well with such a shift of the 2S_i level. With the present precision, we have not yet detected any discrepancy between the Dirac theory and the doublet separation of the P levels. (According to most of the imaginable theoretical explanations of the shift, the doublet separation would not be affected as much as the relative location of the S and P states.) With proposed refinements in sensitivity, magnetic field homogeneity, and calibration, it is hoped to locate the S level with respect to each P level to an accuracy of at least ten Mc/sec. By addition of these frequencies and assumption of the theoretical formula $\Delta \nu = \frac{1}{16}\alpha^2 R$ for the doublet separation, it should be possible to measure the square of the fine structure constant

times the Rydberg frequency to an accuracy of 0.1 percent.

By a slight extension of the method, it is hoped to determine the hyperfine structure of the 2^2S_i state. All of these measurements will be repeated for deuterium and other hydrogen-like atoms.

A paper giving a fuller account of the experimental and theoretical details of the method is being prepared, and this will contain later and more accurate data.

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On Self-Quenching Halogen Counters

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 $\mathbf{S}^{\mathrm{OME}}$ considerations relating the spectroscopic and photochemical properties of polyatomic gases with their use in Geiger-Mueller counters have been developed by the writer.1 The selfquenching counter is able to operate without the usual large resistance because of the absence of secondary emission of electrons when the positive ion sheath reaches the cathode and is neutralized. The neutralization of the ions (at about 10^{-7} cm from the wall) results in neutral atoms or molecules having an excitation energy of $(I-\varphi)$ approximately, where I is the ionization energy and φ the photoelectric work function of the surface. In the case of a monatomic or diatomic (non-quenching) gas this excitation energy is transferred to the metal in about 10⁻¹² sec. and secondary electrons are liberated if $I > 2\varphi$. In the case of most polyatomic gases (with four or more atoms), the neutralized molecules will predissociate (in about 10^{-13} sec.) before they can make an inelastic collision with the wall, and the emission of secondary electrons will be negligible. In order to determine whether a given gas will show self-quenching action, it is sufficient to examine its absorption spectrum at wave-lengths corresponding to an excitation energy of $(I-\varphi)$. Continuous absorption, or a line broadening corresponding to a predissociation lifetime of 10⁻¹³ sec., indicate that the molecule undergoes primary photo-decomposition. Such a gas will make a self-quenching counter. If a mixture of quenching and non-quenching gases is used, the counter will show self-quenching action only if the ionization potential of the non-quenching gas exceeds that of the quenching gas. Under these circumstances electron transfer changes the composition of the positive ion sheath so that, when it reaches the cathode, there is a negligible number of non-quenching ions. A more detailed discussion will be found in reference 1.

We should like to point out here that the mechanism of secondary-emission quenching is compatible, under special circumstances, with the

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¹S. A. Korff and R. D. Present, Phys. Rev. **65**, 274 (1944). The theoretical considerations in this paper were mainly developed by R. D. Present; the experimental work and its interpretation were done mainly by S. A. Korff.

quenching gas being diatomic. The halogens Cl₂, Br₂, and I₂ are examples of diatomic gases which would be expected to show self-quenching action.2 The absorption spectra of these gases have been investigated into the far ultraviolet. The ionization potentials are respectively 13.2, 12.8, and 9.7 volts. If the cathode surface is carbon³ (photoelectric work function ≈5 volts) the values of $(I-\varphi)$ correspond to wave-lengths of 1500, 1600, and 2600A for the three gases, respectively. In this region of the spectrum both Cl₂ and Br₂ show continuous absorption corresponding to primary photo-decomposition. One should expect that these gases would give rise to no secondary emission. The ultraviolet absorption spectrum of I2 shows several bands in the region from 2760 to 1750A.5 Several of these bands are sharp and are accompanied by fluorescence, indicating the absence of predissociation except as induced by collisions. 6 Decomposition of the neutralized I₂ molecules at the cathode surface is not indicated as in the case of the other halogens. Nevertheless, if the cathode surface be of carbon,³ secondary emission cannot occur because the ionization potential is less than twice the work function. The work function of carbon is 4.7 volts for ordinary contamination; however, halogen contamination generally raises the work function by several tenths of a volt,7 For all surfaces for which $I < 2\varphi$ the secondary emission by positive ions is quenched.

³ The inner surfaces of the cathodes used in reference 2

were coated with Aquadag (graphite).

⁶O. Oldenberg, Zeits. f. Physik **25**, 136 (1924); P. Pringsheim and B. Rosen, Zeits. f. Physik **50**, 1 (1928); D. T. Warren, Phys. Rev. **47**, 1 (1935).

⁷C. Ouellet and E. K. Rideal, J. Chem. Phys. 3, 150

The possible effects of electron attachment cannot be neglected when the halogens are used in appreciable concentrations. After the initial ionizing event there will evidently be a small number of negative ions moving in toward the center wire from the outer regions of the counter. When a negative ion reaches the high field region near the wire, an electron will detach itself and initiate a new avalanche unless the field is below the counting threshold. As the positive ion sheath moves outward, in a fast counter the field near the wire increases; the threshold field is reached when the positive ions have traveled the critical distance (about half the distance to the wall⁸). The negative ions in a fast halogen counter must all have been neutralized before the positive ion sheath reaches the critical distance. The reason for this is found partly in the greater mobility of the negative compared to the positive ions.9 Furthermore, the negative ions may be neutralized in crossing the positive ion sheath (the electron affinities of the halogen atoms are less than the ionization potentials of the molecules). If the partial pressure of halogen gas is not too large, it appears likely that the performance of these counters should be unimpaired by multiple pulses and spurious counts arising from negative ions. However, the concentration of halogen must be large enough to quench metastable raregas atoms.² Finally, just as in the case of oxygen counters, 10 attachment of the electrons formed in the initial ionizing event can cause a mean time lag of as much as 10^{-4} sec. between the passage of the ionizing particle and the initiation of the discharge (unless the concentration of halogen is only a few percent). This would make the halogen counter unsuitable for coincidence experiments in which the efficiency must be high and the resolving time low.

10 M. E. Rose and W. E. Ramsey, Phys. Rev. 59, 616

(1941).

² S. H. Liebson, Bull. Am. Phys. Soc. 22, 2 (1947), has recently reported that counters filled with suitable mixtures of halogen and noble gases show self-quenching (fast) counter action.

⁴ Both the Cl₂ and Br₂ continuous absorption regions in the ultraviolet extend down to 1560A (limit of observations) and the maximum of the Cl₂ absorption appears to be near this value. H. Cordes and H. Sponer, Zeits. f. Physik **63**, 334 (1930).

⁶ Predissociation induced by gas collisions would be ineffective in preventing secondary emission since the neutralized molecule would make an inelastic collision with the wall before it could collide with another molecule. The van der Waals field at the surface has a sufficient range to induce predissociation of the neutralized molecule but the interaction is insufficient to reduce the lifetime to less than 10⁻¹¹ sec.

⁸ H. G. Stever, Phys. Rev. **61**, 38 (1942).

⁹ Immediately after electron attachment the halogen molecule ion dissociates into an atomic ion and a neutral atom. Because of its smaller mass and effective cross section the negative atomic ion should have a greater mobility than the positive molecular ion. The discharge terminates before the mobilities can be affected by impurities.