficiently.

For the calculations of Na^+ energies, we arbitrarily choose $\Delta U = 0$. This value includes the case of ground-state reactants going into ground-state

products, which is a reasonable possibility.

For zero scattering angle and $\Delta U = 0$, the lab energies of Na^+ for reactions (a), (b), and (c), respectively, are designated ϵ_a, ϵ_b, and ϵ_c. The energy ϵ_c is calculated under the assumption that the velocities of O and O^- are the same. For reaction (a), ϵ_a is equal to the energy associated with $\vec{v}_3 m$, shown in Fig. 2. In Fig. 3 arrows designate ϵ_a, ϵ_b, and ϵ_c which are, respectively, at Re values (where e is the magnitude of the electronic charge) of 2942 eV, 2948 eV, and 3011 eV.

Consider first the narrow energy distribution between the two plateaus. The peak of the distribution is between these plateaus, i.e., in the range 2938 eV $\leq$ Re $\leq$ 2945 eV. The resolution of the retarding grid is such that a monochromatic beam will appear to have an energy spread of 4 or 5 eV and peak at an Re of about 4 eV less than its energy. Therefore, if the energy associated with the peak is ϵ_a, the peak should occur at 4 eV to the left of the ϵ_a arrow, or at Re = 2938 eV. Within experimental error, the data are consistent with this location. In addition, it appears that the energy distribution about the peak could be attributable to the resolution of the retarding grid.

If we assume that the c.m. velocity associated with the peak is at a scattering angle of 0°, then any discrepancy in the peak location from 2938 eV would be the result of a nonzero ΔU. The greatest difference would be if the peak were at Re = 2945 eV. For such a peak one obtains, using Eq. (2), $\Delta U \approx 0.6$ eV. For the peak at 2938 eV, and thus $\Delta U = 0$, W' is a maximum and is equal to $(W - \Delta U - \Delta H) = 7.29$ eV. If the peak is associated with $\Delta U \approx 0.6$ eV, then $W' \approx 6.7$ eV, or 92% of the maximum W'. Thus, a 7 eV difference in the location of the peak makes little difference in the kinematics of the process.

It is conceivable that the narrow energy distribution and its associated peak could be explained by assuming c.m. scattering angles considerably different from zero. Then $\Delta U < 0$. The angular spread in the center-of-mass system associated with the narrow energy distribution would also be narrow. As an example, if it is assumed that the energy spread in the lab system is 2 eV, then for $\Delta U = -1$ eV, the angular distribution in the center-of-mass system would peak at about 20° and have a spread of just a few degrees. Such an extremely narrow, off-axis angular distribution would be unusual.

We suggest that the very narrow energy distribution and its peak are associated solely with reaction (a). In addition, it seems likely that ΔU is very close to zero, and therefore almost all the excess translational energy of the reactants (i.e., $W - \Delta H$) is converted into translational energy of the products with very little going into internal energy. Finally, because of the very narrow energy distribution about ϵ_a, the products in the center-of-mass system must be confined to a very small angle about the axis of the interaction region. In particular, Na^+ in the center-of-mass system appears to be scattered almost completely in the 0° direction. Apparently the process proceeds via a direct rather than a complex mechanism. The cross section for reaction (a) leading to the formation of Na^+ in this narrow energy distribution will be called Q_a.

Consider now the broader Na^+ distribution. It seems likely that this distribution is associated with reaction (b) even though the solid curve shows ϵ_b to be outside the distribution. However, between about 2944 and 2963 eV, a gentle curve with an inflection could be drawn consistent with the data such that the low-energy limit of the distribution would be extended to the left of ϵ_b. If this were done, the integral of this distribution would be changed very little. Another inflection point at Re $\geq$ 2963 eV would result in a well-defined peak at the point. From Eq. (2) as applied to reaction (b), the ΔU associated with this peak (if it were at Re = 2963 eV) would be about 1.3 eV. This means that at 12 eV, reaction (b) is most probable when 1.3 eV, or 19% of the excess translational energy (i.e., $W - \Delta H = 6.86$ eV) is converted into either KE of the free electron, internal energy of O_2, or both. The significance of such a partition of energy is not known. [Recall that the peak of the energy distribution of reaction (a) could be associated with $\Delta U \approx 0.6$ eV, which would imply that the reaction is most probable when 0.6 eV of the excess translational energy was converted into excitation of O_2^-.] The high-energy tail preceding the kink could be explained by the conversion of translational energy into KE of the electron and internal energy of O_2 (the largest ΔU for the distribution would be about 3.5 eV) and/or by angular scattering of Na^+. The cross section for reaction (b) leading to the formation of Na^+ in the energy distribution discussed above will be called Q_b.

