Ionization of Helium, Neon, and Nitrogen by Helium Atoms*

HOWARD C. HAYDEN AND NYLE G. UTTERBACK†
University of Denver, Denver, Colorado
(Received 22 April 1964)

The ionization cross sections for He and Ne atoms and N_2 molecules on impact with He atoms have been measured over the laboratory energy range from 30 to 1000 eV. The incident atomic He beam was 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. The ionization cross sections obtained for the He-He and He-Ne interactions were one to two orders of magnitude smaller than the N_2-N_2, N_2-O_2, and O_2-O_2 cross sections studied earlier. The He-N_2 cross section was found to be of the same order of magnitude as the N_2-N_2 cross section. Data were also obtained on He^+-in-He charge transfer and secondary-electron emission from a gold surface by He ions and atoms.

INTRODUCTION

THREE previous papers[1–3] have described the development of fast N_2 and O_2 molecular beams and their application to the measurement of the ionization cross sections for N_2-N_2, N_2-O_2, O_2-N_2, and O_2-O_2 (neutrals on neutrals). The present paper reports an extension of this work to the measurement of the He-He, He-Ne, and He-N_2 ionization cross sections.

The technique was the same as used previously,[2,3] and consisted of three basic parts. First, an atomic helium beam was produced having the desired energy. Second, a He, Ne, or N_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 collisions 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[4] 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 chamber surfaces.

HELIUM ATOMIC BEAM

The apparatus used for producing the fast atomic helium beam was similar to that used previously[1] for the N_2 molecular beam. (However, in the present apparatus mercury diffusion pumps were used throughout.) Helium at a pressure of 40 μ Hg was bombarded by 45-eV electrons in the ion source. The resulting ion beam was analyzed with a mass spectrometer.[3] Table I shows a typical ion beam mass spectrum obtained.

TABLE I. Ion beam mass spectrum.

Mass	Amount (%)	Identification
4	97.	He^+
8	<0.1	He_2^+
14	0.1	N^+
18	0.9	H_2O^+
28	2.0	N_2^+ or CO^+

The energy spread in the ion beam was measured by a stopping potential method,[1] and was found to be less than 0.5 eV at half-maximum.

The helium ion beam was neutralized by charge transfer in helium gas. Figure 1 shows stopping potential curves[1] for the slow ions produced by charge transfer in the neutralization chamber. Figure 2 shows the charge transfer cross section for He^+ ions in He, obtained from the curves (extrapolated values) of Fig. 1 by the method used previously.[1,5] In the present measurement it was necessary to include a correction for the secondary electrons ejected by the slow He^+ ions upon collection.

The uncertainty in the absolute values of Fig. 2 is

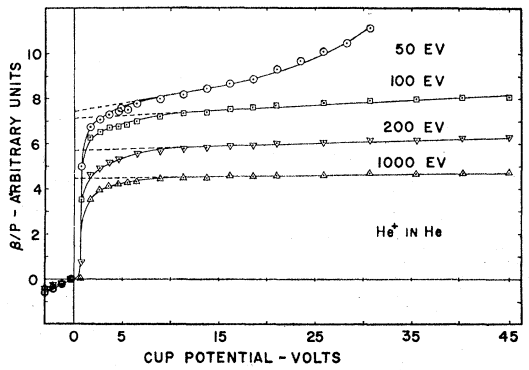

FIG. 1. Ratio β/P versus cup potential.

* Work supported by NASA Grant NsG-392.

† Present address: General Motors Defense Research Laboratories, Santa Barbara, California.

[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] N. G. Utterback, Phys. Rev. 129, 219 (1963).

[4] No distinction was made between ionization and stripping; "ionization cross section" as used here thus includes both processes.

[5] The charge transfer cross section for N_2^+ in N_2 given in Ref. 1 contains a small error due to incomplete suppression of secondary electrons produced by the fast neutral molecules. Elimination of this error changed the shape of the curve slightly, but did not change the absolute values beyond the quoted uncertainty, namely, ±15%.

