Electron Emission of Metals in Electric Fields

II. Field Dependence of the Surface Photo-Effect

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The photoelectric current emitted under the influence of an applied electric field is found to contain a term analogous to the Schottky term for thermionic emission and also a term periodic in the field intensity similar to that recently found and explained for thermionic emission. If frequencies near the threshold are used, then for fields of 3×10^5 volts cm^{-1} the periodic term has a magnitude of about four percent of the nonperiodic part of the current. If the photoelectric threshold frequency for zero field is used to eject the electrons, the resultant plot of the nonperiodic part of the photo-current against the field is a straight line for high field intensities. This line gives the most convenient reference system for observing the periodic term; in addition, the use of the zero field threshold gives the fractional magnitude of the periodic term a relatively large value.

I. INTRODUCTION

In a recent paper[1] the observed[2,3] periodic deviations from the Schottky line are explained as due to a periodic dependency of the transmission coefficient upon the intensity of the applied field. This periodic behavior of the transmission coefficient may be interpreted as the result of interference of the electron waves reflected from the potential barrier at the surface of the metal. Since this same potential barrier is used in the theory of the surface photoelectric effect, and since the transmission coefficient enters the expression for the photo-current in the same way, a periodic dependence of the photo-current on the applied field, similar to the dependence of the thermionic current, is to be expected. In the present paper the influence of an applied field upon the emitted photo-current is investigated, and an expression for the current is derived. It is found that the current contains the expected periodic term, the fractional magnitude being even larger than with thermionic emission. The effect should be most easily observable for frequencies very near the threshold, for then the fraction of the current due to the periodic term has its largest value.

Some indications of the results to be expected for the field dependence of a photo-current may be seen by considering briefly the analogous problem of thermionic emission. In this case one has

$$i=A_0\bar{D}(F)T^2e^{-\chi/kT}$$

or

$$\log\frac{i(F)}{i(0)}=\frac{e^{\frac{3}{2}}}{kT}F^{\frac{1}{2}}+\log\frac{\bar{D}(F)}{\bar{D}(0)},\tag{1}$$

where A_0 is the emission constant $=120$ amp./cm^2; $\bar{D}(F)$ is the transmission coefficient summed over all electron energies greater than that necessary for an electron to escape from the metal; $i(F)$ is the thermionic current at field F and temperature T°K; χ is the thermionic work function at field F. One usually plots $\log i$+const. against $F^{\frac{1}{2}}$. Then, neglecting the variation of $\bar{D}(F)$ with F, one has the result that the plot should be a straight line, known as the Schottky line. The increase of current with field is due to the fact that increasing the field decreases the maximum height of the potential barrier at the metal surface and therefore makes a larger number of electrons available for emission. However, it has been found that the transmission coefficient $\bar{D}(F)$ also varies with F, i.e., with the shape of the barrier; hence, $\bar{D}(F)/\bar{D}(0)\neq1$ and one does not obtain a perfectly straight line from the plot of Eq. (1). Rather, $\bar{D}(F)$ varies periodically with F, so that the plot yields periodic deviations from a straight line. In the theory of photo-emission a similar

[1] E. Guth and C. J. Mullin, Phys. Rev. **59**, 575 (1941).
[2] R. L. E. Seifert and T. E. Phipps, Phys. Rev. **56**, 652 (1939).
[3] D. Turnbull and T. E. Phipps, Phys. Rev. **56**, 663 (1939). Cf. also W. B. Nottingham, Phys. Rev. **57**, 935 (1940).

periodic fluctuation in the photo-current as one changes the intensity of the applied field is to be expected. Experimental data on the field dependence of photo-currents[4] are rather meager and have not as yet disclosed this periodic behavior; in fact, even the photoelectric analog to the Schottky effect does not seem to have been thoroughly investigated.

