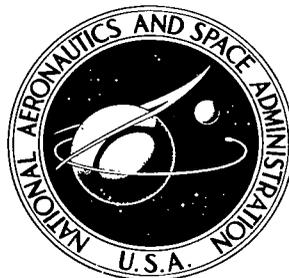


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**MOLECULAR VIBRATION SPECTRA
FROM FIELD EMISSION
ENERGY DISTRIBUTIONS**

by Dennis J. Flood

Lewis Research Center

Cleveland, Ohio



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1. Report No. NASA TN D-5423	2. Government Accession No.	3. Recipient's Catalog No.	
4. Title and Subtitle MOLECULAR VIBRATION SPECTRA FROM FIELD EMISSION ENERGY DISTRIBUTIONS		5. Report Date September 1969	6. Performing Organization Code
7. Author(s) Dennis J. Flood	9. Performing Organization Name and Address Lewis Research Center National Aeronautics and Space Administration Cleveland, Ohio 44135		8. Performing Organization Report No. E-4072
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D. C. 20546	10. Work Unit No. 129-02		11. Contract or Grant No.
15. Supplementary Notes	13. Type of Report and Period Covered Technical Note		14. Sponsoring Agency Code
16. Abstract A calculation is presented which predicts a change in the energy distribution of field emitted electrons due to electron-molecule interactions at the metal-vacuum interface. The derivative of the energy distribution of electrons which undergo such an interaction should yield information on the infrared absorption spectra of the adsorbed molecules.			
17. Key Words (Suggested by Author(s)) Electron emission Molecular spectra	18. Distribution Statement Unclassified - unlimited		
19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages 22	22. Price* \$3.00

* For sale by the Clearinghouse for Federal Scientific and Technical Information
Springfield, Virginia 22151

MOLECULAR VIBRATION SPECTRA FROM FIELD EMISSION ENERGY DISTRIBUTIONS

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SUMMARY

The effect on a field emission current of foreign molecules located at the cathode surface is presented. The electron-molecule interaction is represented by the potential energy of a charged particle in the presence of an electric dipole field. Only the case of a quadratic dispersion law for the electrons in the metal is considered. Results have been obtained which are valid for the low temperature range where the tail of the Fermi distribution function may be neglected. The calculation indicates that the emission current should change by about 1 percent for less than monolayer coverages of the cathode. The total energy distribution of the emitted electrons $P_T(\epsilon)$, and in particular the first derivative of $P_T(\epsilon)$, should give information on the vibrational spectra of the molecular species involved.

INTRODUCTION

It has recently been pointed out (refs. 1 and 2) that vibrational excitations of foreign molecules located in the oxide layer of thin film metal-oxide-metal (MOM) sandwiches produce considerable structure in the current-voltage characteristics of the tunneling current. The effect shows up as a series of peaks in d^2I/dV^2 . The peaks appear because a fraction of tunneling electrons interact inelastically with the molecules, exciting them into one or another of their upper vibrational states. A model calculation (ref. 3), in which the electron-molecule interaction is taken into account by including the molecular dipole field in the potential describing the barrier region, is in good agreement with experimental observation. This report presents a calculation based on the same kind of model for the case of field emission into a vacuum from a metal with a molecular layer on its surface.

DESCRIPTION OF MODEL

The field emission process from clean metallic surfaces can be treated by considering a one-dimensional potential which is assumed to represent the effects of the metal and applied electric field on the conduction electrons. In the free-electron approximation the effective potential energy of the electrons is written as

$$V_0 = 0 \tag{1}$$

inside the metal, and

$$V_0 = W_a - eFx - \frac{e^2}{4x} \tag{2}$$

outside. Figure 1 is an illustration of the form of the effective potential energy. The

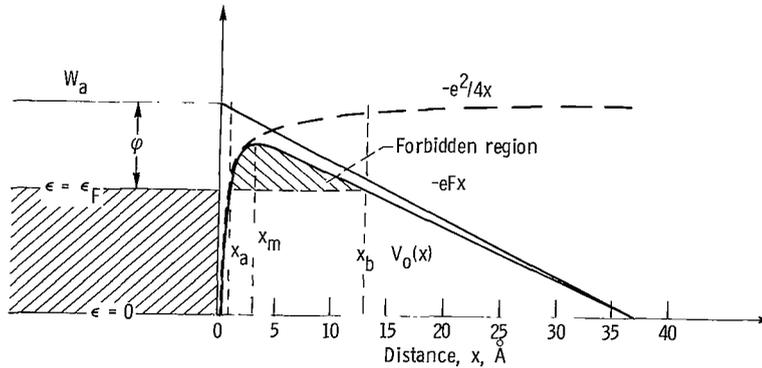


Figure 1. - Effective potential energy of an electron near a metallic surface in vacuum, under the influence of a strong electric field.

origin of the three terms in equation (2) is as follows:

(1) W_a is the height of the potential energy well representing the metal. Energies will be measured from the bottom of the conduction band.

(2) F is the applied electric field and is assumed to be constant as far as surface barrier effects are concerned. The origin of coordinates is chosen to be at the metal-vacuum interface. Positive values of x are measured to the right of, and perpendicular to, the surface of the metal. Under these conditions an electron of charge $-e$ outside the metal will have a potential energy of $-eFx$.

(3) The last term arises from the force exerted on the electron by the image charge induced on the surface of the metal as the electron attempts to escape. With the zero

of energy chosen as indicated, in the absence of an applied electric field an electron at infinity will have an energy W_a .

Figure 1 also shows the classically forbidden region where the potential energy is greater than the kinetic energy of the electrons. The points x_a and x_b are the classical turning points of the motion. The presence of molecules in the barrier region may be taken into account by including in equation (2) a term arising from the Coulomb potential of the molecules and their images. Approximating this potential by a dipole potential, and neglecting the transverse components (i. e., those parallel to the metal surface), the electron-molecule interaction may be represented by

$$V_i(x) = \frac{-2eP_x x}{(x^2 + r_\perp^2)^{3/2}} \quad (3)$$

The effect of this term will be to lower slightly the barrier height in the region where the molecule is located. The quantity P_x is the component of the dipole moment normal to the surface, and r_\perp is the distance in the plane of the barrier of the electron from the molecule. The other components of the dipole field of the molecule and its image effectively cancel each other at distances greater than their separation. This is shown in the appendix.

