

## Ion energy distributions from photon- and electron-stimulated desorption. II. The quasiclassical final state and reneutralization

William L. Clinton and Sipra Pal\*

*Department of Physics, Georgetown University, Washington, D.C. 20057*

Ronald E. Jutila

*Boeing Aerospace Company, P.O. Box 3999, Mail Stop 87-08, Seattle, Washington 98124-2499*

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Franck-Condon overlap integrals are calculated to fit ion energy distributions (IED's) resulting from photon- or electron-stimulated desorption. The WKB or quasiclassical trajectory approximation is used to compute the final-state wave function. The final-state potential consists of a repulsive exponential and an image term. The calculated IED's compare well with those found previously using the reflection or classical trajectory approximation. Both methods agree well with a wide range of experimental IED's all of which are mildly asymmetric Gaussian functions of the ion energy. It is shown how these two approximations are related through the classical limit of the final-state wave function. In addition, the quasiclassical wave function is generalized to include an optical potential giving rise in a natural way to the reneutralization reduction factor. The Gaussian asymmetry in the IED's is usually to the high-energy side reflecting a "normal" exponential repulsion. However, in a few anomalous cases the Gaussian is skewed to the low-energy side of the IED peak. This anomaly cannot be explained by expected influences on the initial-state wave function such as anharmonicities. On the other hand, the reneutralization factor, when it predominates, provides a natural explanation for this effect. In addition, this reneutralization factor can cause significant shifts in the IED peak, away from the Franck-Condon peak.

### I. INTRODUCTION

In a recent report<sup>1</sup> we presented an analysis of ion yields from photon- and electron-stimulated desorption. It was based on the Franck-Condon model using the well-known reflection approximation (RA), where the final-state wave function of the desorbing ion is taken to be a  $\delta$  function, corresponding to its classical trajectory. There it was shown that in the RA model, the ion energy distribution (IED) is a reflection of the square of the initial-state bound vibrational wave function. The final-state potential-energy curve serves as the "mirror" in this graphical process. The IED is essentially a mildly asymmetric Gaussian distribution. The normal asymmetry to the high-energy side is a result of the exponential final-state potential. It was suggested that a more complicated potential based on an effective reneutralization process gives rise to an anomalous asymmetry to the low-energy sides of the IED in some cases. This is observed in Nb-H<sup>+</sup> and Mo-O<sup>+</sup> [see Figs. 1(h) and 1(i)]. In the present work we present an extension of our theory of the IED that results in a more natural and rigorous treatment of reneutralization. This in turn leads to an explanation of the anomalous asymmetry. We do this by looking in detail at the final-state wave function—especially in the neighborhood of the classical turning point. In particular, we show how this quasiclassical state goes formally into a  $\delta$  function in the classical limit. More importantly, however, the final state is also studied in the very important

case of a complex potential where the imaginary part represents the decay of the ion via reneutralization. We show how this naturally leads to a reduction factor in the ion desorption probability.<sup>2</sup> Energy dependence of the form seen in Figs. 2 and 3 gives rise to asymmetries and energy shifts.

We have also found that the existence of the two electronic states, ion and neutral, as the desorption occurs also leads to the possibility of interference phenomena similar to that which is observed in various ion spectroscopies.<sup>3</sup> These interference effects will be the subject of a future communication.

### II. GENERAL FRANCK-CONDON THEORY FOR A REAL FINAL-STATE POTENTIAL

Experimentally determined ion energy and ion angle distributions from electron-stimulated and photon-stimulated desorption have been explained in terms of two processes: (a) initial-state (IS) effects from which structural, spectroscopic, and chemical bond information can be inferred,<sup>4,5</sup> and (b) final-state (FS) effects wherein ion-surface interactions<sup>6-8</sup> determine the classical ion trajectories, using model potentials. In previous work using the Franck-Condon principle theory,<sup>9,10</sup> both IS and FS effects were taken into account and information regarding the initial ground-state adsorbate wave function and final-state potential were inferred. In addition, all trajectory effects (final state—due to ion-surface interactions as