It is here assumed that the potential traversed by the escaping electron is the usual image+applied field potential which has been so successful in the explanation of thermionic emission; i.e.,

$$V=W_a-(e^2/4x)-eFx. \tag{2}$$

Here W_a is the difference in the potential energy of the electron in the metal and at infinity when $F=0$; x is the distance of the escaping electron from the metal surface; F is the intensity of the applied field; W_a' is the maximum barrier height when the field intensity is F. (We do not consider patch effects which come in for fields from 0 to about 5000 volts or higher, depending upon the wire specimen used.) This potential is shown in Fig. 1 of reference 1. It may now be assumed that the current is given by the expression

$$i \propto \int_{W_a'}^{\infty} N(W)P(W,\nu)D(W,F)dW$$

or

$$i \propto \int_0^{\infty} N(\epsilon)P(\epsilon,\nu)D(\epsilon,F)d\epsilon, \tag{3}$$

where W is the normal energy[5] of the electron before it absorbs a photon; $\epsilon=W-W_a'+h\nu$ is the excess of the electron's normal energy $W+h\nu$ (after the electron has absorbed a quantum $h\nu$) over the maximum height of the potential barrier at the emitting surface; $P(\nu,\epsilon)$ is the probability that an electron with normal energy W will absorb a quantum $h\nu$ and become a potential photoelectron; $D(\epsilon,F)$ is the probability that an electron with excess normal energy ϵ over the barrier will escape through the metal surface under the influence of an applied field of intensity F. A particular case of Eq. (3) which is obtained by considering only $F=0$ and assuming that $D(\epsilon,0)=1$ forms the basis of Fowler's[6] well-known theory of the photoelectric effect which is valid for frequencies in the neighborhood of the threshold. *A priori* reasons do not completely justify Eq. (3); however, Mitchell[7] calculated the current by applying the standard perturbation theory and found that Fowler's procedure, and hence (3) also, gives a good approximation in the neighborhood of the threshold frequency.

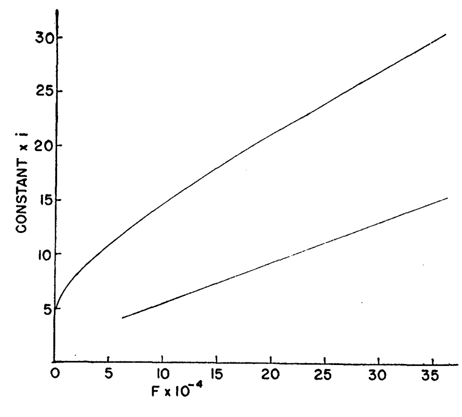

FIG. 1. The photo-current as a function of the applied field. The field intensities F are in volts per cm. The upper curve is for $h\nu-h\nu_0=0.1$ ev, the lower for $h\nu-h\nu_0=0$. Both curves are plotted with $T=500°K$.

In Section II of the present paper Fowler's evaluation of the integral in (3) is generalized to include the application of a field. $D(\epsilon,F)$ is taken as unity and the current increase due to the lowering of the potential barrier because of the applied field F is obtained; this is the photoelectric analog to the Schottky effect. In Section III the variation of $D(\epsilon,F)$ with ϵ and F is considered and the resulting expression (17) is found to contain the expected periodic term.

II. Photoelectric Analog of the Schottky Effect

In the first approximation one may assume that all electrons for which $W+h\nu-W_a'>0$ escape from the metal, i.e., $D(\epsilon,F)=1$ for these electrons; furthermore, if one considers values of

[4] The work of E. O. Lawrence and L. B. Linford [Phys. Rev. **36**, 482 (1930)] was an attempt in this direction. Also Dr. R. J. Cashman has informed us that he is investigating the field dependence of the photo-current experimentally.

[5] Here and in what follows we use the expression "normal energy" to mean the part of the energy corresponding to the normal velocity component of the electron.

[6] R. H. Fowler, Phys. Rev. **38**, 45 (1931); or cf. R. H. Fowler, *Statistical Mechanics* (Cambridge University Press and Macmillan, 1936), second edition, pp. 358 ff.

[7] K. Mitchell, Proc. Roy. Soc. **A146**, 442 (1934), and Proc. Camb. Phil. Soc. **31**, 416 (1935).