Electron Tunneling

The probability per unit time that an electron in a state a on one side of a barrier will make a transition to a state b on the other side is (ref. 4)

$$P_{ab} = \frac{2\pi}{\hbar} |M_{ab}|^2 \rho_b f_a (1 - f_b) \quad (4)$$

where ρ_b is the density of states at b , and f_a and f_b are the probabilities of occupation of the states a and b , respectively. The quantity M_{ab} is the tunneling matrix element for a transition from a to b . Bardeen (ref. 5) has shown that the matrix element may be written as

$$M_{ab} = -i\hbar J_{ab}^{(x)} \quad (5)$$

where $J_{ab}^{(x)}$ is the matrix element of the x component of the current density operator J_x , evaluated in the barrier region:

$$J_{ab}^{(x)} = \langle \psi_a | J_x | \psi_b \rangle \quad (6)$$

and ψ_a and ψ_b are the wave functions which describe the states a and b . M_{ab} vanishes unless the transverse wave number k_t is conserved in the tunneling process. If state a is considered to be on the left of a barrier, the current flowing from left to right is obtained by summing P_{ab} over all states a of fixed k_t , summing over k_t , multiplying by the electronic charge e , and multiplying by 2 to account for spin. Similarly,

$$P_{ba} = \frac{2\pi}{\hbar} |M_{ba}|^2 \rho_a f_b (1 - f_a) \quad (7)$$

is the probability per unit time for a transition from the state b to the state a . The net current density flowing from left to right across the barrier is thus given by

$$\begin{aligned} J &= 2e \sum_{k_t} \int_{-\infty}^{\infty} (P_{ab} \rho_a - P_{ba} \rho_b) d\epsilon \\ &= \frac{4\pi e}{\hbar} \sum_{k_t} \left[|M_{ab}|^2 \rho_b f_a (1 - f_b) \rho_a - |M_{ba}|^2 \rho_a f_b (1 - f_a) \rho_b \right] d\epsilon \end{aligned} \quad (8)$$

The density of states factors allows the sum over the initial states to be replaced by an integral. But since J_x is equal to its complex conjugate J_x^* ,

$$M_{ba} = -i\hbar \langle \psi_b | J_x | \psi_a \rangle = -M_{ab}^* \quad (9a)$$

$$|M_{ba}|^2 = |M_{ab}|^2 \quad (9b)$$

and equation (8) reduces to

$$J = \frac{4\pi e}{\hbar} \sum_{\mathbf{k}_t} \int_{-\infty}^{\infty} |M_{ab}|^2 \rho_a \rho_b (f_a - f_b) d\epsilon \quad (10)$$

where ϵ is the total energy for a fixed \mathbf{k}_t . For the case of field emission from a metal the probability of occupation for a state in the vacuum is zero, and equation (10) becomes

$$J = \frac{4\pi e}{\hbar} \sum_{\mathbf{k}_t} \int_{-\infty}^{\infty} |M_{ab}|^2 \rho_a \rho_b f_a d\epsilon \quad (11)$$

The matrix element M_{ab} has been evaluated by Harrison (ref. 4) in the WKB approximation, and is given by

$$M_{ab} = \frac{1}{2\pi} \rho_a^{-1/2} \rho_b^{-1/2} \exp\left(-\int_{x_a}^{x_b} |k_x| dx\right) \quad (12)$$

where x_a and x_b are the classical turning points of the motion (see fig. 1), and

$$k_x = \left\{ \frac{2m}{\hbar^2} [V(x) - \epsilon_x] \right\}^{1/2} \quad (13)$$

where ϵ_x is the "x-directed" part of the electronic energy of motion, and $V(x)$ is the barrier potential energy.

$$V(x) = V_o(x) + V_i(x) \quad (14)$$

Calculation of the Matrix Element

The complete matrix element of the tunneling transition must be calculated not only between the initial and final electron states, but between the initial and final vibrational states of the molecule as well. If the transition is between the lowest vibrational state and a vibrational level of energy $\hbar\omega_n$, the complete matrix element is $\langle n | M_{ab} | 0 \rangle$. In order to calculate $\langle n | M_{ab} | 0 \rangle$, it is first necessary to evaluate the integral appearing in

the exponential of equation (12). Using equations (13) and (14),

$$I = - \int_{x_a}^{x_b} |k_x| dx = - \int_{x_a}^{x_b} \left\{ \frac{2m}{\hbar^2} [V_o(x) + V_i(x) - \epsilon_x] \right\}^{1/2} dx \quad (15)$$

The energy required to excite a molecule from one of its vibrational states to another is ordinarily a few tenths of an electron volt (infrared region of the spectrum). The barrier height $V_o(x) - \epsilon_x$, on the other hand, is usually not much smaller than the work function of the metal so that $V_i(x) \approx 10^{-1}[V_o(x) - \epsilon_x]$. Setting $V_o(x) - \epsilon_x \equiv \phi_m$, expanding the integrand in equation (15), and retaining only the first order term,

$$I \approx \frac{-(2m)^{1/2}}{\hbar} \int_{x_a}^{x_b} \phi_m^{1/2} \left[1 + \frac{V_i(x)}{2\phi_m} \right] dx \quad (16)$$

$V_i(x)$ is expected to be important only for the range $x < x_m$, where x_m is the point at which $V_o(x)$ reaches a maximum (see fig. 1). In this region ϕ_m may be treated as a constant (i. e., $V_o(x)$ meets the requirements of the WKB approximation). For $x > x_m$, $V_i(x)$ may be ignored completely, but the x dependence of ϕ_m should be considered. Hence, the integration is broken into two parts:

$$I = \frac{-(2m\phi_m)^{1/2}}{\hbar} \int_{x_m}^{x_m} \left[1 - \frac{eP_x x}{(x^2 + r_\perp^2)^{3/2} \phi_m} \right] dx - \frac{(2m)^{1/2}}{\hbar} \int_{x_m}^{x_b} \left(W_a - eFx - \frac{e^2}{4x} - \epsilon_x \right) dx \quad (17)$$

