

secondary electrons. This absorption can itself account for the decrease in the value of  $R$  under consideration. It is also instructive to find out the variation of the ratio  $dR/RdV$  with the atomic number instead of with the density. The kind of absorption in this case may be due to the collisions of the outgoing secondary electrons with the bound orbital electrons within the atoms, while that part of the absorption depending on the grating constant may be due to the collisions of the secondary electrons with the free or valency or structure electrons.<sup>4</sup> The grating constant may be taken as a measure of the probability of the collisions of the secondary electrons with those mentioned above. The experiments of Davisson and Kunsman and later of Davisson and Germer<sup>5</sup> suggest that the largest secondary emission is in the direction of the primary beam when the incidence is normal.

These considerations indicate that the decrease of  $R$  at higher potentials is mainly due to the absorption of the secondary electrons due to their collisions with the bound or partly bound or free electrons. The efficiency of production of the secondary electrons would therefore be a constant after a certain potential is reached (this potential depending on the nature of the metal and the crystal surface) if there were no absorption of the secondary electrons.

#### A Theory of the Ozone of the Lower Atmosphere and Its Relation to the General Problem of Atmospheric Ozone

The observed failure of radiation in the region 2200–2000Å to penetrate the earth's atmosphere has made it of considerable interest to identify the substances which are responsible for the stopping of this radiation lying between the ultraviolet absorption of ozone and that of oxygen. The absorption of light by the molecule  $O_4$ <sup>1</sup> in the earth's atmosphere can account for the removal of the greater part of this radiation. That this is the case may be shown in an approximate way by using the absorption coefficient of  $O_4$  and its dissociation constant computed in Ref. 1, and an oxygen distribution in the atmosphere given over the heights 0 to 11 km by the expression  $n = 5.38 \times 10^{18} e^{-1.12 \times 10^{-6} z}$  molecules/cc, and above 11 km by the expression  $n = 1.57 \times 10^{18} e^{-1.73 \times 10^{-6} z}$  molecules/cc, where  $z$ , the height, is in centimeters, this distribution resembling closely that given in Table 2,

The results mentioned above derive additional support from the fact that adsorption of gases by the crystal surface increases the ratio  $dR/RdV$  considerably. This was found to be the case with the 110 face of a nickel crystal.

Also careful experiments by Nakaya<sup>6</sup> show that a similar saturation effect exists in the photoelectric efficiency curves for soft x-rays at voltages in the neighborhood of 3000 volts for ordinary metals. It is highly probable that if the potentials are carried much higher, these curves may also show a similar fall in value due to the absorption of the photoelectrons in the medium of the photoelectric target.

More accurate work on the secondary electron emission from different metals and crystal faces is necessary to settle these interesting questions.

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<sup>4</sup> O. W. Richardson, Proc. Roy. Soc. **A128**, 63 (1930).

<sup>5</sup> C. J. Davisson and L. H. Germer, Phys. Rev. **30**, 705 (1927).

<sup>6</sup> U. Nakaya, Proc. Roy. Soc. **A124**, 616 (1929).

p. 393, Vol. I, International Critical Tables. These quantities lead to an intensity at the earth's surface of a little less than 1 percent of the initial intensity outside the atmosphere. The absorption will, however, be greater than this, for it was shown by Warburg,<sup>2</sup> on whose experimental work rests the quantitative measurement of the absorption, that in air this unusual oxygen absorption was greater for the same amount of oxygen than in pure oxygen. This was briefly discussed in Ref. 1. The use of Warburg's data on air leads, in much the same way as was done for pure oxygen in Ref. 1, to an equilibrium constant of approximately  $K_p = 0.6$  gm/cc for the dissociation of  $O_4$ , if the molecular absorption coefficient is

<sup>1</sup> Wulf, Jour. Am. Chem. Soc. **50**, 2596 (1928); Proc. Nat. Acad. Sci. **14**, 609 (1928).

