same collector was shifted towards the axis of the tube not only the collector current changed with the change of the discharge current but the influence of illumination from the outside source as well. Metastable atoms in a neon discharge may firstly, ionize the impurities (volume effect) and secondly, liberate electrons from surfaces (surface effect). The collector current at high negative potentials according to Found and Langmuir depends on the sheath conditions. We believe that our experiments lead to the conclusion that the secondary emission is mainly influenced by the metastable atoms.

Pike's[3] calculations which have led him to the conclusion that the efficiency of metastable atoms is small compared with the photoeffect of the radiation hardly may be applied in our and other authors' experimental conditions. Pike bases his calculations on Penning's curves[4] for spark potential referring to high neon pressures (18–20 mm). It is well known however that the changes in the emission from the cold cathode affect the spark potential only at low pressures. At high pressures the volume effect plays the main role.[5] This explains the small value got by Pike for the efficiency of metastable atoms in liberating the electrons from the collector. Measurements with a plane collector placed beyond the column which could be oriented perpendicular and parallel with the axis of the tube showed that for the perpendicular position of the electrode the ion currents were somewhat greater than for the parallel one. Kenty[6] assumes that this increase of the current is one of the evidences of the direct photoeffect from the collector. But in our experiments this difference in the current existed even when the main discharge was switched off. Thus in our experiments the cause of this effect was not the radiation diffusing from the positive column, but the change of the configuration of the gap between the collector and the anode. In the discharge tube with a transparent anode and a collector placed at the axis of the tube beyond the anode and directly affected by radiation from the positive column the ion currents to the collector decreased sharply when a glass wall was approached by the collector from the side opposite to radiation. When the collector was screened from the positive column with various screens the ion current decreased. But this decrease was almost independent of the optical properties of the screens. All these experiments point out the existence of a surface effect under the action of metastable atoms and a comparatively small direct influence of the photoeffect on the secondary emission.

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October 14, 1932.

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[3] E. W. Pike, Phys. Rev. **40,** 314 (1932).

[4] F. M. Penning, Zeits. f. Physik **46,** 335 (1928); **57,** 723 (1929), (Fig. 4).

[5] L. I. Neuman, Proc. Nat. Acad. Sci. **15,** 259 (1929), (Fig. 3).

[6] C. Kenty, Phys. Rev. **38,** 377 (1931).

A Filter for the Study of the Raman Effect

To excite Raman spectra[1] by means of the 4358 mercury line, it is current practice to eliminate the 4047 groups by means of a quinine sulphate solution. Since this solution turns brown upon prolonged exposure, recourse is had to the use of a preliminary filter of pale Noviol glass which absorbs the 3650 line as well as lines of shorter wave-lengths—and which, hence, prolongs the useful life of the quinine solution.

Recently, in developing a series of filters transmitting, respectively, only the ultraviolet, the visible, and the infrared, it was found that a solution of sodium nitrite $NaNO_2$ has a short wave-length transmission limit at about 4050. The behavior of a saturated solution of sodium nitrite in a cell 12 mm thick is shown in the accompanying photographs. Actual measurements, carried out with a quartz monochromator and a Weston Photronic Cell show that while the transmission of the nitrite filter for the 4358 line is

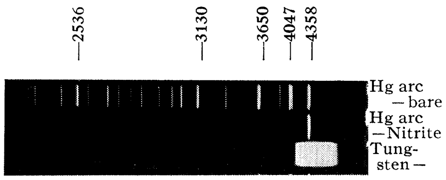

Fig. 1.

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[1] R. W. Wood, Phys. Rev. **38,** 2168 (1931).

65 percent, the transmission for the 4047 line is less than 1 percent. The transmission of the Noviol glass was 56 percent for the 4358 line. This indicated that the sodium nitrite solution would be at least as effective as the quinine sulphate-Noviol combination and possess, in addition, the advantage of permanence. Prolonged exposures to the intense radiation of a quartz mercury arc have failed to show any noticeable effects upon the transmission of the nitrite solution.