The first integral is

$$I_1 = - \frac{(2m)^{1/2}}{\hbar} \phi_m^{1/2} \left\{ (x_m - x_a) - \frac{eP_x}{\phi_m} \left[\frac{1}{(x_a^2 + r_\perp^2)^{1/2}} - \frac{1}{(x_m^2 + r_\perp^2)^{1/2}} \right] \right\} \quad (18)$$

while the second may be written as

$$I_2 = - \int_{x_a}^{x_b} \left[\frac{2m}{\hbar^2} \left(W_a - eFx - \frac{e^2}{4x} - \epsilon_x \right) \right]^{1/2} dx + \int_{x_a}^{x_m} \left[\frac{2m}{\hbar^2} \left(W_a - eFx - \frac{e^2}{4x} - \epsilon_x \right) \right]^{1/2} dx \quad (19)$$

The first integral in equation (19) is a standard expression in the theory of field emission from metals and has been evaluated (ref. 6). It is

$$\frac{-2\sqrt{2m\phi^3}}{3\hbar eF} v \left(\frac{\sqrt{e^3 F}}{\phi} \right) + \frac{\epsilon_x - \epsilon_F}{\hbar eF} \sqrt{2m\phi} t \frac{\sqrt{e^3 F}}{\phi}$$

where ϕ is the work function of the cathode and ϵ_F its Fermi energy; $t(y)$ and $v(y)$ are given below, and have been tabulated by Burgess, Kroemer, and Houston (ref. 7) for typical values of electric field and work function.

$$v(y) = \frac{1}{\sqrt{2}} \left(1 + \sqrt{1 - y^2} \right)^{1/2} \left[E(k) - \left(1 - \sqrt{1 - y^2} \right) K(k) \right] \quad (20a)$$

$$t(y) = v(y) - \left(\frac{2}{3} \right) y \frac{dv(y)}{dy} \quad (20b)$$

$$k^2 = \frac{2\sqrt{1 - y^2}}{1 + \sqrt{1 - y^2}}; \quad y = \frac{\sqrt{e^3 F}}{\phi} \quad (20c)$$

where $K(k)$ and $E(k)$ are the complete elliptic integrals of the first and second kinds, respectively. The second integral in equation (19) is simply

$$\int_{x_a}^{x_m} \left\{ \frac{2m}{\hbar^2} \left[V_o(x) - \epsilon_x \right] \right\}^{1/2} dx = \frac{(2m)^{1/2}}{\hbar} \phi_m^{1/2} (x_m - x_a) \quad (21)$$

since the range of integration is that for which ϕ_m is approximately constant. Collecting results,

$$M_{ab} = \frac{1}{2\pi} \rho_a^{-1/2} \rho_b^{-1/2} \exp \left[\left(\frac{2m}{\varphi_m} \right)^{1/2} \left(-\frac{eP_x}{\hbar} \right) \xi \left(\frac{r_\perp}{x_m} \right) - \frac{g}{2} + \frac{\epsilon_x - \epsilon_F}{2d} \right] \quad (22)$$

where

$$\xi \left(\frac{r_\perp}{x_m} \right) = \frac{1}{x_m} \left[\left(\frac{1 + r_\perp^2}{x_m^2} \right)^{-1/2} - \left(\frac{r_\perp}{x_m} \right)^{-1} \left(\frac{1 + x_a^2}{r_\perp^2} \right)^{-1/2} \right] \quad (23a)$$

$$g = \frac{-4\sqrt{2m}\varphi^3}{3\hbar eF} v \left(\frac{\sqrt{e^3 F}}{\varphi} \right) \quad (23b)$$

$$d = \frac{\hbar eF}{2\sqrt{2m}\varphi t \left(\frac{\sqrt{e^3 F}}{\varphi} \right)} \quad (23c)$$

If P_x is set equal to zero in equation (22) (i.e., there is no interaction), the equation reduces to the usual expression obtained for field emission from clean surfaces into vacuum.

The quantity $\xi \simeq 10^8$, according to equation (23a), and P_x is typically 3×10^{-31} Coulomb-meter (10^{-19} esu-cm) (ref. 2). Hence, the first term in the exponential factor of equation (22) is on the order of 10^{-2} . Using the expansion for $\exp(-x)$ for small x , M_{ab} is finally written as

$$\langle n | M_{ab} | 0 \rangle \simeq \frac{1}{2\pi} \left\langle n \left| \rho_a^{-1/2} \rho_b^{-1/2} \left[1 - \left(\frac{2m}{\varphi} \right)^{1/2} \frac{eP_x}{\hbar} \xi \left(\frac{r_\perp}{x_m} \right) \exp \left(-\frac{g}{2} + \frac{\epsilon_x - \epsilon_F}{2d} \right) \right] \right| 0 \right\rangle \quad (24)$$

This reduces to

$$\langle n | M_{ab} | 0 \rangle \simeq \frac{-1}{2\pi} \rho_a^{-1/2} \rho_b^{-1/2} \left(\frac{2m}{\varphi_m} \right)^{1/2} \frac{e \left(\frac{r_{\perp}}{x_m} \right)}{\hbar} \langle n | P_x | 0 \rangle \exp \left(-\frac{g}{2} + \frac{\epsilon_x - \epsilon_F}{2d} \right) \quad (25)$$

since P_x is the only factor in equation (24) which operates on the wave functions describing the vibrational states of the molecule.

