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Ionization of Nitrogen and Oxygen Molecules by Nitrogen and Oxygen Molecules*

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The ionization cross sections for N_2 and O_2 molecules on impact with N_2 and O_2 molecules have been measured over the laboratory energy range from 20 to 1000 eV. The incident molecular beams were produced by the technique of ionization by electron impact, electrostatic acceleration, and neutralization by charge transfer. The measurements were carried out in a low-pressure parallel plate ionization chamber. Particular attention was paid to the problem of secondary electrons. Ionization was observed a few eV above threshold for all combinations. Cross sections which were obtained ranged from 10^{-20} to 5×10^{-16} cm². The N_2-O_2, O_2-N_2, and O_2-O_2 curves of cross section vs incident particle energy showed no apparent structure, as contrasted with N_2-N_2 case. The N_2-O_2 and O_2-N_2 results were in agreement when corrected to center-of-mass energy.

INTRODUCTION

TWO previous papers[1,2] have described the development of a fast molecular N_2 beam and its application to the measurement of the ionization cross section for N_2 molecules on N_2 molecules (N_2–N_2) near threshold. The present paper reports an extension of this work to the measurement of the N_2–O_2, O_2–N_2, and O_2–O_2 ionization cross sections.

The technique was the same as used previously,[2] and consisted of three basic parts. First, a molecular N_2 or O_2 beam was produced having the desired energy. Second, an N_2 or O_2 gas thin target was provided for this beam between the plates of a parallel plate ionization chamber. Finally, the electrons (or possibly negative ions) produced in ionizing interactions were swept by the electrostatic field between the plates to the collector plate and this current was measured. It was possible to determine the ionization cross section through knowledge of the incident beam intensity, target particle density, guarded collector length, and the collector current. The major experimental difficulty involved verifying that the collector current corresponded to ionization electrons rather than secondary electrons produced at the chamber surfaces.

N_2-O_2 MEASUREMENT

The apparatus used for the N_2–O_2 ionization cross section measurement was the same as used previously[2] for N_2–N_2, but the present measurement differed from the N_2–N_2 case in two respects. First, the neutralization chamber contained some contaminating O_2 as well as the N_2. This O_2 entered from the ionization chamber through the molecular beam exit aperture. Second, the O_2 target gas contained some N_2 which entered the ionization chamber from the neutralization chamber. It was therefore necessary to make corrections for the ionization current which arose from N_2–N_2 ionizing events in the ionization chamber.

The presence of the O_2 in the neutralization chamber made little difference in the N_2 molecular beam. This was checked by first obtaining a normal molecular N_2 beam with no O_2 in the ionization chamber. Oxygen was then admitted to the ionization chamber. The fraction of the N_2 ion beam being neutralized, β, (see reference 1) increased only a few percent on the addition of the O_2, which indicated that only a relatively small amount of N_2^+ in O_2 charge transfer was occurring. The shape of the β/P curve[1] was no different from the case with pure N_2 in the neutralization chamber. A rough measurement of the charge transfer cross section for N_2^+ in O_2 yielded a value of 5×10^{-16} cm², which was about constant over the energy range. This energy dependence is consistent with the results of other investigators,[3,4] and the present absolute value falls between their values. Under usual operating conditions, the pressure of the O_2 impurity in the neutralization chamber was about one-fourth that of the N_2. This, combined with the 6 to 1 ratio between the N_2^+ in N_2 and N_2^+ in O_2 charge transfer cross sections, resulted in the few percent increase in β observed when the O_2 target gas was admitted.

The correction for the N_2 impurity in the O_2 target gas was determined by measuring the N_2 pressure in the ionization chamber before admitting the O_2. Since the gas flow was all in the free molecule regime, adding the O_2 target gas did not change the N_2 pressure. It was thus possible to calculate the amount of ionization current due to the N_2 impurity through knowledge of the beam intensity, N_2 pressure, and the previously determined N_2–N_2 ionization cross section. The N_2 pressure usually amounted to about 10% of the O_2 pressure. Because the N_2–O_2 ionization cross section was greater than that for N_2–N_2 for a given beam energy, the necessary correction was less than 10%. Pressures were determined using a Bayard–Alpert gauge which was linear with pressure in the region of interest. This gauge was calibrated with a McLeod gauge for each gas and mixture used.

