Electron Scattering in Bromine Gas*

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Calculations have been made on the angular dependence of electron scattering in bromine gas with the scattering phases obtained in a recent paper. For the lower energies it is essential that atomic polarization be included in the calculations of the phase defects. The results are compared with previous experimental work by Arnot.

IN a paper recently published,[1] the authors have calculated the fine structure to be expected on the high frequency side of the Br K-absorption edge in gaseous bromine. The position of the transmission band as calculated agrees well with that obtained experimentally by means of a double crystal spectrometer. The calculated intensity, on the other hand, is far too low. As a check on the values of the electron scattering phases used in the previous paper, we have calculated the dependence on angle of the elastic scattering of electrons from the bromine molecule and compared the predicted scattering with the empirical results of Arnot.[2]

THEORY AND CALCULATIONS

The intensity of electron single scattering in a monatomic gas at the angle θ from the direction of the incident beam is given by the expression[3]

$$I(\theta) = \frac{1}{4p^2}\left\{ \sum_{l=0}^{l=\infty} (2l+1)[e^{2i\delta_l}-1]P_l(\cos\theta)\right\}^2,$$

where p is the momentum of the scattered electron, δ_l is the phase shift upon scattering of the partial electron wave of angular momentum l and $p_l(\cos\theta)$ is the lth order Legendre polynomial. If the electron momentum p is measured in "atomic units" $(p=(2E)^{\frac{1}{2}})$ the intensity $I(\theta)$ is said also to be in atomic units.

If the gas is diatomic the molecular scattering I_m is somewhat different from the atomic and is given by[4]

$$I_m(\theta) = 2I_a(\theta)\left[1+\frac{\sin x}{x}\right],$$

where $x = 2pp \sin(\theta/2)$ and ρ is the interatomic distance. In general in the angular region experimentally convenient the corrective term for the molecule is relatively unimportant and the molecular scattering is approximately twice the atomic.[5]

The problem of calculating the electron scattering as well as that of the fine structure of the x-ray absorption edge of bromine is complicated by the fact that the self-consistent field has not as yet been calculated. Two methods have been used for the determination of electron scattering phases—both admittedly only approximate in nature. The first[5] was to obtain a Hartree field for bromine by extrapolation from the known Hartree field for Rb+. The phase defects were then computed by either the Jefferys[6] or the Born[7] approximate formula. The major criticism of this method as used is that the final field so obtained is uncorrected for the polarization of the scattering atom by the scattered electron. The errors in the resulting phases are especially large for the higher values[8] of l. The second method is to assume the Hartree field for krypton corrected for polarization[8] and extrapolate the "exact" phases for krypton to obtain those for bromine by a method given by Henneberg.[9] The major criticism of this method is that the

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[1] T. M. Snyder and C. H. Shaw, Phys. Rev. **57**, 881 (1940).

[2] F. L. Arnot, Proc. Roy. Soc. **A144**, 360 (1934).

[3] N. F. Mott and H. S. Massey *The Theory of Atomic Collisions* (Oxford University Press, New York, 1933), p. 24.

[4] H. S. Massey and E. C. Bullard, Proc. Camb. Phil. Soc. **29**, 511 (1933).

[5] F. L. Arnot and J. C. McLauchlan, Proc. Roy. Soc. **146**, 662 (1934).

[6] F. L. Arnot and G. O. Baines, Proc. Roy. Soc. **A146**, 651 (1934).

[7] N. F. Mott, Proc. Camb. Phil. Soc. **25**, 304 (1929).

[8] J. Holtsmark, Zeits. f. Physik **66**, 49 (1930).

[9] W. Henneberg, Zeits. f. Physik **83**, 555 (1933).

extrapolation formula assumes the Thomas-Fermi form of the atomic field. For low energies the latter method is the better and has been used in the present work.

In applying the second method to bromine the question immediately arises as to whether the atomic polarizability of bromine is the same as that of krypton. The comparison may be made by means of refractive index data. The molar refractivity may be expressed in terms of the atomic refractivity of the constituent atoms as follows:[10]

$$K = \sum_i N_i k_i,$$

where N_i is the number of atoms of type i in the molecule. But

$$k_i = \left(\frac{M}{\rho}\right)_i \frac{n_i^2 - 1}{n_i^2 + 2} \approx \frac{2}{3}\left(\frac{M}{\rho}\right)_i (n_i - 1).$$

Since M/ρ is a constant for all gases, the molar refractivity is given by

$$K = \frac{2}{3}\frac{M}{\rho} \sum_i N_i(n_i - 1).$$

The refractive indices of krypton and bromine have been measured in the region from 4000 to 7000A.[11] Calculation of the atomic refractivities as indicated above shows that k for bromine is about 25 percent greater than that for krypton. In view of the approximate nature of the correction for polarization, it may be concluded, then, that Holtsmark's correction for polarization[12] of krypton may be applied to bromine.