Total Energy Distribution

The part of the current density arising from the electron-molecule interaction is given by

$$J_i = \frac{4\pi e}{\hbar} \sum_{k_t} \int_{-\infty}^{\infty} \frac{2m}{h^2 \varphi_m} e^2 |\langle n | P_x | 0 \rangle|^2 \xi^2 \left(\frac{r_{\perp}}{x_m} \right) \exp \left(-g + \frac{\epsilon_x - \epsilon_F}{d} \right) f(\epsilon') d \quad (26)$$

where $\epsilon' = \epsilon - \epsilon_F$ and $f(\epsilon')$ is the Fermi function $[\exp(\epsilon'/kT) + 1]^{-1}$. In a measurement of the total energy distribution only those electrons which satisfy the minimum energy condition (see fig. 2)

$$\epsilon - \hbar\omega_n \geq \varphi_{col} + \epsilon_F - eV_{col} \quad (27)$$

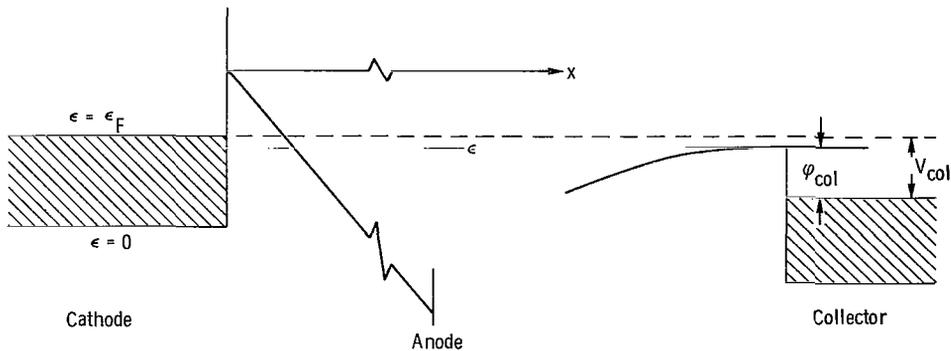


Figure 2. - Schematic representation of field emission energy distribution analyzer. Electrons with energy less than ϵ will not reach collector. Collector is located far enough from anode that tunneling into collector is negligible.

will reach the collector. The quantity $\hbar\omega_n$ is the excitation energy of a vibrational state of the molecule, φ_{col} is the collector work function, V_{col} is the bias voltage between cathode and collector, ϵ is the total energy of an electron incident on the barrier from inside the metal, and ϵ_{F} is the cathode Fermi energy. The total energy distribution of field emitted electrons is defined as

$$P_{\text{T}}(\epsilon) = \frac{1}{e} \frac{dJ}{d\epsilon} \quad (28)$$

From equation (25) for the "interaction" part of the current,

$$P_{\text{T}}^{\text{i}}(\epsilon) = \frac{4\pi}{\hbar} \sum_{\mathbf{k}_{\text{t}}} \frac{2me^2}{\varphi_{\text{m}}} \frac{|\langle n | P_{\text{x}} | 0 \rangle|^2}{h^2} \xi^2 \left(\frac{r_{\perp}}{x_{\text{m}}} \right) \exp \left(-g + \frac{\epsilon - \epsilon_{\perp} - \epsilon_{\text{F}}}{d} \right) f(\epsilon') \quad (29)$$

where r_{\perp} is the "perpendicular" part of the energy: $\epsilon = \epsilon_{\text{x}} + \epsilon_{\perp}$. But at the absolute zero of temperature in the absence of an interaction,

$$J_0 = \frac{2e}{h} \sum_{\mathbf{k}_{\text{t}}} \int_0^{\epsilon_{\text{F}}} \exp \left(-g + \frac{\epsilon - \epsilon_{\perp} - \epsilon_{\text{F}}}{d} \right) d\epsilon \quad (30)$$

Taking the derivative of equation (30) and substituting it in equation (29) results in

$$P_{\text{T}}^{\text{i}}(\epsilon) = \frac{8\pi^2 me}{\varphi_{\text{m}}} \frac{dJ_0}{d\epsilon} \xi^2 \left(\frac{r_{\perp}}{x_{\text{m}}} \right) \frac{|\langle n | P_{\text{x}} | 0 \rangle|^2}{h^2} f(\epsilon') \quad (31)$$

which, in terms of the applied collector voltage in equation (27) becomes

$$P_{\text{T}}^{\text{i}}(V_{\text{col}}) = -\frac{8\pi^2 m}{\varphi_{\text{m}}} \frac{dJ_0}{dV_{\text{col}}} \xi^2 \left(\frac{r_{\perp}}{x_{\text{m}}} \right) \frac{|\langle n | P_{\text{x}} | 0 \rangle|^2}{h^2} f(\varphi_{\text{col}} + \hbar\omega_n - eV_{\text{col}}) \quad (32)$$

The total energy distribution at finite temperatures for the noninteracting part of the current density is simply

$$P_T^0(V_{\text{col}}) = \frac{-1}{e^2} \left(\frac{dJ_0}{dV_{\text{col}}} \right) f(\varphi_{\text{col}} - eV_{\text{col}}) \quad (33)$$

and $P_T(V_{\text{col}})$ for the total field emission current density becomes

$$P_T(V_{\text{col}}) = - \left(\frac{dJ_0}{dV_{\text{col}}} \right) \left[\frac{1}{e^2} f(\varphi_{\text{col}} - eV_{\text{col}}) + \frac{8\pi^2 m}{\varphi_m} \xi^2 \left(\frac{r_{\perp}}{x_m} \right) \frac{|\langle n | P_x | 0 \rangle|^2}{h^2} f(\varphi_{\text{col}} + \hbar\omega_n - eV_{\text{col}}) \right] \quad (34)$$