The second peak and energy distribution in the vicinity of the peak could also be explained via reaction (b) by assuming $\Delta U = 0$ (or, at least, different from 1.3 eV) and a distribution of scattering angles in the center-of-mass system that peaks at an angle different from 0°.

There is no evidence for the kink at 2995 V in Fig. 3. Small signal-to-noise ratios in the vicinity of the kink make it extremely difficult to obtain such evidence. The straight lines meeting at the kink could be smoothed to form one continuous curve that would fit the data. This could be interpreted in two ways: (1) as simply a longer high-energy tail associated with reaction (b) than described above, and (2) for $R > 2995$ V, as a distribution resulting from reaction (c) with the peak of this distribution at about ϵ_c. The high-energy side of this distribution could be explained by assuming

a difference in the velocities of O and O^-. The cross section for reaction (c) leading to the formation of Na^+ in this distribution will be called Q_c.

If the second interpretation is assumed (see Concluding Remarks), then from Fig. 3, $Q_a : Q_b : Q_c \approx 5 : 3.5 : 1$.

Data similar to those shown in Fig. 3 were taken for $W = 8$ and 10 eV. These observations together with those for $W = 12$ eV indicated that signal-to-noise ratios were smaller as W decreased. Further examination showed that this effect was the result of an unexplained increase in O_2 noise with a decrease in W. We define O_2 noise as an apparent signal due only to the presence of the O_2 beam.

Curves confined to 85% confidence limits associated with the points for each R at $W = 10$ eV have an inflection in or very near a plateau analogous to the first plateau for $W = 12$ eV. Inflections indicating two plateaus analogous to those for $W = 12$ eV exist for about 50% confidence limits. Confidence limits for $W = 8$ eV are 50% for the first plateau and less than 50% for both plateaus.

The evidence for plateaus is stronger at 10 eV than at 8 eV, but plateaus are consistent with the data at 8 eV, and their existence will be assumed. As for $W = 12$ eV then, both a narrow and a broad Na^+ distribution would appear to exist at 8 and 10 eV. These can be interpreted in the same fashion as for 12 eV. At both 8 and 10 eV, $Q_a/Q_b \approx 1$.

At $W = 10$ eV, there were no observable signals for Re greater than or equal to the associated ϵ_c. If the high-energy tail at $W = 12$ eV for $R > 2995$ V results from reaction (c), then at 10 eV the absence of signals for $\mathrm{Re} \geq \epsilon_c$ could be due to very small Q_c at such energies. At $W = 8$ eV there was no high-energy tail analogous to that at 12 eV. At 8 eV there is insufficient energy for the onset of reaction (c). Therefore, for $W = 8$ and 10 eV it will be assumed that $Q_c = 0$.

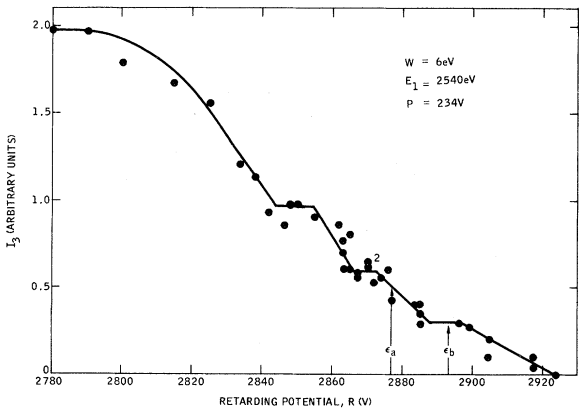

FIG. 4. Na^+ current (I_3) versus R for Na-O_2 collisions at $W = 6$ eV. Symbols have the same meaning as in Fig. 3. The basis for drawing the solid curve is described in the text.

Figure 4 shows I_3 versus R for $W = 6$ eV. We did not obtain data for $R < 2780$ V because we began to get interference from stripped Na in the primary beam. No signals were observed for $R > 2924$ V. For $R > 2872$ V, I_3 was the same for both a 1.27-cm diam hole and the normal hole in the aperture plate. This indicates that any large angle scattering would have been detected.

The solid curve is drawn to be consistent with the data and to show plateaus in about the same positions with respect to ϵ_a and ϵ_b as was the case for $W = 8$, 10, and 12 eV. There is no statistical evidence for the existence of inflections in the vicinity of these plateaus, presumably because of smaller signal-to-noise ratios than for the higher W, as discussed previously. Justification of the solid curve is the rather fair evidence for similar plateaus at higher W. Again $Q_a/Q_b \approx 1$.