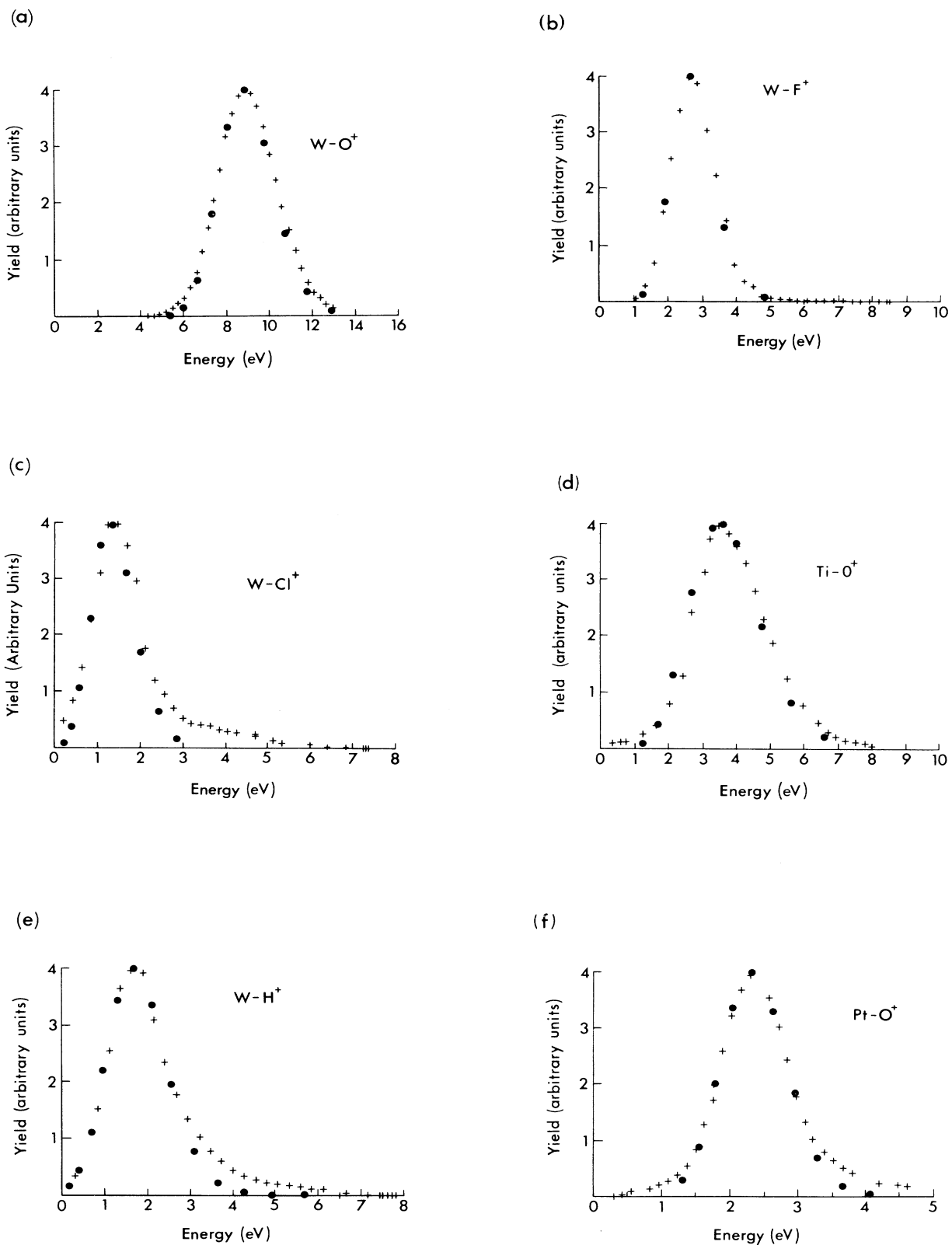


FIG. 1. Comparison of WKB calculated IED with experimental results for a representative set of metal-ion systems. Note anomalous asymmetry in Figs. 1(h) ( $Nb-O^+$ ) and 1(i) ( $Mb-O^+$ ).