ν near the threshold value ν_0, then the probability $P(\nu, \epsilon)$ that an electron will absorb a quantum $h\nu$ and become a photoelectron should be independent of the normal energy W of the electron. With such assumptions Fowler[6] has derived an expression for the photo-current emitted at temperature T and frequency ν. His result is

$$i \propto \frac{4\pi m k^2 T^2}{h^3}\left\{\frac{\pi^2}{6}+\frac{1}{2}\delta^2 - \left[e^{-\delta}-\frac{e^{-2\delta}}{2^2}+\frac{e^{-3\delta}}{3^2}-\cdots\right]\right\}, \quad \delta \geqslant 0$$

and (4)

$$i \propto \frac{4\pi m k^2 T^2}{h^3}\left[e^{-\delta}-\frac{e^{-2\delta}}{2^2}+\frac{e^{-3\delta}}{3^2}-\cdots\right], \quad \delta \leqslant 0$$

where

$$\delta = h(\nu-\nu_0)/kT.$$

If an electric field is applied to the emitting surface, Eq. (4) should again be valid if the zero field threshold ν_0 is replaced by a field dependent threshold ν_0', whose dependence upon the field is given by the relation

$$h\nu_0' = h\nu_0 - e^{\frac{3}{2}}F^{\frac{1}{2}},$$

i.e., we replace δ by

$$\delta' = (h\nu - h\nu_0 + e^{\frac{3}{2}}F^{\frac{1}{2}})/kT. \tag{5}$$

This shift in the threshold frequency arises from the lowering of the potential barrier by the applied field; this corresponds exactly to the decrease of the thermionic work function when the applied field is increased. Since decreasing the barrier height makes more electrons available for emission, an increase in current is expected; this is the analog to the Schottky effect in thermionic emission. There is, however, one essential difference: The number of electrons made available by lowering the barrier is considerably different in the two cases; the thermionic electrons have energies so large that their energy distribution (which determines the number made available by lowering the barrier) is Maxwellian, while on the other hand, the potential photoelectrons have much smaller energies, so that they have a Fermi-Dirac energy distribution. Hence, for photo-currents the current increase observed because of the decrease in the maximum barrier height with increasing field is not expected to be equal to that produced when the same field is applied under similar circumstances to a thermionic filament.

A particularly simple case of the field dependence of the current occurs when

$$\delta' = (h\nu - h\nu_0 + e^{\frac{3}{2}}F^{\frac{1}{2}})/kT \gg 0, \tag{6}$$

so that the bracket term of (4) may be neglected. This condition may be fulfilled for large fields even for values of ν less than ν_0. If this condition is fulfilled, then

$$i \propto \tfrac{1}{6}\pi^2(kT)^2 + \tfrac{1}{2}[h(\nu-\nu_0)]^2 + h(\nu-\nu_0)e^{\frac{3}{2}}F^{\frac{1}{2}} + \tfrac{1}{2}e^3F$$

or

$$i \propto a + bF^{\frac{1}{2}} + cF. \tag{7a}$$

Figure 1 shows the current plotted as a function of F for a particular temperature and for two values of $h(\nu-\nu_0)$. It is to be noted that when $\nu=\nu_0$ the coefficient b in (7a) vanishes, so that the plot of (7a) yields a straight line,

$$i \propto a + cF. \tag{7b}$$

The effect of the field on the current when the condition (6) is not fulfilled may be found by substituting δ' (as given by (5)) for δ in Eq. (4). The expressions (7a) and (7b), and other expressions derived for the field dependency of the current, will hold accurately only for fields above about 10^4 volt/cm, because of the occurrence of patch effects for lower fields.

III. Influence of the Field Dependency of the Transmission Coefficient

If, for convenience, we introduce the following system of atomic units: unit of length $=a = h^2/me^2 = 0.528\text{A}$ = radius of first Bohr orbit in H, unit of energy $= e^2/2a = 13.54$ ev = ionization potential of H, the equation (2) for the potential becomes

$$V = W_a - \frac{1}{2x} - \frac{x}{2x_0^2}. \tag{8}$$

The maximum height of the barrier is then

$$W_a' = W_a - (1/x_0), \tag{9}$$

the term $1/x_0$ being the amount the barrier is lowered by the applied field. The quantity x_0, the position of the potential maximum, is here used as a variable in place of the field F. The relation between x_0 and F is established by the equation

$$x_0=\tfrac{1}{2}(300e/F)^{\frac{1}{2}}10^8 a/0.528, \tag{10}$$

where F is in volts cm^{-1}. For the field intensities of interest the number of electrons which tunnel through the barrier may be neglected; the photocurrent arises from the electrons which surmount the barrier. Thus, in order that an electron with normal energy W be emitted after absorbing a quantum $h\nu$, it is at least necessary that

$$W+h\nu\geqslant W_a'=W_a-(1/x_0).$$

Hence, according to Eq. (3)

$$i\propto\int_0^\infty N(\epsilon)P(\nu,\,\epsilon)D(\epsilon,\,F)d\epsilon$$

with W_a' given by (9).

