Metastable Atoms and Molecules. I. Metastable States Produced in Charge-Exchange Processes

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A beam of ions of energy between 25 and 360 eV was formed, and permitted to pass through the parent gas at pressures between 5 and 100 μ. The beam then emerged into a highly evacuated space (2 to 9×10^{-8} Torr) and impinged on a target of Mo. When the ions of the beam were deflected and prevented from reaching the target, a target current of secondary electrons or ions to the housing surrounding the target disclosed that neutral particles, formed by charge exchange, were reaching the target, and that these neutrals were excited with long lives compared with a microsecond. The behavior was tested in H_2, N_2, Ne, and Ar, all of which were found to contain excited states in the neutral beam. A new variant of the charge-exchange process thus appears to be occurring in the production of excited neutrals. The essential technique is to cause the charge-changing collisions to occur directly in the source. It is believed that different mechanisms are active in different gases, but that collisions between ions and excited atoms or molecules occur commonly under the experimental conditions existing in this study, where very short times exist between electron-atom collisions and ion-atom-exchange collisions.

INTRODUCTION

DURING the period around 1930, the phenomenon of resonant charge exchange was discovered, in which a positive ion in traveling near to a molecule of its own type could steal an electron and become neutralized without having a scattering collision at all.[1] The original ion proceeded unaltered in speed or direction as a neutral particle. This phenomenon has been utilized to produce fast beams of neutral atoms and molecules. Charge exchange has also been observed to occur in nonresonant cases but with a smaller cross section than in the corresponding resonant case and having a maximum cross section at higher ion speeds by contrast with the maximum at or near zero speed in the resonant case. The subject has been studied rather exhaustively.[2] The basic assumption in resonant charge exchange is that an exact interchange occurs between an ion and its neutral counterpart so that no energy is gained or expended in the interchanges. The particle initially an ion thus becomes a ground-state neutral atom.

The present writer has been concerned for some time that he had evidence in the case of mercury that charge exchange was occurring, but was leaving the neutralized beam particles in excited (presumably metastable) states.[3] The evidence was that the neutral beam produced by charge exchange was far too efficient as an emitter of secondary electrons when it struck a metal target than could be expected of ground-state atoms with relatively low kinetic energies. There is both experimental and theoretical evidence in support of the existence of a threshold kinetic energy for secondary emission by ground-state neutral atoms. Results for argon and for helium are described by Kaminsky.[4] For argon, the threshold appears to be just under 500 eV. The combination of secondary emission at much lower kinetic energies (observed in argon in the present work) with high values of the secondary emission coefficient γ (observed in mercury in Ref. 3) strongly support the belief that beams of excited particles are produced in these cases. A somewhat different comparison is possible in nitrogen. Utterback and Miller[5] report that γ for nitrogen neutrals on a gold-plated surface with a value of 1 at 600 eV declines very steeply even in a log-log plot to 10^{-2} at 100 eV and curves toward an even faster decline at still lower beam energy. By contrast, present results show secondary effects in nitrogen declining only weakly with the applied accelerating potentials in the source. While no measure of neutral particle flux is possible in the present work, there is at least a qualitative suggestion that γ is large. Finally, since times of flight of the neutrals from their formation point to the target in the experiments to be described were in the range of a microsecond, the excited states would appear to have long lives.

DESIGN OF SOURCE

A simple and compact ion source was accordingly built as shown schematically in Fig. 1. The complete source is housed within a Kovar cup which also serves as the negative electrode. It has a pinhole 0.006 in. in diam designated A, through which ions and neutrals formed by charge exchange emerge with some speed and through which some neutral gas also flows out into the pump. The pump used is a Varian Vac-Ion pump with a rating of 140 liters/sec of air.

Inside the cup is a filament F of 0.008 in. tungsten and an anode or plate P. P is positive relative to F by a potential V_1; F is positive to A by a potential V_2. When the filament is heated, thermionic electrons are drawn

[1] H. Kallmann and B. Rosen, Z. Physik **61**, 61 (1930); **64**, 806 (1930).
[2] J. B. Hasted, *Physics of Atomic Collisions* (Butterworths Scientific Publications Ltd., London, 1964), Chap. 12.
[3] R. W. Rostron, J. Appl. Phys. **35**, 2291 (1964).
[4] M. Kaminsky, *Atomic and Ionic Impact Phenomena on Metal Surfaces* (Academic Press Inc., New York, 1965), Chap. 14.
[5] N. G. Utterback and G. H. Miller, Rev. Sci. Instr. **32**, 1101 (1961).