The data of Fig. 4 are not shown to support the existence of plateaus analogous to those at higher W. These data are the poorest in that respect. The purpose of Fig. 4 is to show the rise in I_3 as R is decreased below values associated with the plateau immediately to the left of ϵ_a. (The two plateaus shown in this rise may or may not exist; a statistical analysis of the data in this region has not been made.) Evidence of such a rise is also noted in Fig. 3. If our explanation of the first plateau is valid, it is likely from Fig. 2 and Eq. (2) that the rise is associated with reaction (a) and $\Delta U < 0$. This means that some O_2 is excited and that there is a conversion of some of this internal energy into translational energy of the products.

Data similar to those of Figs. 3 and 4 were taken for $W = 4.71$ eV. For this case $E_1 = 2579$ eV and $P = 275$ V. The largest R for which there was a non-negligible I_3 was about 2970 V. As R was decreased below 2970 V, I_3 became larger. The threshold for reaction (a) is 4.71 eV, and $\epsilon_a = 3025$ V. On the basis of our explanations for previous data, we would expect to observe no Na^+ for $\mathrm{Re} \geq 3025$ eV. The data for $W = 4.71$ eV are consistent with this expectation. The rise of I_3 below 2970 V is evidence again for excited states of O_2 and $\Delta U < 0$.

Figure 5 shows I_3 versus R for $W = 6, 8, 10$, and 12 eV. Only the data for those Re values in the vicinity of ϵ_a and the plateau immediately to the left of ϵ_a are shown. No plateaus were observed for $W = 15$ and 25 eV.

Figure 6 shows relative Q_0 as a function of W, where Q_0 is defined as $Q_a + Q_b + Q_c$. At a given W, the Q_0 is proportional to the I_3 of the first plateau (see Fig. 5). The relative Q_0 of Fig. 6 were obtained by measuring the appropriate I_3 one after another as rapidly as possible and normalizing the measurements to the same primary beam currents. Source conditions (except E_1) for all measurements were kept the same. At $W = 10$ eV, an absolute Q_0

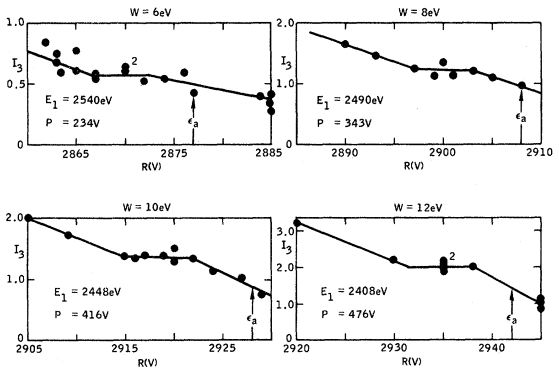

FIG. 5. Na^+ current (I_3) versus R for $W=6, 8, 10$, and 12 eV. I_3 is in arbitrary units. Symbols have the same meaning as in Fig. 3. The basis for drawing the solid curves is described in the text.

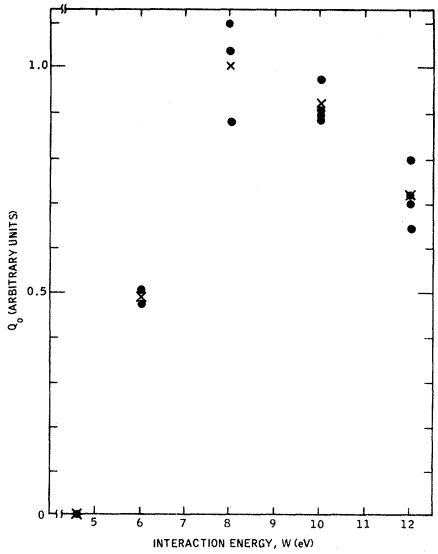

FIG. 6. Relative Q_0 versus W. Q_0 is the cross section for the formation of Na^+ in Na-O_2 collisions for $\Delta U \geq 0$. Each dot represents a value obtained for a single measurement. Crosses are arithmetic averages of dots. Q_0 was chosen as unity for the cross at $W=8$ eV.

has been calculated as 0.1 Å^2 with an estimated error of +35% to −50%. The primary beam currents used in this calculation were those measured at the neutral beam monitor.