Figure 1 shows collector current saturation with

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* Supported by NASA Grant NsG–50–60.

[1] N. G. Utterback and G. H. Miller, Rev. Sci. Instr. **32**, 1101 (1961).

[2] N. G. Utterback and G. H. Miller, Phys. Rev. **124**, 1477 (1961).

[3] R. F. Potter, J. Chem. Phys. **22**, 974 (1954).

[4] R. F. Stebbings (private communication), General Atomic Report GA–2768 (unpublished).

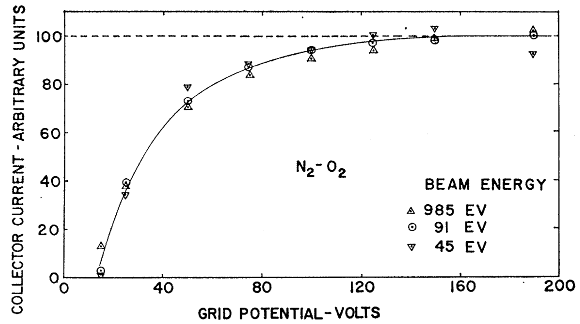

FIG. 1. N_2–O_2 collector current saturation curves.

respect to the negative grid potential in the ion chamber. There is no significant change from the N_2–N_2 curve obtained previously.[2] A check of this curve at a grid potential of 300 V showed that the current was insignificantly different at 190 and 300 V. Because the ionization measurements were made at a grid potential of 95 V, a 10% correction to the collector current was made in order to obtain the saturation values.

Figure 2 shows the ionization cross-section values obtained as a function of ion chamber pressure. The N_2 pressure in all cases was about 0.15×10^{-4} mm Hg. Again, these curves are not significantly different from those obtained previously for N_2–N_2. The ionization measurements were made at about 1.5×10^{-4} mm Hg, and a 10% correction was made to the cross sections to obtain the extrapolated values. As before,[2] these curves indicate that secondary electron effects did not preclude making meaningful measurements.

Measurements made with back plate-to-grid potential differences of 0, 30, and 50 V gave about the same results as obtained with N_2–N_2, again indicating that secondary electron emission from the grid was not a serious problem.

Figure 3 shows the final results for the N_2–O_2 ionization cross section. Ionization cross section values, σ_i, were obtained from

$$\sigma_i = 3.05\times10^{-20}(i/PB)\,\text{cm}^2, \qquad (1)$$

where i is collector current (corrected for the N_2–N_2 current) in units of 10^{-16} A, P is the O_2 pressure in the ionization chamber in units of 10^{-4} mm Hg, and B is the neutral beam equivalent current in units of 10^{-10} A. The collector length was 10 cm and the temperature was 22°C. The current values were corrected for voltage saturation and pressure effects as indicated above.

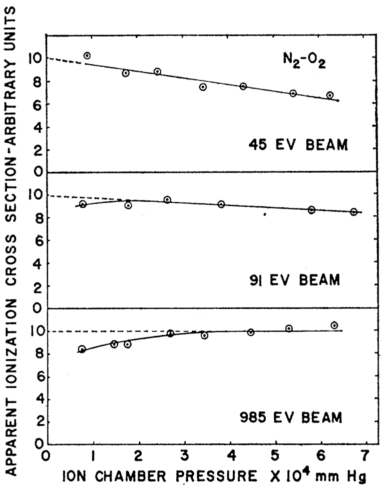

FIG. 2. N_2–O_2 pressure saturation curves.

The energy scale for Fig. 3 is the energy in the center-of-mass system minus 12.2 eV, the ionization potential for O_2. The error flags at the low end of the curve indicate random errors in σ_i, which were due mostly to uncertainties in i. Beam energy uncertainty also became important near threshold, and is estimated to have been ±0.25 eV (c.m. system). At higher energies the random uncertainties were a few percent.