The value of $N(\epsilon)$ is given by the Fermi-Dirac distribution,[8] and the value of $D(\epsilon,\,F)$ has been worked out[1] for the barrier of Fig. 1 of reference 1. We give only the results here.

$$N(\epsilon)=\frac{4\pi mkT}{h^3}\log[1+\exp(-[\epsilon+h(\nu_0'-\nu)]/kT)], \tag{11}$$

$$D(\epsilon,F)=\frac{1}{1+\exp[-2\pi(x_0^3/2)^{\frac{1}{2}}\epsilon]}-\frac{\sqrt{W_a}}{2}\cdot\frac{\exp[-\pi(x_0^3/2)^{\frac{1}{2}}\epsilon]}{(1+\exp[-2\pi(x_0^3/2)^{\frac{1}{2}}\epsilon)^{\frac{3}{2}}]}\cdot\cos v$$
$$-\frac{W_a^4}{16(\epsilon+W_a')^3}\cdot\frac{1}{(1+\exp[-2\pi(x_0^3/2)^{\frac{1}{2}}\epsilon]^2)^2}, \tag{12}$$

with

$$v=\frac{4\sqrt{2}}{3}x_0^{\frac{1}{2}}-\frac{2}{\sqrt{W_a}}+\tan^{-1}\frac{\sqrt{W_a}}{4}-(\gamma+2\log 2)\left(\frac{x_0^3}{2}\right)^{\frac{1}{2}}\epsilon,$$

where ν_0' is the threshold frequency at field F and is related to the zero field threshold ν_0 by the relation $h\nu_0'=h\nu_0-(1/x_0)$; and $\gamma=$ Euler's constant $=0.5772$.

Thus the only unknown quantity in the expression (4) for the current is the transition probability $P(\nu,\,\epsilon)$. The work of Mitchell shows that near the threshold the transition probability is independent of the electron energy. Hence, the emitted current is given by the relation

$$i\propto\frac{4\pi mkT}{h^3}\int_0^\infty D(\epsilon,\,F)\log[1+\exp(-[\epsilon+h(\nu_0'-\nu)]/kT)]d\epsilon \tag{13}$$

with $D(\epsilon,\,F)$ given by (12).

We may expand the log into the following forms

$$\log[1+\exp(-[\epsilon+h(\nu_0'-\nu)]/kT)]=\sum_{n=1}^{\infty}\frac{(-1)^{n+1}}{n}\exp(-n[\epsilon+h(\nu_0'-\nu)]/kT)\quad\text{if}\quad\begin{matrix}\nu_0'\geqslant\nu\\0\leqslant\epsilon\leqslant\infty\end{matrix}$$

$$\log[1+\exp(-[\epsilon+h(\nu_0'-\nu)]/kT)]=-\frac{\epsilon}{kT}+\frac{h(\nu-\nu_0')}{kT}+\sum_{n=1}^{\infty}\frac{(-1)^{n+1}}{n}\exp(n[\epsilon-h(\nu-\nu_0')]/kT)$$
$$\text{if}\quad\begin{matrix}\nu\geqslant\nu_0'\\0\leqslant\epsilon\leqslant h(\nu-\nu_0')\end{matrix} \tag{14}$$

$$\log[1+\exp(-[\epsilon+h(\nu_0'-\nu)]/kT)]=\sum_{n=1}^{\infty}\frac{(-1)^{n+1}}{n}\exp(-n[\epsilon-h(\nu-\nu_0')]/kT)\quad\text{if}\quad\begin{matrix}\nu\geqslant\nu_0'\\h(\nu-\nu_0')\leqslant\epsilon<\infty.\end{matrix}$$

[8] Cf. R. H. Fowler, *Statistical Mechanics*, (second edition), pp. 341 ff.