A freshly prepared solution of sodium nitrite in water shows turbidity which is not removed by filtering. If the solution be allowed to stand for several days, the suspended matter settles out and leaves the solution quite clear. For most cases a saturated solution in a 12 mm layer will suffice. For use in Wood's system of filters, it is suggested that 2 parts of water be added to 1 part of the saturated nitrite solution and that the mixture be used to fill the glass tube of 3.6 cm internal diameter.

Actual Raman spectrograms taken by Professor Wood showed that the necessary time of exposure with the nitrite filter was no greater than that required by the quinine-Noviol filter and that the nitrite filter did not change its color.

A. H. PFUND
The Johns Hopkins University,
October 22, 1932.

Note on Perturbation Theory ot Molecules Formed from Two 2*p* Atoms

The various methods which can be used to estimate (either quantitatively or qualitatively) the energy levels of diatomic molecules do not always give concordant results for the ordering of the levels. Professor Van Vleck has suggested that a comparison of these methods might yield information of some value; this note gives the results of such a comparison in a particular instance. The case chosen is that of a molecule formed from two similar atoms, each containing a single 2*p* electron (plus perhaps non-bonding closed inner shells). We shall neglect the "hybridization" of the 2*s*, 2*p* levels; for, though important in hydrogenic atoms because of degeneracy, it is usually less important in heavier atoms. The various schemes of calculation include the following:

1. The Heitler-London perturbation method, inclusive of the electron repulsion term, e^2/r_{12}, in the potential energy. This has been done, to the first order approximation, by Barlett;[1] his results, corrected as suggested in a later paper,[2] are shown in Fig. 1. This is the method leading to the concept of "electron pairs."
2. The Heitler-London perturbation method, exclusive of the electron repulsion term. The results, readily calculated from Bartlett's tables, are indicated in Fig. 2.
3. The "two-center" or "molecular orbital" method, also exclusive of detailed electronic interaction. This is the method used extensively in the "Aufbauprinzip" of Hund and Mulliken. It consists essentially of adding the attractive energies of the separate electrons, each calculated as for the one-electron two-center problem, to the repulsive energy of the nuclei. It will be necessary for us to distinguish the two following ways of applying (3):

(3a) First order perturbation theory, neglecting electronic repulsion, with unperturbed wave functions of the type $[a_i(1)\pm b_i(1)]\times[a_j(2)\pm b_j(2)]$. The choice of sign for each electron's orbital determines whether it is *gerade* or *ungerade*. (Notation: $a_i(1)$ refers to the wave function of electron 1 on nucleus a in the state $m_l=i$, etc.) This method, like (1) and (2), has the disadvantage that it is applicable only for large internuclear distances. It has been worked out by Lennard-Jones;[3] the results for our two-electron case are given in Fig. 3.

(3b) Semi-empirical methods of Hund[4] and Mulliken,[5] which are guided by correlation of the configurations and levels of known molecules with those of the united atoms and

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[1] J. H. Bartlett, Jr., Phys. Rev. **37**, 507 (1931).

[2] W. H. Furry and J. H. Bartlett, Jr., Phys. Rev. **39**, 211 (1932).

[3] J. E. Lennard-Jones, Trans. Faraday Soc. **25**, 668 (1929). As a check, the same results have been found with the aid of Bartlett's tables.

[4] F. Hund, Zeits. f. Physik **73**, 577 (1932).

[5] R. S. Mulliken, Rev. Mod. Phys. **4**, 1 (1932); particularly Fig. 43, which is here taken as a standard by which to judge the accuracy of the perturbation methods.

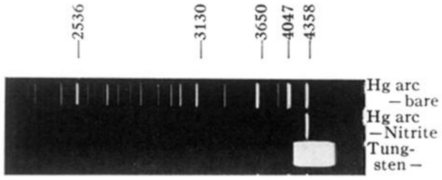

Fig. 1.