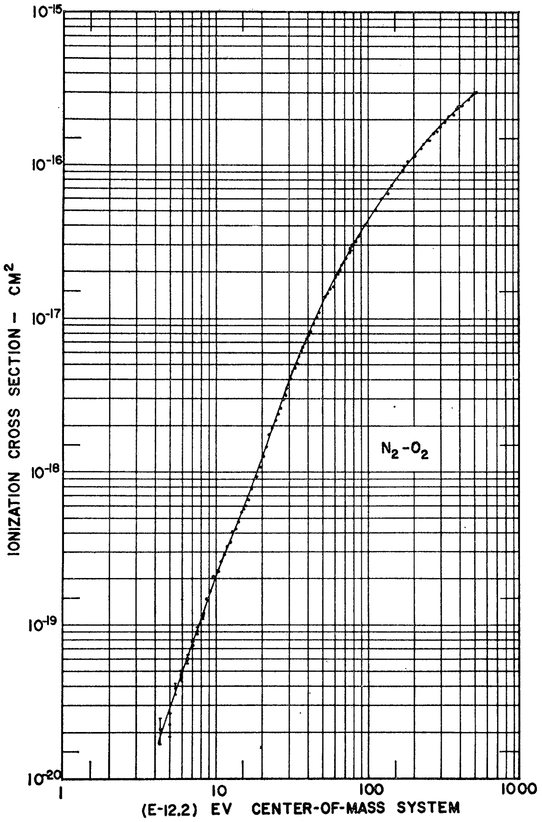

FIG. 3. N_2–O_2 ionization cross section.

The largest systematic uncertainty in σ_i was due to the molecular beam intensity, B, which was known to within ±20%.[1] The pressure uncertainty was ±10%. Other uncertainties should not have been over a few percent, so the results are assigned a systematic uncertainty of ±25%.

O_2-O_2 AND O_2-N_2 MEASUREMENTS

Essentially the same apparatus was used in obtaining the O_2–O_2 and O_2–N_2 ionization cross section data as was used in the N_2–N_2 and N_2–O_2 cases. However, minor modifications in the ion source were necessary in order to obtain an O_2^+ ion beam. The tungsten filament was replaced with a thoria-coated iridium ribbon filament, and the ion source cone walls were covered with gold foil. Although the ion source was operable, it was possible to obtain only one-tenth as much O_2^+ as N_2^+. Furthermore, filaments lasted only a few hours. The energy spread in the extracted O_2^+ beam was as good as the N_2^+ case, having less than 0.5 eV width at half maximum. The average energy of the O_2^+ ions extracted from the source was about 1.5 eV lower than the N_2^+ ions for a given ion source-to-neutralization region potential difference.

It was not possible to operate the ion source with a low enough filament-to-case potential to prevent the ionizing electrons from reaching the appearance potential energy for the production of O^+. However, it was possible to reach a potential (21 V) at which less than 0.1% of the beam was O^+. The O_2^+ ion beam was 98% mass 32, with the major contaminants being mass 18 (H_2O) and mass 28 (CO or N_2). This will be discussed further in the next section.

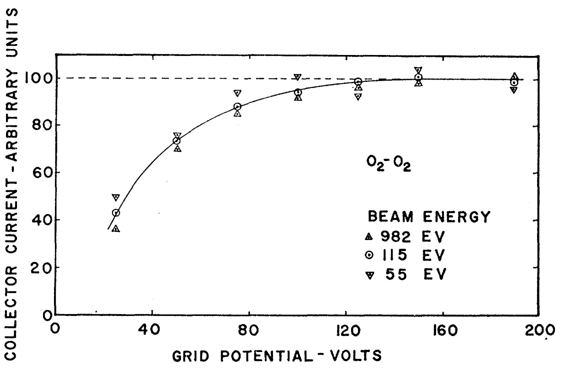

FIG. 4. O_2–O_2 collector current saturation curves.

Oxygen was used as the neutralizing gas. A rough measurement of the O_2^+ in O_2 charge transfer cross section indicated that it was about half (15×10^{-16} cm^2 at 100 eV) as great as the N_2^+ in N_2 charge transfer cross section, while the energy dependence was about the same. This energy dependence is consistent with that found by other investigators,[3–5] and the absolute value is consistent with the latter two.[4,5]

Except for the lower ion beam intensity obtainable and the lower charge transfer cross section, the beam-producing apparatus appeared to behave the same for the O_2 molecular beam as for the N_2 molecular beam.