Relative Q_a, Q_b, and Q_c versus W can be obtained from Fig. 6 and the known ratios (at given W) Q_a: Q_b: Q_c. At 4.71 eV, $Q_0 = Q_a \approx 0$. Since the ratios Q_a: Q_b: Q_c are approximately 1:1:0 at $W=6, 8$, and 10 eV, the relative Q_a and Q_b are the same as the measured relative Q_0. The ratio of Q_0 at 10 eV to Q_0 at 12 eV is approximately 1.2. The corresponding ratios of Q_a and Q_b are about 1.1 and 1.6, respectively. (The absence of any effect from reaction (c) in these experiments would be equivalent to setting the ratios Q_a: Q_b: Q_c = 10:9:0 at 12 eV. The corresponding ratios at $W=6, 8$, and 10 eV would remain the same since it was already assumed that reaction (c) had no effect at these energies. The only change in the ratios quoted above would be that Q_b at 10 eV to Q_b at 12 eV is about 1.2 instead of 1.6. Figure 6 would remain the same since Q_0 depends only on the measured I_3 of the first plateau.) Crossing of potential curves could contribute to the fall-off of Q_a and Q_b with increasing W above 8 eV. It is not known whether quantitative agreement with the data could be achieved through such a consideration.

The threshold energy in Fig. 6 could not be obtained with less than 0.5 eV uncertainty since the signal-to-noise ratio was very small in the vicinity of threshold. As a result, the electron affinity for O_2 could not be obtained accurately.

As mentioned previously, $Q_0 \approx 0.1$ Å^2 at $W=10$ eV. Therefore, at this same energy $Q_a \approx Q_b \approx 0.05$ Å^2. (These cross sections apply, of course, when the specific states of the reactants and their abundances are the same as exist in this experiment.) Since the states of the molecular reactant and product are unknown, the experimental results only shed light on the ΔU of a process. From the results it appeared that $\Delta U = 0$ for the process with cross section Q_a. This reaction is a charge transfer process, and presumably the Franck-Condon principle applies. Since the equilibrium internuclear distances for the ground state of O_2 and O_2^- are nearly equal,[7] the conversion of ground-state O_2 to ground-state O_2^- has a favorable Franck-Condon factor in addition to satisfying the condition that $\Delta U = 0$. If it is reasonably assumed that ground-state O_2 to ground-state O_2^- was the only significant process occurring, then the cross section for this case would be 0.05 Å^2 if all of the O_2 had been in the ground state. If only a fraction of the O_2 had been in the ground state, the cross section would be proportionately larger.

REARRANGEMENT EXPERIMENTS

Reactions (d) and (e) were studied using the same method and procedure as for reactions (a), (b), and (c) except that the components of the detector assembly were tuned for the passage of NaO^+ (by using a K^+ impurity beam from source 1). A signal attributable to NaO^+ was obtained. This signal could have resulted from reaction (d) and/or (e). The first experimental evidence for the existence of NaO^+ was recently reported by Rol and Entemann.[8] In the present experiment, the curve of the cross section for the formation of NaO^+ as a function of W rose from zero at about 5.5 eV, reached a maximum at 7 eV, and became zero again at about 8.5 eV. An upper limit to the cross section at $W=7$ eV was estimated to be 0.004 Å^2.

CONCLUDING REMARKS

There is rather good experimental evidence for the existence of a "first plateau" in retarding potential curves of Na^+ at $W=12$ and 10 eV and of a "second plateau" at 12 eV. In addition, the two energy distributions of Na^+ indicated by the first and second plateaus can be nicely explained as resulting from reactions (a) and (b). Although the experimental evidence is weaker for the second plateau at 10 eV and the first and second plateaus at 8 and 6 eV, the data are consistent with the existence of such plateaus.

A long tail at large R (i.e., $R>2995$ V) exists at $W=12$ eV. This tail does not appear in similar curves for $W=6, 8$, and 10 eV. If the tail at 12 eV were due to the formation of Na^+ from reaction (c), a similar tail would not be expected at 6 and 8 eV because the threshold for the reaction is 8.78 eV. The absence of the tail at 10 eV, which is only 1.22 eV from threshold, could be due to a small Q_c at this energy. It is therefore conceivable that Na^+ from reaction (c) was observed at $W=12$ eV. If the tail at 12 eV were due to reaction (b) instead, calculations would give the same Q_0 and Q_a and about a 30% larger Q_b.

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Population Distributions. II. Charge-Exchange Capture by Protons Incident Upon Ground-State Atoms*

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The ratios of the excited captures to the total captures have been computed for charge-exchange collision of protons incident upon each of the elements in their ground state. The calculations have been performed for incident proton energies of 5 to 140 keV and employing a simplified form of the Brinkman-Kramers matrix element. Generally speaking the extremes of behavior of the population distributions occur for charge-exchange collisions with the alkalis and with the inert gases; the population distributions for the other target elements fall smoothly within these extremes. The main variations of the population ratios and the primary trends for different target elements agree reasonably well with available experimental data.

I. INTRODUCTION

In an earlier paper,[1] expressions were given for the cross sections for electron capture by protons incident upon hydrogenlike targets. Using these expressions it was possible to deduce some of the features of the population distributions of the excited atoms formed by protons incident upon different elements. In particular, the calculations showed that the excited-state population ratios