We then have the following expressions for the current

$$i \propto \frac{4\pi mkT}{h^3}\left\{\int_0^{h(\nu-\nu_0')} D(\epsilon, F)\left(\frac{h\nu - h\nu_0' - \epsilon}{kT}\right)d\epsilon + \int_0^{h(\nu-\nu_0')} D(\epsilon, F)\sum_{n=1}^{\infty}\frac{(-1)^{n+1}}{n}\exp(n[\epsilon - h(\nu-\nu_0')]/kT)d\epsilon\right.$$

$$\left. + \int_{h(\nu-\nu_0')}^{\infty} D(\epsilon, F)\sum_{n=1}^{\infty}\frac{(-1)^{n+1}}{n}\exp(-[\epsilon - h(\nu-\nu_0')]/kT)d\epsilon\right\} \quad \nu \geqslant \nu_0' \tag{15}$$

and

$$i \propto \frac{4\pi mkT}{h^3}\int_0^{\infty} D(\epsilon, F)\sum_{n=1}^{\infty}\frac{(-1)^{n+1}}{n}\exp(-n[\epsilon + h(\nu_0'-\nu)]/kT)d\epsilon \quad \nu \leqslant \nu_0'. \tag{16}$$

For the purposes of summing over the electron energies we may neglect the term $[W_a^4/16(\epsilon+W_a')^3]\cdot(1+\exp[-2\pi(x_0^3/2)^{\frac{1}{2}}\epsilon])^{-2}$; furthermore, we make the approximation

$$(1+\exp[-2\pi(x_0^3/2)^{\frac{1}{2}}\epsilon])^{-\frac{1}{2}} \sim (1-\tfrac{1}{2}\exp[-2\pi(x_0^3/2)^{\frac{1}{2}}\epsilon])\sum_{n=0}^{\infty}(-1)^n\exp[-2n\pi(x_0^3/2)^{\frac{1}{2}}\epsilon].$$

With these approximations we may write

$$D(\epsilon, F) \sim \sum_{k=0}^{\infty}(-1)^k\exp[-2k\pi(x_0^3/2)^{\frac{1}{2}}\epsilon] - \frac{\sqrt{W_a}}{2}\exp[-\pi(x_0^3/2)^{\frac{1}{2}}\epsilon](1-\tfrac{1}{2}\exp[-2\pi(x_0^3/2)^{\frac{1}{2}}\epsilon])$$

$$\sum_{k=0}^{\infty}(-1)^k\exp[-2k\pi(x_0^3/2)^{\frac{1}{2}}\epsilon]\cdot\cos v.$$

The integrations of (15) and (16) may now be carried through in a straightforward manner. The resulting formulae give particularly simple and interesting results when $h(\nu-\nu_0')/kT \gg 0$ so that the condition $\exp[-h(\nu-\nu_0')/kT] \ll 1$ is fulfilled. Note that even if one takes $\nu=\nu_0$, the threshold at zero field, the condition is fulfilled for all values of the field above some relatively small value (since ν_0' decreases as F is increased). For large values of F the condition may be fulfilled with ν chosen even less than ν_0. In the case that $\exp[-h(\nu-\nu_0')/kT] \ll 1$, the integration of (7) yields with good approximation:

$$i \propto \frac{4\pi mk^2T^2}{h^3}\left\{\frac{\pi^2}{6}+\frac{1}{2}\left[\frac{h(\nu-\nu_0')}{kT}\right]^2 - \frac{\sqrt{W_a}}{2}\frac{h(\nu-\nu_0')}{(kT)^2}\frac{\cos u}{\{[\pi(x_0^3/2)^{\frac{1}{2}}+1/kT]^2+(\gamma+2\log 2)^2x_0^3/2\}^{\frac{1}{2}}}\right\}, \tag{17}$$

where

$$u = \frac{4\sqrt{2}}{3}x_0^{\frac{1}{2}} - \frac{2}{\sqrt{W_a}} + \tan^{-1}\frac{\sqrt{W_a}}{4} - \tan^{-1}\frac{(\gamma+2\log 2)(x_0^3/2)^{\frac{1}{2}}}{[\pi(x_0^3/2)^{\frac{1}{2}}+1/kT]}.$$