Figures 4 and 5 show the voltage and pressure saturation curves for O_2–O_2 corresponding to Figs. 1 and 2 for N_2–O_2. Figures 1 and 4 are insignificantly different. It appears from Fig. 5 that secondary electron effects are slightly less important for the O_2–O_2 case as compared to the N_2–O_2 case of Fig. 2. A 10% voltage saturation correction and a 7% pressure extrapolation correction were made to the O_2–O_2 ionization data as described in the preceding sections for N_2–O_2.

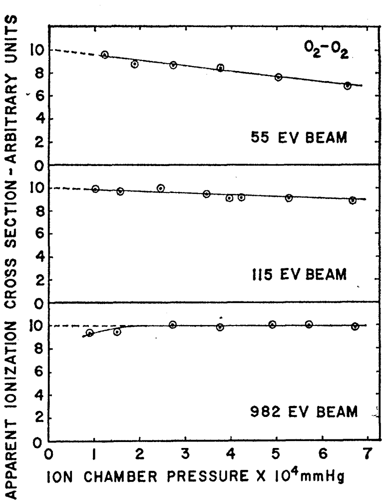

FIG. 5. O_2–O_2 pressure saturation curves.

Figure 6 shows the final results for the O_2–O_2 ioniza-

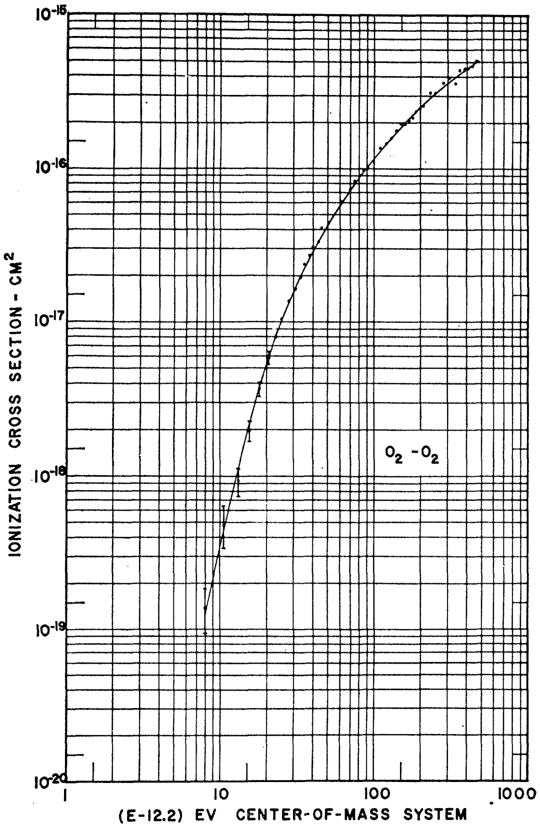

FIG. 6. O_2–O_2 ionization cross section.

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[5] S. N. Ghosh and W. F. Sheridan, J. Chem. Phys. 27, 1436 (1957).

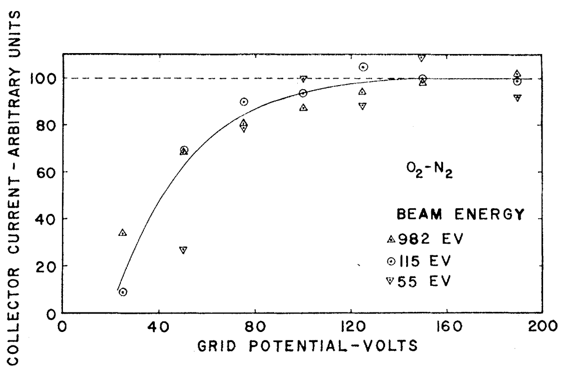

FIG. 7. O_2–N_2 collector current saturation curves.

tion cross section. Cross-section values were obtained from Eq. (1) as in the preceding section. The energy scale is the same as for Fig. 3. Beam energy uncertainty for the O_2–O_2 case is estimated to have been ±0.5 eV (c.m. system). The systematic uncertainty in the ionization cross section was again ±25%. Because of the lower O_2 molecular beam intensity, it was not possible to make measurements to as low cross-section values as was possible with the nitrogen beam.