From equation (34)

$$\begin{aligned} \frac{dP_T}{dV_{\text{col}}} = \frac{d^2 J_0}{dV_{\text{col}}^2} P_T(V_{\text{col}}) \left(\frac{dJ_0}{dV_{\text{col}}} \right)^{-1} - \frac{dJ_0}{dV_{\text{col}}} \left[\frac{1}{e^2} \frac{df(\varphi_{\text{col}} - eV_{\text{col}})}{dV_{\text{col}}} + \frac{8\pi^2 m}{\varphi_m} \xi^2 \left(\frac{r_{\perp}}{x_m} \right) \right. \\ \left. \times \frac{|\langle n | P_x | 0 \rangle|^2}{h^2} \frac{df(\varphi_{\text{col}} + \hbar\omega_n - eV_{\text{col}})}{dV_{\text{col}}} \right] \end{aligned} \quad (35)$$

At low temperatures the derivative of the Fermi function behaves like a Dirac delta function, and equation (35) may be rewritten as

$$\begin{aligned} \frac{dP_T}{dV_{\text{col}}} \approx \frac{d^2 J_0}{dV_{\text{col}}^2} P_T(V_{\text{col}}) \left(\frac{dJ_0}{dV_{\text{col}}} \right)^{-1} - \left(\frac{dJ_0}{dV_{\text{col}}} \right) \left[\frac{1}{e^2} \delta(\varphi_{\text{col}} - eV_{\text{col}}) + \frac{8\pi^2 m}{\varphi_m} \right. \\ \left. \times \xi^2 \left(\frac{r_{\perp}}{x_m} \right) \frac{|\langle n | P_x | 0 \rangle|^2}{h^2} \delta(\varphi_{\text{col}} + \hbar\omega_n - eV_{\text{col}}) \right] \end{aligned} \quad (36)$$

Equations (34) and (36) represent the final result for the case where a single molecule with a single upper vibrational energy level of energy $\hbar\omega_n$ interacts with the tunneling current. If N foreign molecules per unit area have been deposited on the cathode, the average "interaction" current density may be found by integrating equation (26) over the

surface area of the cathode and multiplying the result by N . Such an averaging process assumes that the molecules do not interact with each other to alter their dipole fields. In order for the dipole approximation to remain valid, then, the density N must be low enough that an electron emerging from the metal sees the field of a single molecule. For the idealized case considered here (an infinite plane representing the metal surface), the electric field F and work function φ are constants independent of r_{\perp} . Hence, the average "interaction" current density may be written as

$$\langle J_i \rangle = \frac{8\pi^2 e^3 N}{h^3} \left(\frac{2m}{\varphi_m} \right) \sum_{k_t} \int_{-\infty}^{-\infty} |\langle n | P_x | 0 \rangle|^2 \exp \left(-g + \frac{\epsilon - \epsilon_{\perp} - \epsilon_F}{d} \right) \times f(\epsilon') d\epsilon \int_{-\infty}^{\infty} \xi^2 \left(\frac{r_{\perp}}{m} \right) 2\pi r_{\perp} dr_{\perp} \quad (37)$$

The lower limit of integration over r_{\perp} has been set at some point r_0 in the vicinity of the molecule. (Near the molecule the approximation for the interaction energy fails because the transverse components of the dipole moment no longer cancel.) The integral over r_{\perp} is

$$I = 2\pi \int_{r_0}^{\infty} \left\{ \frac{r_{\perp}}{\left(r_{\perp}^2 + x_a^2 \right)} - \frac{2r_{\perp}}{\left[\left(r_{\perp}^2 + x_a^2 \right) \left(r_{\perp}^2 + x_m^2 \right) \right]^{1/2}} + \frac{r_{\perp}}{\left(r_{\perp}^2 + x_m^2 \right)} \right\} dr_{\perp} \\ = 2\pi \left\{ \ln \frac{\left[\left(r_{\perp}^2 + x_a^2 \right) \left(r_{\perp}^2 + x_m^2 \right) \right]^{1/2}}{\left[r_{\perp}^4 + r_{\perp}^2 \left(x_m^2 + x_a^2 \right) + x_m^2 x_a^2 \right]^{1/2} + r_{\perp}^2 + \frac{x_m^2 + x_a^2}{2}} \right\}_{r_0}^{\infty} \quad (38)$$

Evaluation at the upper limit may be accomplished by noting that

$$\lim_{r_{\perp} \rightarrow \infty} \left\{ \ln \frac{\left(1 + \frac{x_a^2 + x_m^2}{r_{\perp}} + \frac{x_a^2 x_m^2}{r_{\perp}^4} \right)^{1/2}}{\left[\left(1 + \frac{x_a^2 + x_m^2}{r_{\perp}^2} + \frac{x_a^2 x_m^2}{r_{\perp}^4} \right)^{1/2} + 1 + \frac{x_m^2 + x_a^2}{2r_{\perp}^2} \right]} \right\} = \ln \frac{1}{2}$$

Thus

$$I = 2\pi \ln \frac{\left[r_o^4 + r_o^2(x_m^2 + x_a^2) + x_m^2 x_a^2 \right]^{1/2} + r_o^2 + \frac{x_m^2 + x_a^2}{2}}{2 \left[r_o^4 + r_o^2(x_m^2 + x_a^2) + x_m^2 x_a^2 \right]^{1/2}} = 2\pi \ln \beta \quad (39)$$

The exact value of r_o is unimportant since it enters only in the logarithm. Inserting equation (39) back into equation (37) gives

$$\langle J_i \rangle = \frac{32\pi^3 e^3 N m}{h^3 \varphi_m} \ln \beta \sum_{k_t} |\langle n | P_x | 0 \rangle|^2 \int_{-\infty}^{\infty} \exp\left(-g + \frac{\epsilon - \epsilon_1 - \epsilon_F}{d}\right) f(\epsilon') d\epsilon \quad (40)$$