The formula (17) gives the desired expression for the photo-current. An expression for the current when the condition $h(\nu-\nu_0')/kT \gg 0$ is not fulfilled is readily obtained from (11) and (12). However, the resulting expressions are rather lengthy and complicated and hence difficult to analyze. For a study of the field dependence of the photo-current using light of a fixed frequency, an analysis of the simple expression (17) is sufficient. In deriving (17) a small temperature-independent term has been neglected in the coefficient of the cosine. This neglect is justified as long as T is more than a few degrees absolute. However, an examination of (17) shows that if T is allowed to become zero, then the neglected term, which is a function only of the field, must be considered in order that the periodic term should not vanish when $T=0$. Thus, if T is so small that

$$\frac{h(\nu-\nu_0')(\pi(x_0^3/2)^{\frac{1}{2}}+1/kT)}{2\{(\pi(x_0^3/2)^{\frac{1}{2}}+1/kT)^2+(\gamma+2\log 2)^2x_0^3/2\}} \ll \frac{1}{\pi^2x_0^3} \tag{18}$$

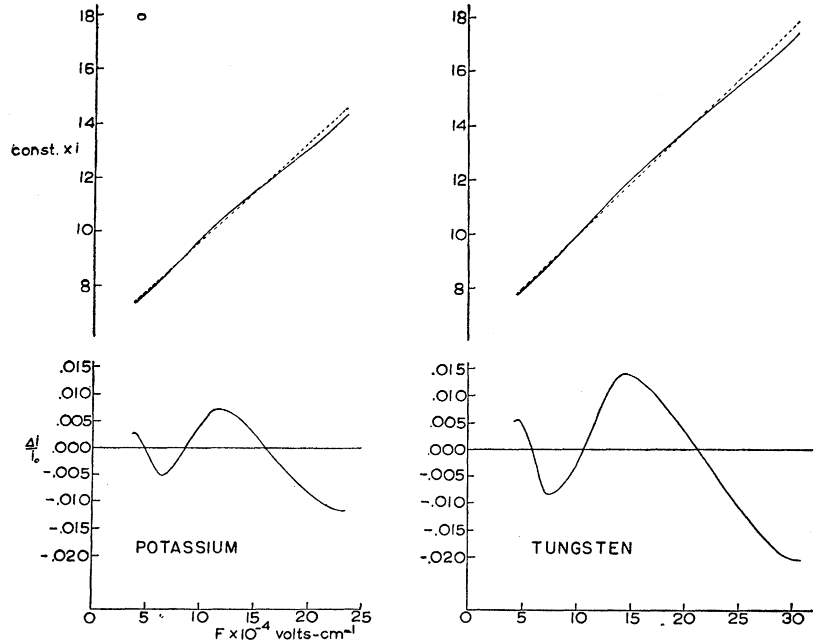

FIG. 2. Field dependence of the photoelectric current. The periodic fluctuation in the current is seen in the upper diagrams. The dotted line shows the nonperiodic part of the current. The lower diagrams show the fractional magnitude of the periodic term, i.e., the periodic term divided by the nonperiodic term. All diagrams are for $\nu=\nu_0$ and $T=300°\mathrm{K}$.

a consideration of the term neglected in (17) gives

$$i\propto\frac{\pi^2}{6}(kT)^2+\frac{1}{2x_0^2}-\frac{\sqrt{W_a}}{\pi^2x_0^3}\cos u. \tag{19}$$

Even for the highest fields considered the inequality (18) is satisfied only if T is very near to the absolute zero.

IV. Discussion of the Results

A comparison of (17), which was obtained by considering the transmission coefficient, and (7), which was obtained by assuming the transmission to be unity, yields the expected result that the change in the transmission coefficient as the shape of the barrier is changed gives rise to a periodic term which causes deviations from the current expected from Eq. (7a). These deviations have values as large as four percent of the total current for fields of 3×10^5 volt/cm. The deviations could be observed most easily in the case where the incident light has a frequency equal to the zero field threshold for the metal; for in this case the equation for the expected current (neglecting the periodic term) has the form

$$i\propto\frac{\pi^2}{6}(kT)^2+\frac{1}{2x_0^2} \tag{20}$$

or since $x_0=\mathrm{const.}\times1/F^{\frac{1}{2}}$

$$i\propto a+cF, \tag{21}$$

where a and c are independent of F. This is the same result as that obtained in Eq. (7b) by assuming that $D(\epsilon, F)=1$. Hence, it is seen that the periodic term arises from the dependence of the transmission probability on energy and field. Equation (21) shows that if $\nu=\nu_0$, a plot of i *versus* F should give a straight line, the simplest reference for observing the deviations. In this case Eq. (17) has the simple form

$$i\propto\frac{\pi^2}{6}(kT)^2+\frac{1}{2x_0^2}-\frac{\sqrt{W_a}}{2x_0}\times\frac{\cos u}{\{(\pi(x_0^3/2)^{\frac{1}{2}}+1/kT]^2+(\gamma+2\log2)^2x_2^3/2\}^{\frac{1}{2}}}. \tag{22}$$

