due to secondary electrons. In the course of some experiments on sputtering by positive ions of neon, it was observed that the energy delivered to a sputtered wire target was much less than that calculated from the current and the voltage drop at the electrode.

This was ascribed to the fact that part of the measured current was due to secondary emission by metastable atoms. As Oliphant's results show that the difference in energy between the metastable state and the work function of the metal is taken up by the emitted electron, we may assume that the total energy to the target is carried by positive ions. Thus the positive ion current may be calculated from measurement of energy delivered to the target and the relation between secondary electron current and positive ion current determined.

A second method of calculating the contribution of secondary electrons to collector currents is the space charge equation developed by Langmuir and Mott Smith (G. E. Rev. 1924). If the secondary emission is due to metastable atoms, it will be proportional to the collector area, whereas the positive ion current is proportional to the sheath area. It has been proved by Langmuir that the secondary electron emission from a negatively charged collector does not vary by more than 0.1 percent per volt. A change of this magnitude can be neglected when dealing with a cylindrical collector of small diameter. If, with such a collector, we choose conditions such that the sheath area is large (i.e., low discharge currents and high voltages) we may assume as a first approximation that the current is due entirely to positive ions. On this basis an approximate value of sheath thickness can be calculated. By comparing the rate of change of collector current to the rate of change of sheath area, the random positive ion current density can be determined by a series of approximations. From this value, the contributions of secondary electrons to collector current is readily computed. Calculation by this method shows that in the positive column of a neon tube of 5 cm diameter at 300 barves pressure and operating at 0.4 amperes discharge current, the secondary electron emission from a tungsten wire is 7.5 m.a./cm² compared to a random positive ion current density in the discharge of 0.82 m.a./cm². This means that a wire collector of 0.005 cm diameter and 3.5 cm long, 100 volts negative to the discharge, receives a positive ion current of 0.91 m.a. and emits a secondary electron current of 0.42 m.a. Results giving the secondary electron current as a function of discharge current and pressure will be given in a future publication.

CLIFTON G. FOUND

Research Laboratury, General Electric Company, Schenectady, New York, December 12, 1929.

Frequency Distribution in Raman Spectra

If we grant that most of the lines in the Raman spectra of organic compounds correspond to fundamental frequencies in the molecule, it is possible to explain the distribution of the frequencies in the spectra by assuming that the non-polar chemical bond always has about the same elastic constants independent of the atoms which it joins or their position in the molecule. In other words variations in frequency appear to be due in most part to the variations in the masses of the particles vibrating rather than to variations in bond strength when the bonds involved are non-polar single bonds.

We have taken the following values as representing the average state of the nonpolar single bond: $k_1=4\times10^5$ dynes per cm for streching the bond; $k_1=0.66$ dynes per cm for bending the bond. In other words k_1 is the restoring force on an atom when it is moved unit distance along the line in which we think the bond to act, and k_2 is the restoring force when the atom is moved perpendicular to this line, the rest of the molecule being held still. This implies; (1) that the bond is a definite localized force closely analogous to a spring, at least for the small displacements involved in thermal vibration which are of the order of 0.2A; (2) that all bonds have a common mechanism as was first suggested by G. N. Lewis when he proposed the electron pair theory.

These assumptions lead us to expect the following groups of frequencies in the Raman spectra of typical organic molecules. (Values are in cm^{-1} .)

- I. Hydrogen attached to C, O, or N vibrating
 - a) along bond: calc. 2730; obs. 2830-3050
 - b) perpendicular to bond: calc. 1500-1200; obs. 1500-1200.
- II. Vibration of groups of C, O, and N atoms a) along bonds:
 - 1. Simple pairs 1068-1000
 - Example: C–O; calc. 1000; obs. 1031 (in CH₃OH)
 - 2. Several bonds restricting one atom. 1300-1000.
 - 3. Motions involving several atoms such as in long chains: 1000-400 or lower depending on length of chain.
 - 4. Single groups attached to heavy radical. 150-250.
 - Example: CH₃-C₆H₄ obs. 215. b) Perpendicular to bonds:
 - In straight chains: 450-150 or lower depending on length of chain.

Example: CH_3CH_2OH calc. 415; obs. 450.

 In ring structure: 600-300. Example: Benzene calc. 612, 306; obs. 605, 360.

To the Editor of the Physical Review Dear Sir:

It has been called to my attention that the experiment described in the last paragraph of my "Letter" of November 15, Phys. Rev. 34, 1392 (1929) really proves nothing at all. For it appears that the copper gauze used as an electrostatic shield also effectively decreases the electromagnetic field inside the tube. As a matter of fact, the electrostatic shield originally suggested to me by Dr. Breit consisted of a system of wires running parallel to the tube. I used, instead, the more convenient copper gauze, for at the time it did not occur to me that the electromagnetic forces inside the tube would be decreased because of the eddy currents set up in the gauze.

Accordingly, I have recently repeated that experiment using an electrostatic shield similar to the one originally suggested by Dr. Breit. It consisted of a set of parallel wires about 1 cm apart, joined at each end by a ring with a small gap in it. The eddy currents induced

- III. Heavy atoms such as Cl, Br, and I or groups such as NO₂, COOH.
 - a) Vibration along bond.
 - Example: Cl-C $_6H_5$ calc. 540; obs. obs. 607.
 - b) Vibration perpendicular to bond. Example: $Cl-C_6H_5$ calc. 215; obs. 195.

The observed spectra are almost without exception in accord with the above scheme. Slight deviations may be due to the fact that actually the strength of a bond may vary by twenty percent from the average value and that exact analysis of the motion involved in many types of vibration is impossible. Further confirmation is given by the fact that with the help of the above the heat capacity can be calculated as a sum of Einstein and Debye functions, and the optically observed frequencies can be assigned in quite a definite and unequivocal manner to the different degrees of freedom. The values so calculated agree well with the experimentally observed values in the dozen cases for which data are available.

DONALD H. ANDREWS Department of Chemistry, Johns Hopkins University, December 10, 1929.

in such a shield would be negligible. Consequently it would function purely as an electrostatic shield. It was found that as soon as the tube was surrounded by this shield, the discharge ceased. Hence, we must conclude, as before, that the electrodeless discharge is principally an electrostatic phenomenon.

There seems to be one exception to this conclusion. In a recent paper, K. A. MacKinnon [Phil. Mag. 8, 605, (1929)], has shown that the luminous annular ring which appears in electrodeless discharge under certain conditions of excitation is undoubtedly produced by electromagnetic forces. It seems that only spark excitation (i.e. damped waves) will produce this "ring." I have always used c.w. excitation and consequently, have never observed it.

> Very truly yours, Charles J. Brasefield

University of Michigan, December 11, 1929.