As in the N_2–O_2 case, the O_2–N_2 measurements involved mixed neutralization and target gases. The presence of the N_2 impurity in the neutralization chamber had little effect on the O_2 beam. A rough measurement of the O_2^+ in N_2 charge transfer cross section yielded 2×10^{-16} cm^2 at 100 eV. The cross section appeared to be decreasing with decreasing energy. This value falls below the results of other investigators,[3,4] and the decrease with decreasing energy is different, although expected because of the nonresonant character of the interaction. Because of the ratio of the charge transfer cross sections between O_2^+ in O_2 and O_2^+ in N_2, and the O_2 to N_2 pressure ratio in the neutralization chamber, only a few percent of the neutralization was due to O_2^+ in N_2 charge transfer.

The presence of a small amount of O_2 impurity in the N_2 target gas was very important however. For the lower beam energies used, the O_2–O_2 ionization cross section was as much as a factor of 6 greater than the O_2–N_2 ionization cross section. Thus, if the O_2 impurity pressure was one-tenth that of the N_2, over one-third of the ionization current was due to O_2–O_2 ionization. Corrections of this order were usual at the lower energies, and were made in the same manner as in the N_2–O_2 case. Figures 7 and 8 show the voltage and pressure saturation curves for O_2–N_2, corresponding to Figs. 1 and 2 for N_2–O_2. The low-energy curve for Fig. 8 has not been included because the large uncertainties due to the O_2 impurity correction and low beam intensity do not allow a meaningful curve to be drawn. The points obtained, however, are not inconsistent with Fig. 2. Figures 1 and 7 and Figs. 2 and 8 are similar enough so that the same voltage saturation and pressure extrapolation corrections were made to the O_2–N_2 results as to the N_2–O_2 results.

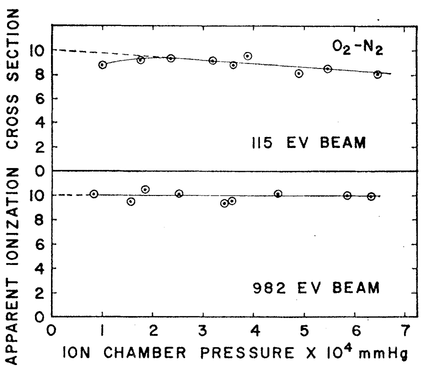

FIG. 8. O_2–N_2 pressure saturation curves.

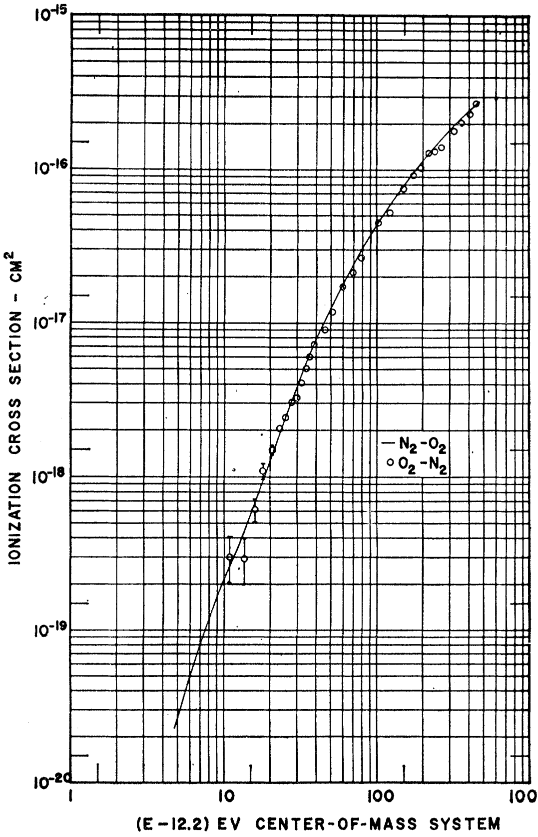

FIG. 9. O_2–N_2 ionization cross section.

Figure 9 shows the final results for the O_2–N_2 ionization cross section. The solid line is the N_2–O_2 curve from Fig. 3, and the circles are the O_2–N_2 cross sections plotted on the same energy scale. Equation (1) was again used to obtain the cross section values, with i corrected for the O_2–O_2 ionization, and P being the N_2 pressure. The flags indicate random errors, which in

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[6] W. Paul, H. P. Reinhard, and U. von Zahn, Z. Physik **152**, 143 (1958).