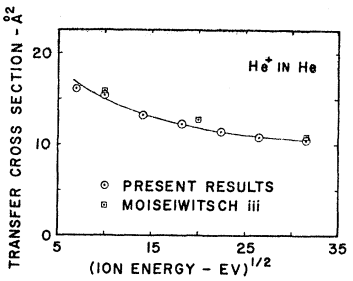

FIG. 2. Charge transfer cross section for He^+ in He.

±15%. Some values from the calculation by Moiseiwitsch[6] are shown for comparison, and the agreement is seen to be good. Figure 2 is also consistent with experimental values reported by other investigators.[7,8]

Figure 3 shows the secondary electron emission coefficients for helium atoms and ions (γ^0 and γ^+, respectively) incident on a contaminated gold surface. The surface was treated only by washing in detergent. The background gas during the measurement was largely helium, and the pressure was 10^{-5} to 10^{-6} mm Hg.

The secondary electron emission coefficients were measured in the same manner as described previously.[1] It was necessary to modify the technique slightly for energies above 300 eV in the γ^+ case because of ion or metastable reflection. Above 300 eV, i_+ was determined by deflecting the ion beam onto the collector plate as in measuring i_1 for the neutral beam case. Below 300 eV, i_1 (deflected beam) and i_+ (on gold surface) were equal to within a few percent, while at 1000 eV i_+ was 15% less than i_1.

Earlier measurements by Rostagni[9] are plotted on Fig. 3 for comparison. Rostagni used copper and brass surfaces, and found no significant difference between them. The present measurement using a gold surface is in excellent over-all agreement. Ghosh and Sheridan[10] and Hagstrum[11] have also measured γ^+ for He on brass and tungsten, respectively, and the agreement is good.

In the present γ^0 measurements, no corrections to B, the neutral beam intensity (see Ref. 1), were made for either the neutralization occurring just in front of and after the neutralization chamber, or for the β/P extrapolated values. The secondary electrons ejected from the neutralization chamber grid upon collection of the slow He^+ ions (i_3, Ref. 1) just compensated these effects.

Figure 3 shows that γ^+ and γ^0 were equal to within 20% at kinetic energies above 400 eV (at least to 1000 eV). This constitutes a consistency check on the method of measuring the neutral beam intensity, under the assumption that γ^+ and γ^0 should be approximately equal at kinetic energies much higher than the ion potential energy.[12] This check is not as clear-cut over the energy range studied here for the He beam as it was for the N_2 beam.[1] The estimated uncertainty in the neutral beam intensity B will be taken to be ±20%.

IONIZATION MEASUREMENTS

The ionization chamber electrodes differed from those used previously[2,3] only in the grid wire spacing. In the present case of the He-He, He-Ne, and He-N_2 measurements, it was found that the background problem[2] due to secondary emission from the ionization chamber grid was serious. For this reason it was necessary to use two different grid spacings in order to make the necessary corrections by comparing grids of different transmission. The 0.0007-in.-diam grid wires were spaced 0.14 in. apart for one grid, and 0.29 in. apart for the other.

The grid corrections for the higher transmission grid were negligible for the He-N_2 case. For the He-Ne case with the same grid, the correction was negligible at high energy but increased to a factor of ½ at the lowest energy. In the case of He-He, a 15% correction was necessary at high energy, which increased to a factor of ½ at low energy. The uncertainties in the grid corrections are included in the uncertainties to be quoted for the ionization cross sections.

In the present measurements, it was found necessary to use much higher collecting voltages (and therefore fields) than previously[2,3] in order to obtain saturation

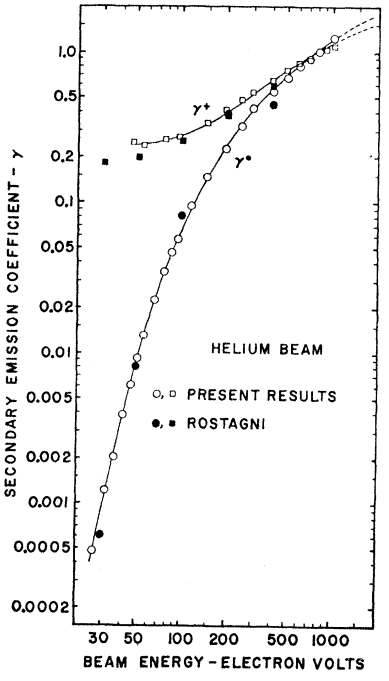

FIG. 3. Secondary electron emission coefficients for He^+ and He.