A molecule ordinarily possesses more than a single vibrational level above its ground state. The expression for the "interaction" part of the current density given by equation (40) must therefore be summed over all such levels, and $P_T(V_{col})$ and $dP_T(V_{col})/dV_{col}$ finally become

$$P_T(V_{col}) = - \left(\frac{dJ_o}{dV_{col}} \right) \left[\frac{1}{e^2} f(\varphi_{col} - eV_{col}) + N \frac{32\pi^3 m}{h^2 \varphi_m} \ln \beta \sum_n |\langle n | P_x | 0 \rangle|^2 f(\varphi_{col} + \omega_n - eV_{col}) \right] \quad (41)$$

and

$$\frac{dP_T(V_{col})}{dV_{col}} = \left(\frac{d^2 J_o}{dV_{col}^2} \right) P_T(V_{col}) \left(\frac{dJ_o}{dV_{col}} \right)^{-1} - \left(\frac{dJ_o}{dV_{col}} \right) \left[\frac{1}{e^2} \delta(\varphi_{col} - eV_{col}) + N \frac{32\pi^3 m}{h^2 \varphi_m} \ln \beta \sum_n |\langle n | P_x | 0 \rangle|^2 \delta(\varphi_{col} + \omega_n - eV_{col}) \right] \quad (42)$$

Calculation of the Collector Current Density

The total average current density is given by

$$\langle J \rangle = \frac{2e}{h} \sum_{k_t} \int_{-\infty}^{\infty} \exp\left(-g + \frac{\epsilon - \epsilon_1 - \epsilon_F}{d}\right) f(\epsilon') d\epsilon + N \frac{32\pi^3 m e^3}{h^3 \varphi_m} \ln \beta \sum_n |\langle n | P_x | 0 \rangle|^2 \times \sum_{k_t} \int_{-\infty}^{\infty} \exp\left(-g + \frac{\epsilon - \epsilon_1 - \epsilon_F}{d}\right) f(\epsilon') d\epsilon \quad (43)$$

The average collector current is obtained by integrating over the range of total energies for which the electrons are collected. The sum over k_t may be converted to an integral as follows:

$$\sum_{k_t} \rightarrow \frac{1}{4\pi^2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dk_y dk_z \rightarrow \frac{1}{4\pi^2 \hbar^2} \int_0^{\infty} \int_0^{2\pi} m d\epsilon_{\perp} d\theta \rightarrow \frac{2\pi}{h^2} \int_0^{\infty} m d\epsilon_{\perp} \quad (44)$$

Considering only the zero temperature limit for simplicity,

$$\begin{aligned}
\langle J_{\text{col}} \rangle &= \frac{2\pi m e}{h^3} \exp(-g) \int_{\varphi_{\text{col}} + \epsilon_{\text{F}} - eV_{\text{col}}}^{\epsilon_{\text{F}}} \exp\left(\frac{\epsilon - \epsilon_{\text{F}}}{d}\right) d\epsilon \int_0^{\epsilon} \exp\left(-\frac{\epsilon_{\perp}}{d}\right) d\epsilon_{\perp} + N \frac{64\pi^4 m^2 e^3}{h^5 \varphi_{\text{m}}} \\
&\times \ln\beta \sum_{\text{n}} |\langle \text{n} | \mathbf{P}_{\text{x}} | 0 \rangle|^2 \exp(-g) \int_{\varphi_{\text{col}} + \hbar\omega_{\text{n}} + \epsilon_{\text{F}} - eV_{\text{col}}}^{\epsilon_{\text{F}}} \exp\left(\frac{\epsilon - \epsilon_{\text{F}}}{d}\right) d\epsilon \int_0^{\epsilon} \exp\left(-\frac{\epsilon_{\perp}}{d}\right) d\epsilon_{\perp}
\end{aligned} \tag{45}$$

from which

$$\begin{aligned}
\langle J_{\text{col}} \rangle &= \frac{2\pi m e d}{h^3} \exp(-g) \left\{ (\varphi_{\text{col}} - eV_{\text{col}}) \exp\left(-\frac{\epsilon_{\text{F}}}{d}\right) + d \left[1 - \exp\left(\frac{\varphi_{\text{col}} - eV_{\text{col}}}{d}\right) \right] \right\} \\
&+ N \frac{64\pi^4 m^2 e^3 d}{h^5 \varphi_{\text{m}}} \exp(-g) \ln\beta \sum_{\text{n}} |\langle \text{n} | \mathbf{P}_{\text{x}} | 0 \rangle|^2 \left\{ (\varphi_{\text{col}} + \hbar\omega_{\text{n}} - eV_{\text{col}}) \exp\left(-\frac{\epsilon_{\text{F}}}{d}\right) \right. \\
&\left. + d \left[1 - \exp\left(\frac{\varphi_{\text{col}} + \hbar\omega_{\text{n}} - eV_{\text{col}}}{d}\right) \right] \right\}
\end{aligned} \tag{46}$$

The quantity d ranges in value from a few hundredths of an electron-volt to a few tenths of an electron-volt for stable field emission. Since for most metals of interest as field emission cathodes ϵ_{F} is on the order of 5 or 6 electron volts, the linear term in each pair of braces may be neglected. (The factor $\exp(-\epsilon_{\text{F}}/d)$ will almost always be less than 10^{-4} .)

DISCUSSION

Figure 3 is a sketch of $\langle J_{\text{col}} \rangle$ as a function of collector voltage. The dashed curve represents the noninteracting part of the collector current density. As indicated in the figure, an increase in current occurs whenever the bias voltage is such that electrons which have lost energy in the electron-molecule interaction can be collected. The threshold voltage for each onset of additional current should be exactly equal to