Table I. Ion beam mass spectra.

Mass	Amount (%)	Identification
	N_2 beam	
14	<0.05	N^+
18	0.7	H_2O^+
28	99.	N_2^+
32	<0.05	O_2^+
40	0.1	Ar^+
44	0.1	CO_2^+
	O_2 beam	
16	<0.1	O^+
18	0.5	H_2O^+
28	0.8	N_2^+ or CO^+
32	98.	O_2^+
34	0.3	O_2^+
40	0.1	Ar^+
44	0.3	CO_2^+
48	0.2	O_3^+

this case were due to uncertainties in both the current and the O_2 impurity correction. The energy uncertainty is estimated to have been ±0.5 eV (c.m. system).

ION BEAM AND GAS PURITY

The N_2 and O_2 gases fed to the ion source were Matheson pre-purified nitrogen ($>99.99\%$ N_2) and Matheson research grade oxygen ($>99.9\%$ O_2). The same gas supplies were used for the neutralizing and target gases.

The ion beam mass spectra are given in Table I. An rf quadrupole mass spectrometer[6] was used in obtaining these spectra. The spectrometer entrance aperture was placed at the exit aperture of the neutralization chamber (no neutralizing gas). The spectrometer behaved according to specifications,[6] and was always operated under 100% transmission conditions with respect to the ions passing through the entrance aperture. Table I shows all discernible peaks occurring between mass 2 and 92. The total current was taken as the sum of the peak currents. Usual conditions of ion source operation were employed.

Since it was not possible to bake the ion source, the impurity concentration changed markedly with time after pump down. For example, the water concentration was as much as 3 times as great just after pump down. The values in Table I are taken after several hours of operation, corresponding to most of the ionization measurements. (No time dependence of the σ_i values was ever noted.)

Mass 29 in the nitrogen beam ($N^{14}N^{15}$) was not resolved since it fell on the tail of the very much larger peak for 28.

The usual tungsten filament was used for the nitrogen beam, and the usual thoria-coated iridium filament was used for the oxygen. Mass analysis of a nitrogen ion beam using the coated iridium filament showed the appearance of a 5% peak at mass 30, which was presumably NO.

Because mass 28 corresponds to both N_2 and CO, it would be possible to have CO impurity in the nitrogen ion beam without detecting it. However, the oxygen beam result would seem to limit the CO impurity to less than 1%.

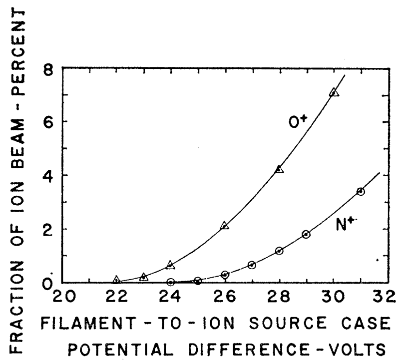

Fig. 10. Atomic ion concentration.

The best evidence that impurities had insignificant effect on the final results is given by the close agreement of the N_2–O_2 and O_2–N_2 ionization cross-section results, Fig. 9. It would be exceedingly fortuitous if the impurity concentrations, charge transfer cross sections, and ionization cross sections were all just right to give agreement in the center-of-mass system. Furthermore, the small impurity concentrations present would imply unreasonably large final ionization cross sections.

Figure 10 shows the N^+ and O^+ concentrations as a function of filament-to-ion source case potential difference for the N_2^+ and O_2^+ beams, respectively. The energy spread of the electrons is characteristic of the tungsten and the coated iridium filaments, and no corrections to the energy have been made. This figure is, therefore, not intended to imply appearance potentials, but only to indicate the performance of the present source as a function of the filament-to-case potential difference. In the nitrogen case the water concentration was monitored along with the N^+, and was found to vary little with filament-to-case potential difference. The ratio of N^+ to N_2^+ was surprisingly high (up to 20% at 60 V), and it appears that the ion source discriminates in favor of the atomic ion. Filament-to-case potential differences of 22 and 21 V for the N_2 and O_2 beams, respectively, were used in obtaining the ionization cross sections.