[6] B. L. Moiseiwitsch, Proc. Phys. Soc. (London) **A69**, 653 (1956).
[7] W. H. Cramer and J. H. Simons, J. Chem. Phys. **26**, 1272 (1957).
[8] H. B. Gilbody and J. B. Hasted, Proc. Roy. Soc. (London) **A238**, 334 (1957).
[9] A. Rostagni, Z. Physik **88**, 55 (1934).
[10] S. N. Ghosh and W. F. Sheridan, J. Chem. Phys. **26**, 480 (1957).
[11] H. D. Hagstrum, J. Appl. Phys. **31**, 897 (1960).
[12] P. M. Stier, C. F. Barnett, and G. E. Evans, Phys. Rev. **96**, 973 (1954).

of the collected current. This was due to the much lower ionization cross section. Fifteen hundred volts was used typically between grid and collector, and four hundred volts between grid and back plate. Voltage saturation curves similar to those obtained previously[2,3] were obtained for the three target gases. No voltage saturation corrections were necessary in the present measurements.

Target pressure saturation curves were also obtained here, and were similar to those obtained previously.[2,3] Pressures typically employed were 0.6 μ Hg for He-He, 0.3 μ Hg for He-Ne, and 0.2 μ Hg for He-N_2. Under these conditions no pressure saturation corrections were necessary.

In the He-Ne and He-N_2 measurements, the effect of the small amount of helium neutralizing gas which leaked into the target gas was negligible. The ratio of impurity helium pressure to target gas pressure was small and the He-He ionization cross section was always smaller than He-Ne or He-N_2 for a given beam energy.

In the He-Ne measurement, the target Ne present in the neutralization chamber accounted for almost none of the neutralization. The He^+ in Ne charge transfer cross section was measured and found to be negligible. This is consistent with other work.[13] On the other hand,

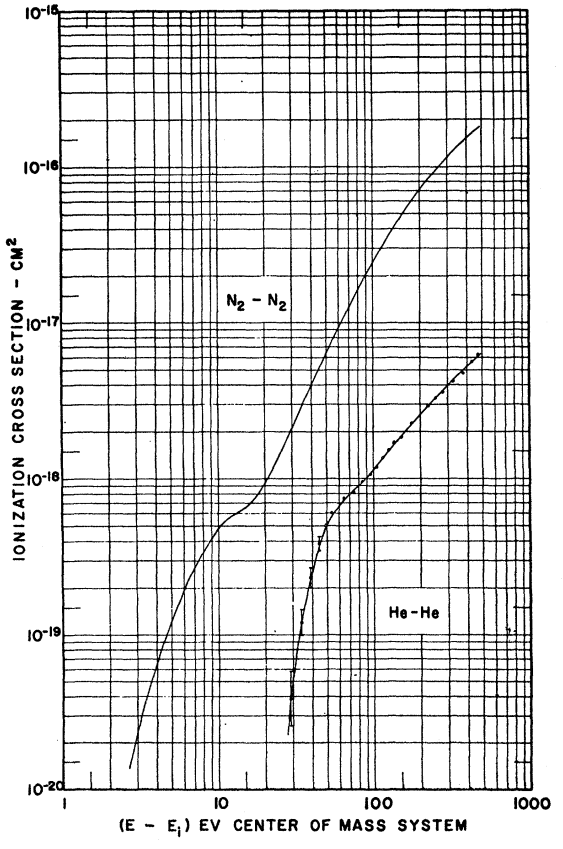

FIG. 4. He-He ionization cross section.

[13] W. H. Cramer, J. Chem. Phys. 28, 688 (1958).