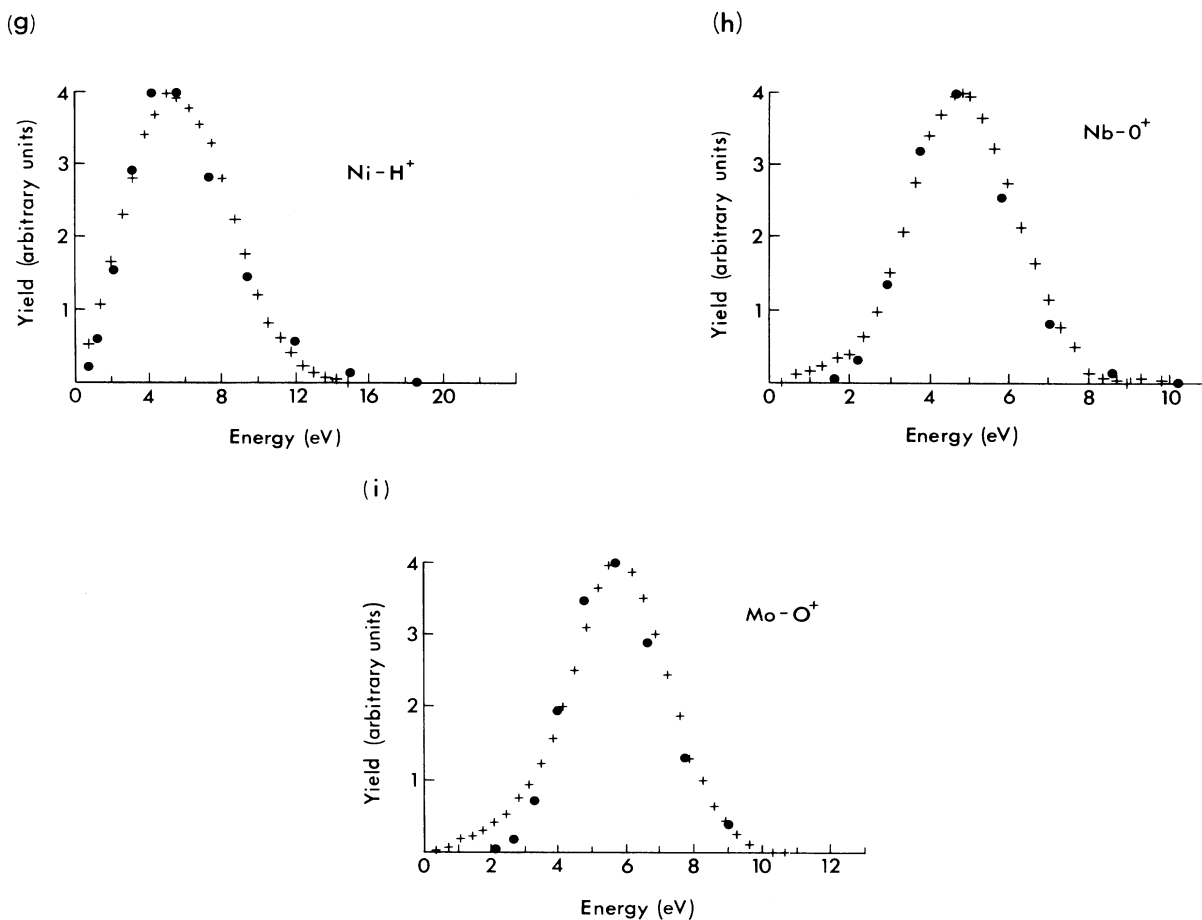


FIG. 1. (Continued).

well as modifications due to reneutralization) were introduced into the theory. In the following we give a brief review of our previous formalism.

#### A. General formulation of the desorption cross section

From the viewpoint of formal scattering theory the processes of electron- and photon-stimulated desorption (ESD and PSD) can be described by a transition matrix element of the form

$$T_{fi} = \int d\mathbf{r} \int d\mathbf{R} \psi_f^*(\mathbf{r}, \mathbf{R}) T \psi_i(\mathbf{r}, \mathbf{R}), \quad (1)$$

where  $\mathbf{r}$  represents the coordinates of all electrons and  $\mathbf{R}$  the coordinates of all of the nuclei. The transition operator  $T$ , in general, operates on all coordinates of the system but to first approximation it can be assumed to operate only on the electronic coordinates. For electronic excitations the  $T$  operator can be derived from the Coulomb potential, namely