DISCUSSION

The question of possible excitation in the molecular beams arises immediately when one considers this investigation. Although few data are available which might indicate the extent of excitation in the ion beam, and, although essentially nothing is known of the charge transfer properties of the various states, it is possible to make some general statements concerning the extent of excitation. The low energy of the ionizing electrons rules out many possible states in the ion beams. Furthermore, since ground-state gases are used for the neutralizing gases, the charge transfer is resonant with ground-state ions only. It would, therefore, be expected that, at least at the lower beam energies, a ground-state (electronic) beam would be favored.

Attempts were made to see excitation effects by varying the ionizing electron energy (filament-to-ion source case potential difference). The N_2–N_2 ionization cross section, σ_i, was measured for filament-to-case potential differences between 21 and 24 V. At most a hint of variation was noted for the smallest cross sections measureable. However, in the O_2–O_2 measurement, a significant increase in σ_i was noted for a filament-to-case potential difference of 24 V. At 30.5 V a much larger increase was found. For example, at 30.5 V the O_2–O_2 σ_i value at 15.4 eV (energy scale from Fig. 6) was about 50% greater than for 21 V filament-to-case potential difference. No significant change was noted between 20 and 22 V. The change in σ_i at the high filament-to-case potential difference decreased for increasing beam energy, and no change was evident at the highest beam energies. A similar effect was noted for the O_2–N_2 ionization cross-section measurement.

Although excitation might account for these changes, the production of O^+ seems a more likely explanation. Figure 10 indicates that the O^+ concentration was very small up to 22 V potential difference. It then rose rapidly with potential difference, and was about 8% at 30.5 V. If one assumes a reasonable charge transfer cross section[3,4] for O^+ in O_2, namely, two-thirds of the O_2^+ in O_2 transfer cross section, the O atomic beam would have been about 5% of the total beam at 30.5 V. If one then assumes that the changes in σ_i between 21 and 30.5 V potential difference were due to σ_i for O–O_2, and uses 5% as the concentration of O in the neutral beam, a σ_i value for O–O_2 of 1.8×10^{-17} cm^2 is obtained for an energy of 24.6 eV. (Energy scale from Fig. 6. Note "center-of-mass system" in this case refers to the O–O_2 system.) Although higher than σ_i for O_2–O_2, the inferred σ_i value for O–O_2 is not unreasonable by comparison. Because of the gross nature of the assumptions, the σ_i value for O–O_2 is intended only to show a reasonable alternative explanation to excitation, rather than to give a precise value for the O–O_2 ionization cross section.

The close agreement of the N_2–O_2 and O_2–N_2 results (Fig. 9) indicates clearly that for the nitrogen molecule–oxygen molecule interaction, either few beam molecules were excited or the excitation present had negligible effect on the ionization cross sections over the energy range compared. It would be very fortuitous if an excited O_2 beam would have had exactly the same effect on the cross section as an excited N_2 beam.

The close agreement of the N_2–O_2 and O_2–N_2 results also gives assurance that ionization events, rather than secondary electrons, were indeed being observed. For example, the N_2–O_2 ionization cross section, σ_i, for an N_2 beam of 80 eV (laboratory system) was measured to be 3.8×10^{-18} cm^2. On the other hand, σ_i for O_2–N_2 for an O_2 beam of 80 eV (laboratory system) was measured to be 2.2×10^{-18} cm^2. However, as seen from Fig. 9, the ionization cross sections for N_2–O_2 and O_2–N_2 agree within a few percent when the center-of-mass energy is used. It is improbable that the secondary electron emissions in the two cases would have had just the right relationship to give agreement after the center-of-mass energy correction.

The absence of obvious structure in the ionization cross section vs energy curves for N_2–O_2, O_2–O_2, and O_2–N_2, as contrasted with the N_2–N_2 case, is rather striking. There is a hint of structure in the N_2–O_2 curve, but it is not outside the experimental uncertainty. Without a theoretical model of the interactions with which to make comparisons, one can say little in explanation of the structure or its absence. Work is now in progress in this laboratory toward making mass spectrometric analyses of the heavy-ion products. It is hoped that these analyses will lead to a model of the interactions and an explanation of the structure and cross-section magnitudes.

ACKNOWLEDGMENT

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