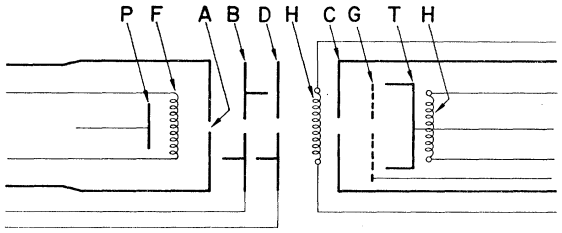

FIG. 1. Schematic diagram showing arrangement of electrodes. The aperture in the Kovar cup which constitutes the ion source is designated A. F is the source filament and P is the anode or plate whose potential relative to F accelerates the electrons. B and D are deflecting electrodes to remove ions from the beam emerging from A but to permit neutrals to continue on to the target T. C is the electron collector surrounding the target and G is a grid for controling the fields at the surfaces of both C and T. The filaments marked H are electron sources for bombardment heating for both C and T.

toward P, ionizing and exciting the gas. The positive ions are drawn toward and past F to A. The source is thus a crude type of ion source which is far from ideal for use in mass spectrographs as the ions may have virtually any kinetic energy from $e(I+V_2)$ to $e(V_1+V_2)$, where I is the ionization potential. The occurrence of charge exchange can spread this energy down to nearly zero. The source was employed, however, for a basically different reason: If a relatively high pressure in the range of 10 to 50 μ is sustained within the cup, a charge exchanging collision between an ion and an atom or molecule becomes reasonably probable. In addition, since the exchanging region coincides with the ionization region in part and is in its entirety within $\frac{1}{2}$ cm of the ionization region, a new possibility is introduced for collisions between ions and atoms or molecules which have also incurred electron collisions and are still in excited states. This feature is believed to provide the essential experimental mechanism for the production of not only a neutral atom beam mixed with the ion beam but a neutral atom beam containing some atoms (or molecules) in excited states of long enough life to suggest the assumption that they are metastable.

BEAM DETECTOR

A mixed beam of ions, neutral ground-state atoms or molecules, and metastables emerges through the pinhole into the high vacuum space. About 6 cm from the pinhole is a rather standard secondary emission target assembly. It consists of a Faraday cup (T in Fig. 1) of Mo 0.010-in. thick as target proper covered by a grid G of Lektromesh with an opening for the beam. The grid has 80 lines/in. and 85% transmission. Surrounding the grid is a collector C completely enclosing the grid and target except for an aperture for admission of the beam.

Between the pinhole in the source and the target assembly is a set of deflector plates which removes positive ions from the beam but permits neutral particles to continue to the target. This arrangement is designated B in the schematic plan of Fig. 1. An additional collimating disc with aperture in the line of flight, labeled D in Fig. 1, was installed to stop off stray ions, secondary electrons produced by them outside of the target assembly, and finally, to be operated at various potentials to collect charges anywhere in the vicinity of the target assembly and keep them out of the sensitive detection volume. In practice, it was found that this electrode could be operated at potentials ranging from 100 to -100 V without alteration of the secondary current readings within the collector. The target assembly finally was provided with two tungsten filaments, labeled H in Fig. 1, which could be used to provide electrons for bombarding the target T and the collector C to flash heat them for degassing and cleaning. In normal use, a bombarding current of 150 to 300 mA at 600 V struck the target heating it to white heat in a few seconds. If this operation had not been done for 16 h, a surge of gas pressure observable on the ionization gauges was produced. No such surge was noticeable in subsequent flashings in the next hour's time.

The entire assembly of Fig. 1 is mounted inside a 4-in. stainless-steel flange pipe with glass connectors to the gas-filling system. The system is standardly baked out before use, and the electrodes P, T, and C are heated by electron bombardment.

Using neon in the source, an ion current to the target approaching 10^{-8} A could be produced. Electrodes A, B, and D were at zero voltage for this observation. By making the grid and housing structure alternately positive and negative relative to the target, secondary electrons could be drawn off the target, causing the target meter to show the sum of incident ions arriving plus secondary electrons leaving, or could be retained on the target causing the meter to show the positive-ion current alone. The secondary electrons from neon ions were found by this method to disclose the degree of dirtying fo the Mo target as described by Hagstrum.[6] The value of γ_i was somewhat over 0.20 for the clean target and dropped to about 0.10 overnight. Since the background pressure was between 2 and 9×10^{-8} Torr during runs, the target was believed to be atomically clean for at least a minute or two after flashing.