The current, as given by (22) is plotted in Fig. 2 as a function of the field for potassium and tungsten; the dotted portion gives the straight line obtained by neglecting the periodic term. If the periodic term is Δi, and the nonperiodic part of the current i_0, the quantity $\Delta i/i_0$ is then a measure of the fractional deviation from the nonperiodic current; this is also shown in Fig. 2 for potassium and tungsten. It is to be noted that the period of the deviations is the same for both metals; the positions of the maxima and minima are different because of the difference of W_a values. Both for tungsten and for potassium the W_i values ($W_i = W_a - \chi =$ width of the Fermi band at absolute zero), which are needed to obtain the W_a values, were calculated from the free electron model of a metal, assuming one free electron per atom. This probably gives a good value for potassium, but a value slightly too large for tungsten. The values of χ used were: $\chi = 4.53$ for tungsten, and $\chi = 2.24$ ev for potassium. The quantity $\Delta i/i_0$ is seen to increase as F is increased or as $\nu - \nu_0$ is decreased. Δi itself is nearly independent of temperature, but the temperature dependence of the nonperiodic i_0 makes the fractional deviation $\Delta i/i_0$ dependent on temperature.

Part III of this work on the transition from thermionic to cold emission will appear in the near future.

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Species Classification and Rotational Energy Level Patterns of Non-Linear Triatomic Molecules*

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With the object of making existing knowledge more readily available, the quantized energy levels of symmetrical and asymmetrical tops are discussed from the viewpoint of their classification into species defined by symmetry operations; and simple species nomenclatures are proposed. These are then applied in a discussion of the rotational levels of symmetrical non-linear triatomic molecules AB_2. With SO_2 as an example, the pattern of rotational levels is studied as a function of the apex angle 2α (near-prolate-symmetrical case for large α, oblate or near-oblate case for intermediate α, second near-prolate case for small α). The classification of the *over-all* wave functions with respect to behavior for exchange of equal nuclei and for inversion is then considered. This gives rise to level patterns like those of diatomic and linear molecules in the first near-prolate case, but of interesting unfamiliar types (expected also in molecules such as BCl_3 or NH_3) in the oblate case, and of relatively unfamiliar types (known for the molecule H_2CO) in the second near-prolate case. Rotational-vibrational and rotational-electronic perturbations are discussed in relation to the species classifications. The concept of gyrovibronic species, and a corresponding nomenclature, are introduced. Top selection rules are discussed, using a convenient tabular formulation. Tables are given, for the case of symmetry C_{2v}, showing what types of transitions are allowed by the vibronic selection rules for every type of electronic transition, allowed or forbidden; the use of these tables is illustrated by application to the near-ultraviolet absorption spectrum of formaldehyde. Finally, non-linear ABC molecules are considered.

I. INTRODUCTION

TRIATOMIC molecules AB_2 fall into two types, linear and bent. The quantized rotational and electronic energy levels of *linear* molecules are like those of diatomic molecules, but the vibrational levels introduce new complexities. *Bent* AB_2 molecules rotate like asymmetrical tops, and their rotational levels are arranged and classified accordingly. Often, however, the level patterns are not very different from those of symmetrical-top molecules.

In connection with a program of investigation of electronic spectra and structures of AB_2 molecules, it became desirable to obtain as clear a view as possible of the classification and arrangement of the energy levels as a function of the shape and masses. Although everything necessary is contained either explicitly or implicitly in existing literature,[1,2] these discussions are for the most part not in a form readily available for application. Tables and figures

* Assistance in the preparation of materials was furnished by the personnel of Works Project Administration Official Project No. 665-54-3-387.

[1] See especially D. M. Dennison, Rev. Mod. Phys. **3**, 280 (1931), and references given there.

[2] A. V. Bushkovitch, Phys. Rev. **45**, 545 (1934): bent AB_2 molecules.