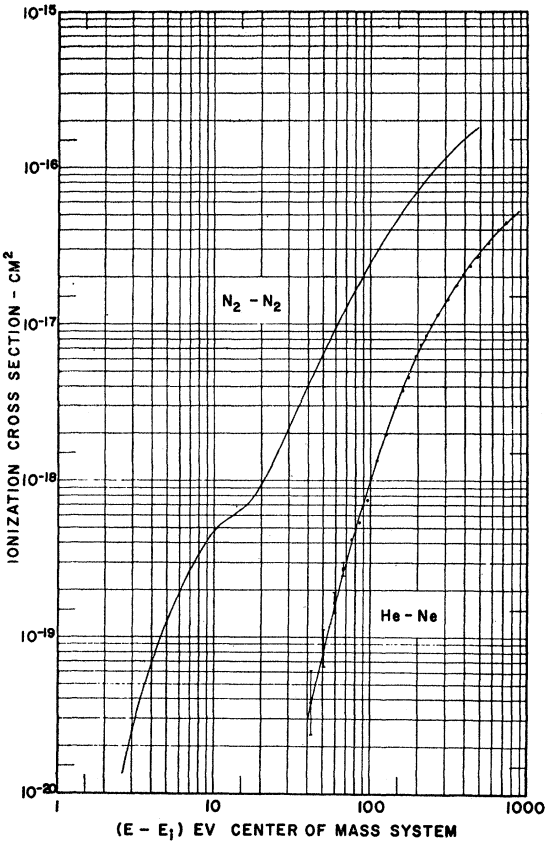

FIG. 5. He-Ne ionization cross section.

in the He-N_2 case, the target N_2 present in the neutralization chamber did account for a small amount of the neutralization. The He^+ in N_2 charge transfer cross section was measured and was found to be consistent with the results of Stebbings *et al.*[14] No inconsistencies were found in the target pressure saturation curves due to variations in the amount of He^+ in N_2 neutralization. However, when N_2 was used entirely as the neutralizing gas, the ionization cross section at high energy agreed with the results with He neutralization but was only $\frac{1}{3}$ as great as the results with He neutralization at low energy. This indicates that considerable scattering takes place when He^+ is neutralized in N_2 at the low energies.

RESULTS

Ionization cross-section values were obtained from

$$\sigma_i = 3.05 \times 10^{-20} (i/PB) \text{cm}^2,$$

where i is collector current in units of 10^{-16} A, P the ionization chamber pressure in units of 10^{-4} mm Hg, and B the neutral beam equivalent current in units of 10^{-10} A. The collector length was 10 cm and the temperature was 22°C.

[14] R. F. Stebbings, A. C. H. Smith, and H. Ehrhardt, J. Chem. Phys. 39, 968 (1963).

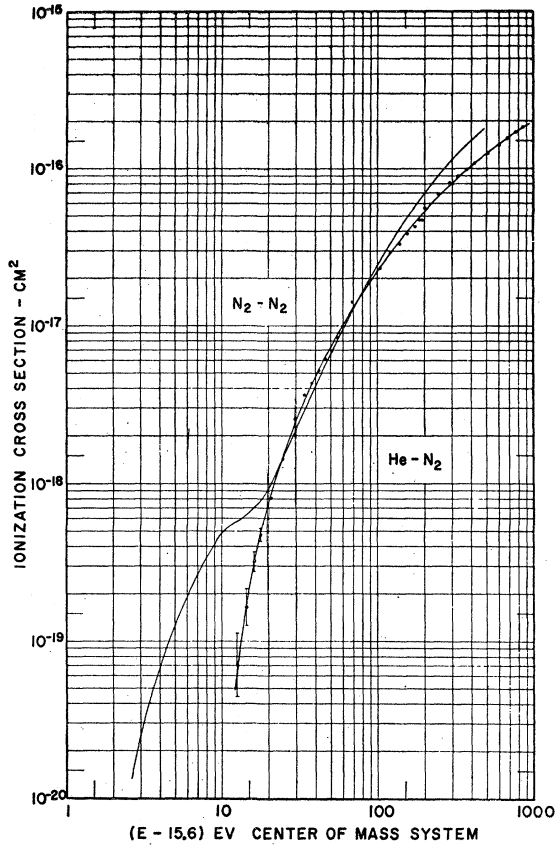

FIG. 6. He-N_2 ionization cross section.