$$V = \frac{1}{2} \sum_{\substack{i,j \\ (i \neq j)}} 1/|\mathbf{r}_i - \mathbf{r}_j|,$$

and for excitations due to photons, from **A·P**. In the

Born-Oppenheimer approximation the wave function is factorizable as  $\psi(\mathbf{r}, \mathbf{R}) = \psi_e(\mathbf{r}, \mathbf{R}) \phi_{ev}(\mathbf{R})$ , thus  $T$  can be written as

$$T_{fi} = \int d\mathbf{R} \phi_{e_f v_f}^* \phi_{e_i v_i} \left[ \int d\mathbf{r} \psi_{e_f}^* T \psi_{e_i} \right]. \quad (2)$$

The vibrational wave function  $\phi_{ev}(\mathbf{R})$  requires two indices to label it since the nuclei move in the field created by the electron-charge cloud and thus in effect depend on  $e$ . The ESD and PSD differential cross section  $\sigma(e_f v_f, e_i v_i)$  can therefore be written as

$$\sigma(e_f v_f, e_i v_i) = \sigma_e(e_f v_f, e_i v_i, \mathbf{R}_e) |I_{FC}(e_f v_f, e_i v_i)|^2, \quad (3)$$

where  $\sigma_e$  is the electronic contribution to the cross section, i.e.,

$$\sigma_e(e_f v_f, e_i v_i, \mathbf{R}) = \left| \int d\mathbf{R} \psi_{e_f}^*(\mathbf{r}, \mathbf{R}) T \psi_{e_i}(\mathbf{r}, \mathbf{R}) \right|^2. \quad (4)$$

In obtaining Eq. (3) it has been assumed that  $\sigma_e$  is a slowly varying function of  $\mathbf{R}$  and is therefore evaluated at the equilibrium position  $\mathbf{R}_e$ . The Franck-Condon overlap integral  $I_{FC}$  is given by

$$I_{FC} = \int d\mathbf{R} \phi_{e_f v_f}(\mathbf{R}) \phi_{e_i v_i}(\mathbf{R}). \quad (5)$$