With the beam cleared of ions by the application of voltages to the ion deflectors, a secondary current could be observed for all gases tried to date (H_2, N_2, Ar, Ne). The secondary current was of the order of magnitude of 10^{-2} to 10^{-3} of the positive-ion current reaching the target without the deflector voltage. The nature of this secondary current is described in paper II[7] because it constitutes a separate set of findings.

ANALYSIS OF THE NEUTRAL BEAM

The primary analysis of the neutral beam reaching the target was made by the secondary electron emission.

[6] H. D. Hagstrum, Phys. Rev. **104**, 1516 (1956).
[7] R. N. Varney, following paper, Phys. Rev. **157**, 116 (1967).

Secondary emission currents ranged from 10^{-14} to 10^{-10} A. Values of the total applied voltage, V_1+V_2, in the source ranged from 25 to 360 V. The neutral beam kinetic energy, while subject to variations depending on the exact point at which each ion lost its charge, could not exceed $e(V_1+V_2)$. With the deflecting voltages applied to electrodes B and D, there was no flux of incident charged particles onto the target, a matter which could be verified by proper use of potentials on the grid of the particle detector to suppress secondary emission. The appearance of the secondary current, combined with the low kinetic energy of the neutrals (well below 500 eV), is the primary evidence that excitation of beam particles exists.

A concern arises as to whether part or all of the incident neutrals striking the target might be photons from the source. The role of photons in the secondary emission was shown to be less than 1% by time-of-flight studies. The voltage V_1 in the source, responsible for giving kinetic energy to the electrons and ionizing the gas initially, was applied only in pulses. The pulses were 0.2-μsec long with a repetition rate of 10^5/sec. The voltage on the grid in the target assembly was made negative to suppress secondary emission except during an overriding positive pulse also of 0.2-μsec duration which could be applied at controlled interval after the source pulse. The meter in the target circuit thus measured secondary emission only if the emission occurred during the time the secondary collector pulse was on. The meter in this case read the accumulated current of the rapidly repeating pulses. With the time interval between the source pulse and the detector pulse set for zero, no detectable reading was shown by the meter for any of the gases used. The time of flight of photons should have been 2×10^{-10} sec, hence essentially zero on the time scale of the pulses. Current was observed, however, with the detector pulse in the range of 0.5 to 2 μsec later than the source pulse, the normal time of flight for the appropriate massive particles, neutral atoms and molecules with 100 eV of kinetic energy, a reasonable mean value to be expected from the value of V_1+V_2 used. The time-of-flight measurements could not be used to identify, for example, whether the particles in hydrogen were H or H_2, because the velocity was too uncertain. However, hydrogen, nitrogen, and neon particles could be discerned to have significantly different times of flight.

The time-of-flight studies also confirm that the metastable particles are much faster than thermal particles. Times of flight for thermal metastables of the gases treated in this paper would have ranged from 30 to 100 μsec. The metastables thus appear clearly to arise from the process of charge exchange, that is, that they acquired kinetic energy as ions and then became neutralized.

One further experimental feature was introduced. The entire target and collector assembly of Fig. 1 was replaced by a new target set obliquely to the incident beam with a collector differing from C of Fig. 1 in having an opening on the side so that particles leaving the target at right angles to the beam could escape. Opposite this opening, a Varian Residual Gas Analyzer (a quadrupole mass spectrometer with an electron multiplier as the detector element) was mounted. This arrangement disclosed that the primary, neutral beam striking the target not only released secondary electrons but also caused emission of positive ions, negative ions, and photons under various circumstances.

CONCLUSIONS

In this paper, a variation of the production of neutral beams by the familiar method of ion-molecule charge exchange is described. The method differs from the common one of separating the ion source from the charge-exchanging region in the respect that the two regions are actually combined into one single small chamber. The modification greatly shortens the time interval between ion formation and charge exchange, and it also allows a chance of exchanges between ions and metastable neutrals. The strong activity of the neutral beams on striking a target, even at low kinetic energies, is construed to be evidence that the neutral beam contains excited particles, presumably in metastable states, because in at least several known cases, the older method yields no secondary activity at the target. Analysis of the beam by its target activity is presented in paper II.

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