Figures 4, 5, and 6 give the final results for the He-He, He-Ne, and He-N_2 cases, respectively. The previous results[2] for N_2-N_2 are shown for comparison. The abscissa values are the energies in the center-of-mass system (for the species involved) minus the ionization potential for the target. Thus, E_i is 24.5 eV for He-He, 21.5 eV for He-Ne, and 15.6 eV for He-N_2 and N_2-N_2.

The error flags at the low end of the curves indicate random errors in σ_i and are due mostly to uncertainties in i and the grid corrections. The systematic uncertainties in σ_i were estimated to be $\pm 25\%$. The beam energy uncertainty was within ± 1 eV (lab system).

DISCUSSION

The He-He ionization cross section at low energies has been theoretically calculated[15] and experimentally measured[16] by other investigators. The present measurements give a cross section smaller by a factor of five at 200 eV (lab system) and a factor of one hundred at 100 eV (lab system). The reason for this large discrepancy is not apparent. It might be speculated that some secondary electrons were measured as ionization in the earlier measurement. This problem becomes very important at low energies and tends to increase the observed cross sections.

Recent measurements of the He-He and He-N_2 ionization cross sections in the laboratory energy range 15 to 180 keV have been reported.[17] The results of these measurements are plotted on Fig. 7 for comparison with the present results. The ionization cross section for He-He reported here includes both stripping and ionization; the He-He cross section reported in Ref. 17 has therefore been multiplied by two to include both ionization and stripping so a direct comparison can be made. The direct comparison of He-N_2 (Fig. 7) assumes that the stripping was negligible compared to ionization of the target N_2. The work of Barnett and Stier[18] indicates that stripping was negligible by comparison with ionization of the target for both He-Ne and He-N_2 in the present work.

Other measurements[18,19] of He-He at high energy have been reported which are up to 30% lower than Ref. 17 at the highest energies. This difference has been attributed by some to the presence of significant amounts of metastable helium atoms in the beam. Although the 30% difference at the highest energy has no bearing on the comparison intended in Fig. 7, the possibility of excited helium atoms in the present measurements should be considered. Other measurements[20] by one of the present authors (on He-H_2, H_2-He, and He-Ar) have indicated that the helium beam contained a few tenths percent metastables at beam energies above

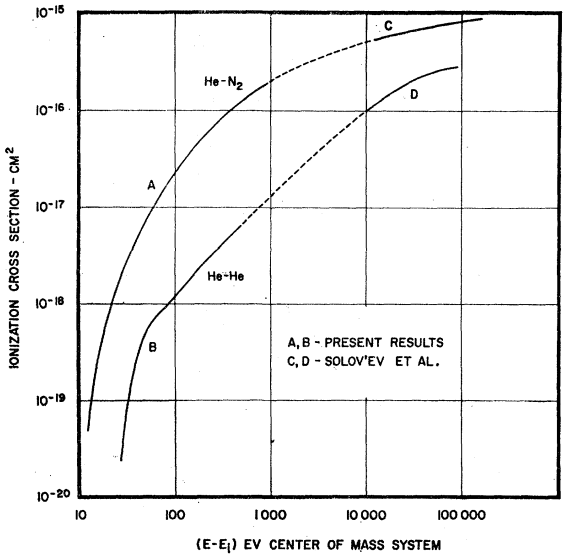

FIG. 7. Comparison of ionization cross-sectiom measurements.

[15] P. Rosen, Phys. Rev. **109**. 348 (1958).
[16] A. Rostagni, Nuovo Cimento **11**, 621 (1934).
[17] E. S. Solov'ev, R. N. Il'in, V. A. Oparin, and N. V. Fedorenko, *Atomic Collision Processes*, edited by M. R. C. McDowell (North-Holland Publishing Company, Amsterdam, 1964).
[18] C. F. Barnett and P. M. Stier, Phys. Rev. **109**, 385 (1958).
[19] S. K. Allison, Phys. Rev. **110**, 670 (1958).
[20] N. G. Utterback, Phys. Rev. Letters **12**, 295 (1964).

50 eV, increasing perhaps to a few percent at 1000 eV. It is hard to see why such small amounts of metastables would have had a significant effect on the He-He and He-Ne results, since the Penning ionization cross section is zero in these cases. A small effect might have been present in He-N_2, but it was not apparent. (In the He-H_2 and He-Ar measurements,[20] characteristic structure was present due to metastables.)