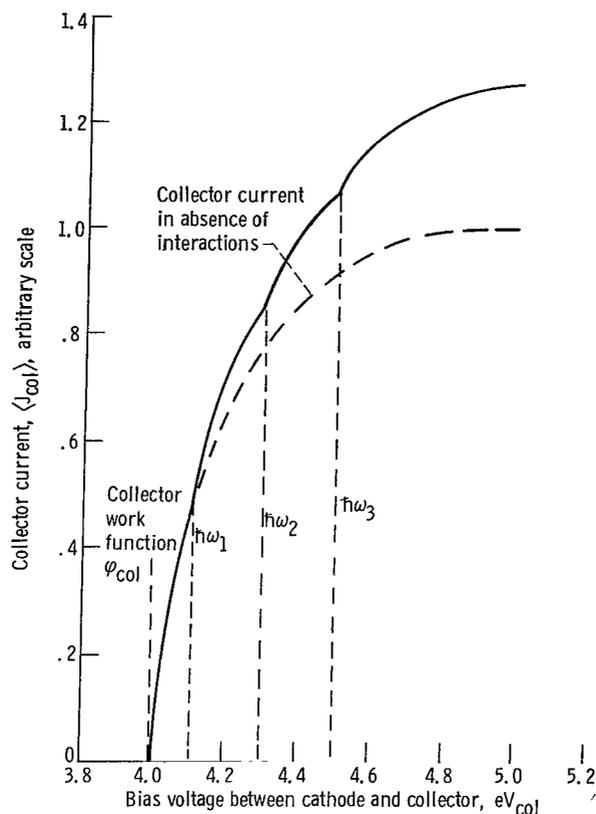


Figure 3. - Collector current as function of collector voltage. Temperature, 0 K.

$e^{-1}(\phi_{col} + \hbar\omega_n)$, where $\hbar\omega_n$ is the energy of the vibrational level to which the molecule makes a transition (assuming the molecule was initially in its ground state).

Sketches of the total energy distribution and its derivative are shown in figures 4 and 5. Each increase in $\langle J_{col} \rangle$ is accompanied by a corresponding increase in $P_T(V_{col})$ for the same values of collector voltage. The threshold voltages are marked by the appearance of a "spectral line" in $dP_T(V_{col})/dV_{col}$. At finite temperatures the lines will not be perfectly sharp, as shown in the figure, but will be broadened by the appearance of a thermal tail on the distribution function.

An order of magnitude estimate of the ratio of the "interaction" part of the collector current density to the noninteracting part is of interest. As indicated in figure 1, $x_m \approx 3 \times 10^{-8}$ centimeter and $x_a \sim 0.5 \times 10^{-8}$ centimeter. From equation (39), $\ln\beta$ ranges from approximately 0.7 for $r_0 = 0$ to about 1.4 for $r_0 = 3 \times 10^{-8}$ centimeter, and can be set equal to 1 for this estimate. A reasonable value for $\sum_n |\langle n | P_x | 0 \rangle|^2$ is 10^{-61} Coulomb²-meter² (10^{-38} (esu)²-cm²) (ref. 2). Again, from figure 1, ϕ_m is ordinarily a

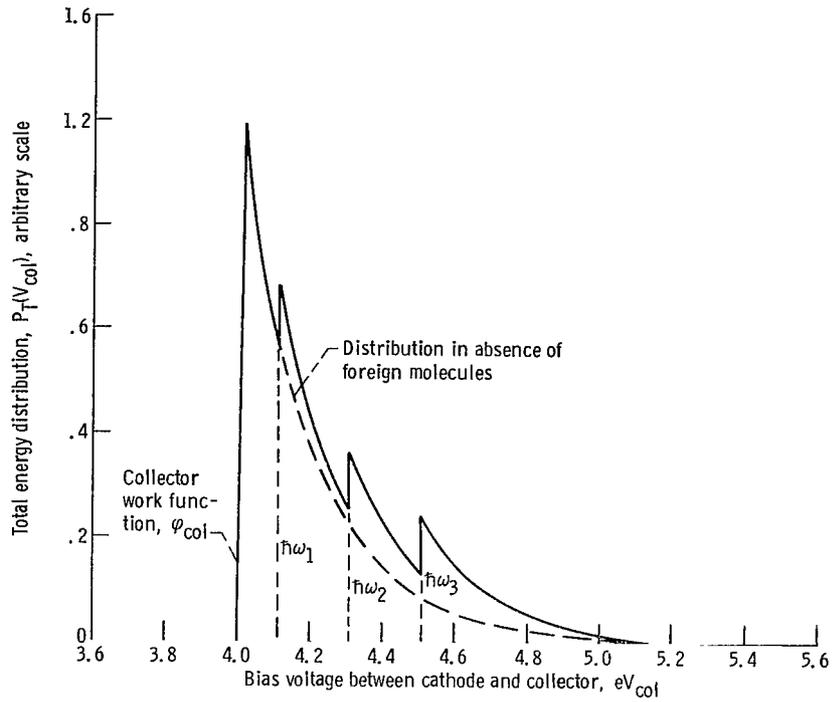


Figure 4. - Total energy distribution from figure 3, indicating presence of electron-molecule interactions. Temperature, 0 K.

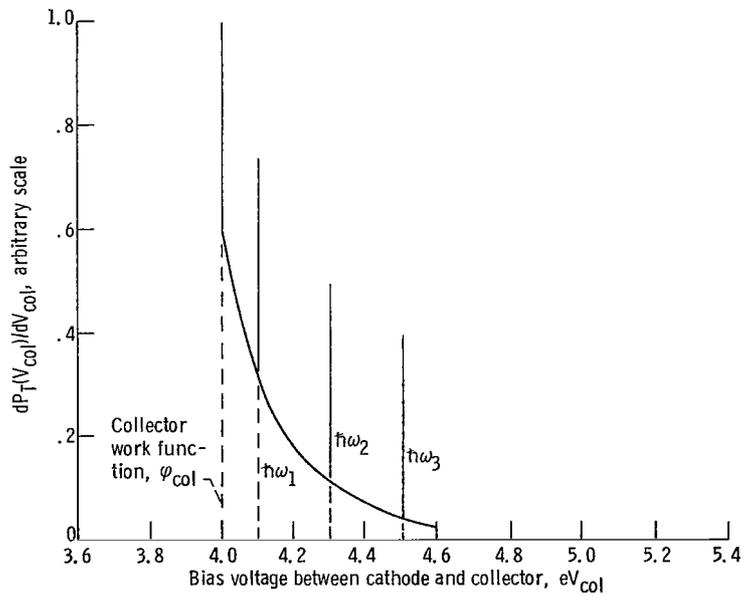


Figure 5. - Derivative of total energy distribution of figure 4, showing existence of "spectral lines" corresponding to molecular excitations. Temperature, 0 K.