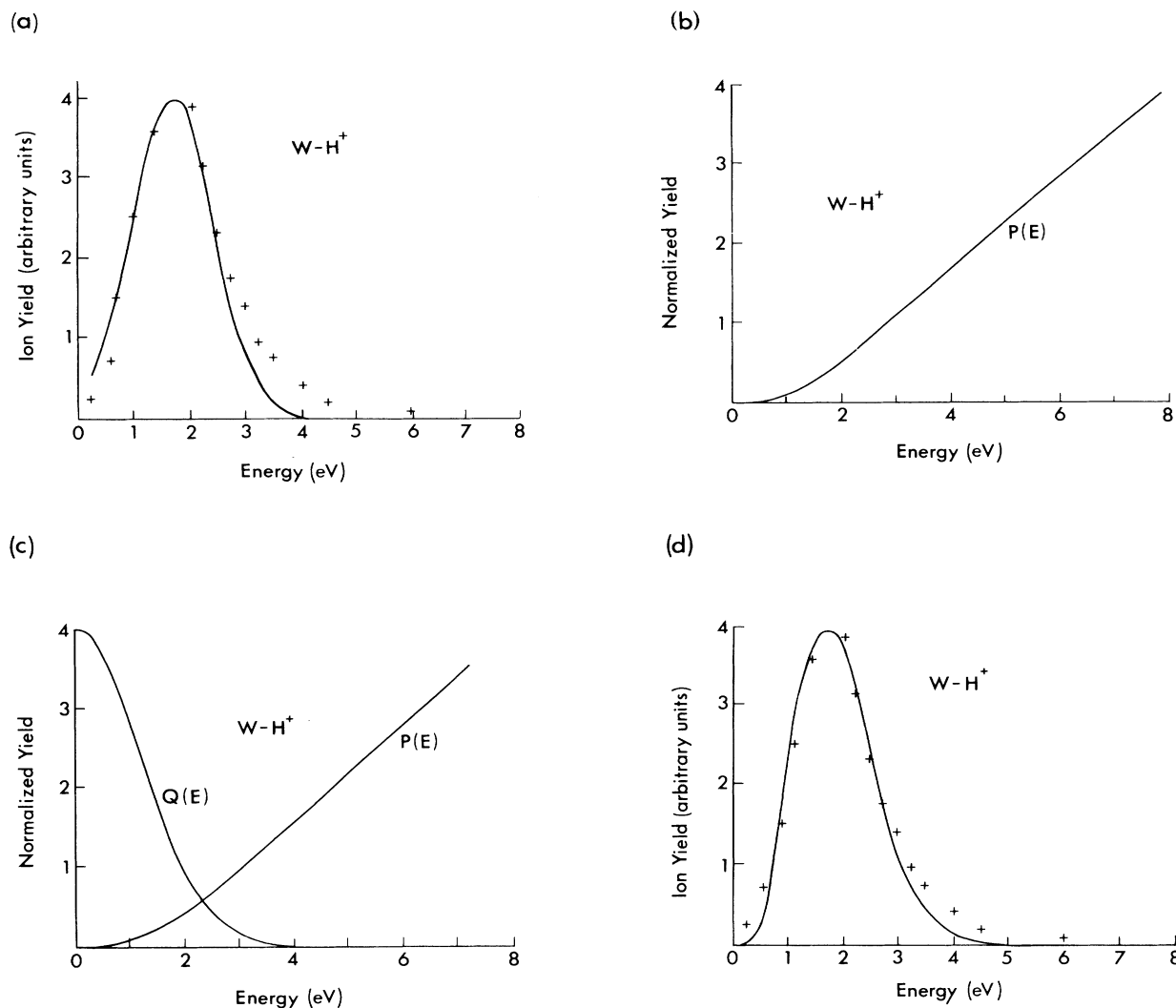


FIG. 2. (a) Comparison of the experimental data (+) to the theoretical (—) Franck-Condon factor  $Y = \exp[-(E - E_p)^2/2\Delta^2]$ , where  $E_p = 1.7$  eV, full width at half maximum (FWHM) is 1.7 eV, and  $\Delta^2 = 0.5231$  eV<sup>2</sup>. (b) Plot of the reduction factor  $P(E) = \exp(-A/E^{1/2})$  where  $A = 5.65$  eV<sup>1/2</sup>. (c) Plot of  $P(E) = \exp(-A/E^{1/2})$  and  $Q(E) = \exp[-(E - E_i)^2/2\Delta^2]$ , where  $A = 5.65$  eV<sup>1/2</sup>,  $E_i = 0.16$  eV, and  $\Delta^2 = 1.2$  eV<sup>2</sup>. (d) Comparison of the experimental data (+) to the theoretical (—) IED cross section including reneutralization.  $Y = \exp[-(E - E_i)^2/2\Delta^2] \exp(-A/E^{1/2})$ , where  $\Delta^2 = 1.2$  eV<sup>2</sup>,  $A = 5.65$  eV<sup>1/2</sup>, and  $E_i = 0.16$  eV. These fitting parameters were calculated for the known value of  $Y = 10^{-6}$  for W-H<sup>+</sup> system.

The overlap integral between the adsorbate vibrational state and the final scattering state wave function is a result of the initial photon or electron impact on the adatom producing a bond breakage, resulting in a change of the potential-energy curve from, for example, a harmonic well to a repulsive exponential. This change occurs in a time much shorter than the nuclear vibrational period such that the instantaneous value of the nuclear coordinate  $\mathbf{R}$  and momentum  $\mathbf{p}_R$  remain unchanged (Franck-Condon principle). The above model of obtaining the cross section works for all the different mechanisms of bond breaking<sup>11</sup>

and the distinct electronic processes involved in the desorption resides in the calculation of  $\sigma_e$ .