<sup>2</sup> Warburg, Berl. Ber., p. 230, 1915.

taken to be unchanged. The atmosphere is approximately a 79% N<sub>2</sub> and 21% O<sub>2</sub> mixture over the altitudes of appreciable O<sub>4</sub> absorption. Carrying out the same calculations as mentioned above, with the same distribution of oxygen but with this O<sub>4</sub> dissociation constant appropriate to air, one finds that radiation in the vicinity of 2100Å will be reduced to roughly 10<sup>-5</sup> of its original value. At a height of 4 km the intensity proves to be a few percent of the original, this being mentioned here because experiment has shown that no detectable radiation of these wavelengths occurs even at this height.<sup>3</sup> Qualitatively these calculations do not, of course, depend upon the interpretation of this absorption as being due to the molecule O<sub>4</sub>, it being sufficient that there is this density-dependent absorption in oxygen, that is, this absorption which does not follow Beer's Law. The above is not intended to imply that O<sub>4</sub> is the only absorbing substance, but simply that its absorption cannot be entirely neglected. Ozone and the molecule O<sub>2</sub> undoubtedly also absorb weakly in this region.

At the same time this absorption accounts, at least in part, for the ozone in the lower atmosphere recently measured by Götz and Ladenburg.<sup>4</sup> For the absorption of this radiation leads to photochemical ozone formation as also has been shown by Warburg.<sup>5</sup> This ozone formation from O<sub>4</sub> occurs chiefly in the troposphere, because the greater part of the absorption lies in these relatively low altitudes. This ozone is in a singular position photochemically, being protected from radia-

tion most active in its decomposition by the ozone formed at higher altitudes from O<sub>2</sub>. In view of the observation that no detectable radiation in the region 2200–2000Å reaches even a height of 4 km, the photochemical formation of this ozone of O<sub>4</sub> origin apparently occurs for the most part at moderate heights. No inconsistency enters here with the observations on the ozone content of the atmosphere close to the earth, however, since the troposphere is a stirred atmosphere, convection distributing the ozone more or less uniformly throughout it. The formation of ozone from O<sub>4</sub> depends evidently upon atmospheric density, not merely upon the total oxygen in the path, and hence will be related to latitude and weather conditions. The above considerations are obviously related to the general problem of atmospheric ozone, especially to its distribution, though further work is required to determine the quantitative importance of these relations.

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<sup>3</sup> Lambert, Déjardin and Chalonge, *Compt. Rend.* **177**, 757 (1923).

<sup>4</sup> Götz and Ladenburg, *Die Naturwissenschaften* **19**, 373 (1931); see also Fabry and Buisson, *Comp. Rend.* **192**, 457 (1931).

<sup>5</sup> Warburg, *Berl. Ber.* p. 746; 1911, p. 216; 1912, p. 872; 1914; *Z. Elektrochem.* **26**, 54 (1920); **27**, 133 (1921).

#### The Raman Spectra of Two Liquid Phases of Nitrobenzene

M. Wolfke and J. Mazur have found an irregularity in the heating curve<sup>1</sup> and also abrupt temperature variation of the dielectric constant and density<sup>2,3</sup> of mononitrobenzene, at a temperature of 9.5°C, i.e., slightly above the freezing point. Their results seem to imply a definite intra-molecular energy change in the liquid state at 9.5°, and, therefore, presumably the Raman spectrum should be modified at that transition temperature. An attempt was made to find such a modification, but exposures taken above and below 9.5° failed to show any evidence of one.

<sup>1</sup> M. Wolfke and J. Mazur, *Nature* **127**, 741 (1931).

<sup>2</sup> J. Mazur, *Nature* **126**, 993 (1930).

<sup>3</sup> J. Mazur, *Nature* **127**, 893 (1931).

Three types of modification of the Raman spectrum were looked for: (1) shift of one or more of the lines, (2) intensity changes, (3) disappearance of one or more of the lines in one or the other phase.

Shifts of the order of 0.2Å could have been observed in the region of the Raman lines but no shift of any line was found.

At the lower temperatures, a marked increase in the intensity of all the lines in the blue end of the spectrum was observed but, by several other experiments, this was found to be due to a large but continuous change in the absorption coefficient of nitrobenzene with temperature.

Exposures up to one and a half hours were taken at 6.0°C and room temperature but