The two percent N_2^+ impurity in the He^+ ion beam (before neutralization) had negligible effect on the present measurements. It was found that N_2^+ did not charge transfer in He or Ne, and therefore the neutral beam contained no N_2 in the He-He and He-Ne cases. A similar argument should hold for the water impurity. In the He-N_2 case, the presence of some N_2 in the neutralization chamber did produce one or two percent N_2 in the He neutral beam. However, the N_2-N_2 cross section is not large enough to cause a significant effect on the results.

It appears that structure is present in the He-He ionization cross section versus energy curve. Berry[21] has reported structure in the ionization electron energy distribution for He-He ionizing interactions. It is probable that these effects are related.

[21] H. W. Berry, Phys. Rev. **121**, 1714 (1961).

PHYSICAL REVIEW VOLUME 135, NUMBER 6A 14 SEPTEMBER 1964

Time-Relaxed Probability Densities and Correlation Functions for Moderately Dense Fluids*

RALPH NOSSAL†
Department of Nuclear Engineering, University of Michigan, Ann Arbor, Michigan‡
(Received 13 April 1964)

Kinetic equations are obtained for the purpose of describing the temporal evolution of two-time (conditional) probability densities for locating subsets of particles moving within an equilibrium assembly. The reduction and solution of the equation for the single-particle density is investigated in considerable detail. Information concerning the short-time evolution of the probability densities is explicitly retained, in order that the applicability of the equations for studying the properties of relatively dense systems be preserved. The expressions for probability densities are used to study the properties of certain associated correlation functions. Expressions for the momentum autocorrelation function are derived. Similarly, certain features of the cross sections for the scattering of slow neutrons are investigated.

I. INTRODUCTION

THE statistical mechanical foundations of linear transport processes and irreversible thermodynamics are now firmly established.[1,2] Parameters appearing in the latter macroscopic theories may be related, quite generally, to appropriate time-relaxed correlation functions describing the motions of the constituent particles of a given system of interest. On the other hand, these general relationships are, in a certain sense, only definitions; there yet remains a rather difficult problem, only partially resolved, of how best to evaluate these expressions when performing explicit calculations.

A related difficulty appears in the calculation of cross sections for the scattering of slow neutrons. It has been shown that the latter can be obtained from expressions for time-relaxed probability densities $G(\mathbf{r},t)$ describing the spatial motion of constituent particles of the scattering medium.[3,4] In general, when attempting to calculate $G(r,t)$ by considering *only* the spatial motion of the particles of the system, semiphenomenological kinetic equations or models are employed.[5,6] However, at least in principle, the spatial probability density may be obtained in a more general fashion by performing appropriate integrations over a probability density function defined, as well, over the momentum space of the particles. The advantage of this procedure is that the latter may be obtained by reduction from an n-particle Liouville equation.

Similarly, the correlation functions mentioned in the previous paragraphs, i.e., those appropriate to analyses of macroscopic transport, may also be obtained from generalized time-relaxed probability densities. Although it is often profitable to devise individual calculational programs specifically for the direct calculation of a

* Based in part on a dissertation submitted to the Faculty of the Graduate School of the University of Michigan in partial fulfillment of the requirements for the Ph.D. degree. Research supported in part by the U. S. Atomic Energy Commission.
† Atomic Energy Commission Predoctoral Fellow.
‡ Present address: Faculté des Sciences, Université Libre de Bruxelles, Bruxelles, Belgium.
[1] M. S. Green, J. Chem. Phys. **20**, 1287 (1952); **22**, 398 (1954).
[2] R. Kubo, J. Phys. Soc. Japan **12**, 570 (1957).
[3] L. Van Hove, Phys. Rev. **95**, 249 (1954).
[4] R. J. Glauber, Phys. Rev. **98**, 1692 (1955).
[5] A. Rahman, K. S. Singwi, and A. Sjolander, Phys. Rev. **126**, 997 (1962).
[6] S. Yip, dissertation, University of Michigan, 1962 (unpublished).