The angular distribution of electrons elastically scattered in bromine vapor has been investigated experimentally by Arnot.[2] He used electron

TABLE I. *Scattering phases.*

PHASE	ARNOT AND McLAUCHLAN 15 v	41 v	SHAW AND SNYDER 15 v	41 v
δ_0	11.02	10.20	10.71	9.78
δ_1	7.75	7.23	8.13	7.47
δ_2	3.36	3.94	4.12	4.28
δ_3	0.035	0.535	0.30	0.96
δ_4	0	0.092	0.13	0.34
δ_5	0	0.024	0	0.18
δ_6	0	0	0	0.085

[10] J. H. Van Vleck, *Electric and Magnetic Susceptibilities* (Oxford University Press, 1932) p. 82.
[11] Landolt-Börnstein, *Tabellen II*, p. 961.
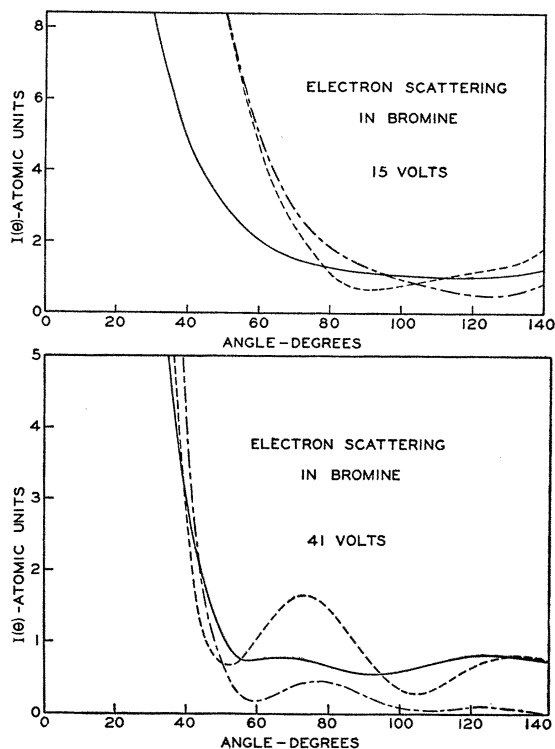[12] J. Holtsmark, Zeits. f. Physik **55**, 437 (1929).

FIG. 1. —————— theory—Arnot and McLauchlan; ———————— theory—Shaw and Snyder; ——————— experiment—Arnot. The scale of the experimental curve is adjustable by an arbitrary multiplying constant.

energies of 15, 41, 80, and 121 ev. Table I lists the scattering phases used by Arnot and McLauchlan[5] and those of the present paper.[1] As discussed in a previous paragraph, the difference is especially marked for the higher order phases and is due to the fact that polarization was included in the latter work. Calculations were not completed for 80 and 121 ev because it was found for these voltages that phases higher than the sixth were required.

Figure 1 shows the experimental data of Arnot, the theoretical curve of Arnot and McLauchlan, and the theoretical curve of the present authors. That the agreement between experiment and theory is not closer may be due both to the approximations in the theory and to errors in the experiments. Errors in the experiments would probably be due to the effects of space charge and to low resolving power. Arnot considered the effects of the radial field produced by the electron beam[13] and came to

[13] F. L. Arnot, Proc. Camb. Phil. Soc. **27**, 73 (1931).

the conclusion that errors from this source were negligible for his experiments in mercury vapor. However, since the electron affinity of the halogens is large it is possible that an appreciable space charge might be built up through the formation of negative ions by electron capture.

Assuming a simplified form for the molecular field, Fisk[14] extended the quantum mechanical method of Allis and Morse[15] to the calculation of the total cross section for elastic scattering of slow electrons from diatomic molecules. He has completed calculations for nitrogen, oxygen, hydrogen and chlorine. Excellent agreement between experiment and theory was obtained

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[14] J. B. Fisk, Phys. Rev. 49, 167 (1936); 51, 25 (1937).
[15] W. P. Allis and P. M. Morse, Zeits. f. Physik 70, 567 (1931).

for the first three gases, but wide deviations were found for chlorine, for which the total cross section for scattering (elastic and inelastic) was measured. The discrepancy was interpreted as meaning that considerable inelastic scattering was present.

It would be instructive to apply Fisk's method to bromine, for which Arnot has made measurements for *elastic* scattering. The agreement for low energies would probably not be very good in view of the strong effect of atomic polarization, which in Fisk's theory is ignored. The agreement, however, should be considerably better than that for chlorine because of the absence of inelastically scattered electrons in the experimental work.

Scattering of Fast Electrons in Helium

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Failure of the quantum mechanical theory of elastic scattering to account for experimental results of Kuper on scattering of 50- to 80-kilovolt electrons in helium has been explained by neglect of the inelastic scattering. Computation of the cross sections including inelastic as well as elastic collisions by an approximate method yields satisfactory agreement without requiring any modification of the theory.

MEASUREMENTS by Kuper[1] on the scattering of fast electrons (50 to 80 kilovolts) in rare gases were in satisfactory accord with the quantum mechanical theory for elastic scattering in the cases of argon and neon. In helium, however, the observed scattering cross sections were much larger and increased more rapidly at the smaller angles than the elastic scattering theory predicted.

In spite of the fact that the resolving power of the electrostatic energy analyzer was such as to permit passage of electrons which had lost as much as 100 electron volts it was assumed that

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[1] J. B. H. Kuper, Phys. Rev. 53, 993 (1938).

inelastic scattering was absent for two reasons. First it was thought that at these energies the losses would be large compared to 100 electron volts, and second that if only elastic scattering was found in neon and argon the same would be true in helium. Both of these assumptions seem to be wrong. The first would be true if we were dealing with larger angles but at angles smaller than 2° the predominant energy losses will be well under 100 electron volts. This can readily be seen by considering the momentum changes involved. The second assumption neglects the fact that while the inelastic cross section (for losses not exceeding 100 ev) will vary approxi-