few electron volts, so the ratio $\langle J_{\text{col}} \rangle_i / \langle J_{\text{col}} \rangle_o$ is $\sim 2 \times 10^{-17} N$. As indicated earlier, the expression obtained for the average current density is valid only when the surface density of molecules is low. In computing the matrix element M_{ab} , it was mentioned that the interaction could be assumed to be negligible for distances greater than x_m . Hence, a value for N of 1 molecule per $20(a)^2$ is well within the limits required by the approximation made previously to obtain $\langle J_{\text{col}} \rangle$. The final result is that $\langle J_{\text{col}} \rangle_i / \langle J_{\text{col}} \rangle_o \sim 10^{-2}$. This estimate, although of the same order of magnitude as the calculated size of the effect in metal-oxide-metal tunneling, seems surprisingly small in view of the dramatic effects observed in field emission microscopes when foreign molecules are adsorbed on the cathode surface. The reason for the difference is, of course, the approximation used for the interaction potential energy $V_i(x)$, and the attendant restrictions to assure its validity. Other types of electron-molecule interactions which have been considered to explain the larger changes in current density have been discussed in the literature (refs. 6, and 8 to 11). None of them, however, have considered the particular effect discussed here. Since the dipole potential is essentially a small perturbation on the barrier potential, it is not unreasonable to expect that the effect will still be present even when other, larger interactions are included.

CONCLUSION

The present calculation indicates that electron-molecular dipole interactions should give rise to structure in field emission currents, just as they do in tunneling currents in metal-oxide-metal sandwiches with impurities trapped in the oxide layer. The magnitude of the effect for low surface coverage of foreign molecules is estimated to be of the order of 1 percent. The first derivative of the total energy distribution of the emitted electrons is directly proportional to the dipole spectral weight function of the molecular species on the cathode surface, and should yield a series of "lines" corresponding to each vibrational transition.

Lewis Research Center,
 National Aeronautics and Space Administration,
 Cleveland, Ohio, June 30, 1969,
 129-02-05-14-22.

APPENDIX - ELECTRIC FIELD OF A DIPOLE AT A METAL-VACUUM INTERFACE

From figure 6 the field at a point P in the vicinity of the charge distribution shown is

$$\vec{E} = \frac{q}{r_1^3} \left(\vec{r}_1 - \frac{\vec{r}_2 r_1^3}{r_2^3} \right) - \frac{q}{(r_1')^3} \left[\vec{r}_1' - \frac{\vec{r}_2' (r_1')^3}{(r_2')^3} \right] \quad (47)$$

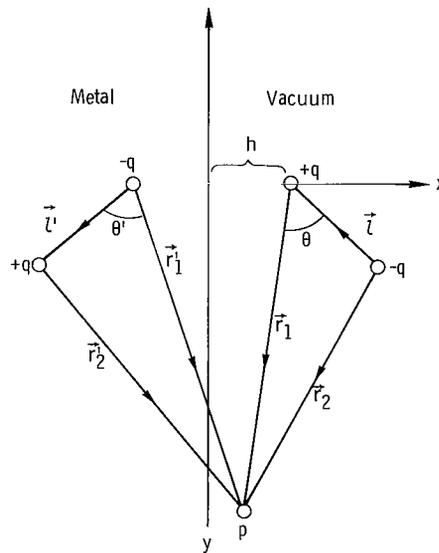


Figure 6. - Dipole and its image at a conducting plane.

From trigonometry

$$r_2^2 = r_1^2 + l^2 - 2r_1 l \cos \theta \quad (48)$$

and if $|\vec{l}| \ll |\vec{r}_1|$,

$$\left(\frac{r_2}{r_1} \right)^{-3} = \left(1 + \frac{l^2}{r_1^2} - \frac{2l}{r_1} \cos \theta \right)^{-3/2} \simeq \left(1 + \frac{3l}{r_1} \cos \theta \right) \quad (49)$$

Similarly,

$$\left(\frac{r'_2}{r'_1}\right)^{-3} \approx \left(1 + \frac{3l}{r'_1} \cos \theta\right) \quad (50)$$

Since $\vec{r}_2 = \vec{r}_1 + \vec{l}$, and $\vec{r}'_2 = \vec{r}'_1 - \vec{l}$,

$$\vec{E} \approx \left(\frac{q}{r_1^3}\right) \left[\vec{r}_1 - (\vec{r}_1 + \vec{l}) \left(1 + \frac{3l}{r_1} \cos \theta\right) \right] - \frac{q}{(r'_1)^3} \left[\vec{r}'_1 - (\vec{r}'_1 - \vec{l}) \left(1 + \frac{3l}{r'_1} \cos \theta'\right) \right] \quad (51)$$

from which

$$\vec{E} \approx \frac{q}{r_1^3} \left(-\vec{l} - \frac{3l\vec{r}_1}{r_1} \cos \theta \right) - \frac{q}{(r'_1)^3} \left(\vec{l}' - \frac{3l\vec{r}'_1}{r'_1} \cos \theta' \right) \quad (52)$$

But

$$\vec{r}' = \hat{i}(x+h) + \hat{j}y + \hat{k}z \quad (53a)$$

$$\vec{r}_1 = \hat{i}(x-h) + \hat{j}y + \hat{k}z \quad (53b)$$

and

$$\vec{l}' = -\hat{i}l_x + \hat{j}l_y + \hat{k}l_z \quad (54a)$$

$$\vec{l} = \hat{i}l_x - \hat{j}l_y + \hat{k}l_z \quad (54b)$$

so that near the conducting plane, where $\theta \sim \theta'$, and for distances such that $r_1 \approx r'_1 \gg h$,

$$\vec{E} \approx \frac{q}{r_1^3} \left[2\hat{i}l_x + \frac{3l\hat{i}(2h)}{r_1} \cos \theta \right] \approx \frac{2ql}{r_1^3} \hat{i} = \frac{2P_x \hat{i}}{r_1^3} \quad (55)$$

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