#### B. Evaluation of $I_{FC}$ via the reflection approximation

The evaluation of the Franck-Condon overlap integral requires a knowledge of both the ground-state (vibrational) and the final-state (desorbing) wave function of the adsorbate. The ground-state function  $\phi_{e_i, v_i}(\mathbf{R})$  can for most purposes be taken to be a Gaussian since the particle can be thought to be bound in the ground state of an harmon-

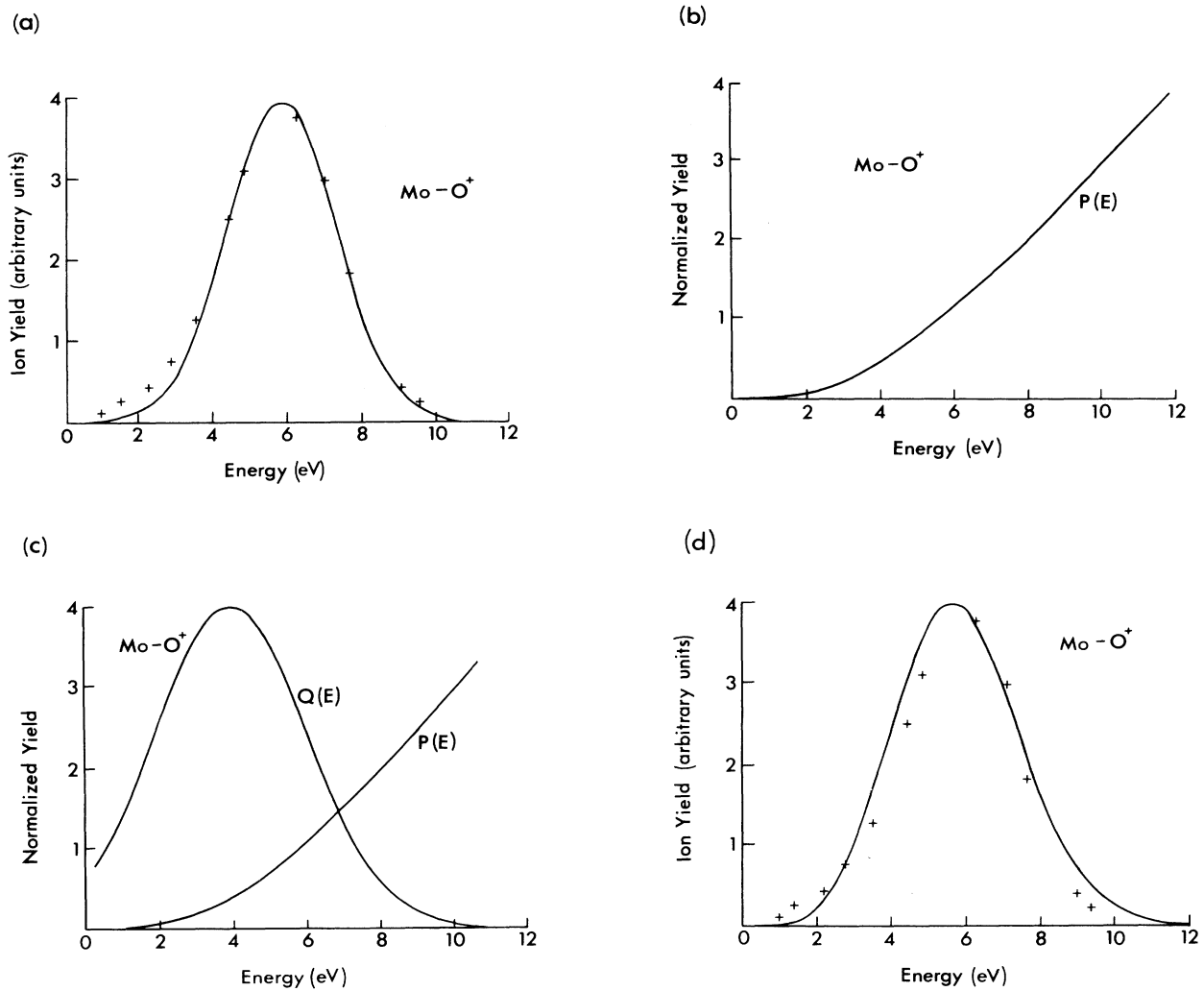


FIG. 3. (a) Comparison of the experimental data (+) to the theoretical (—) Franck-Condon factor  $Y = \exp[-(E - E_p)^2/2\Delta^2]$ , where  $E_p = 5.75$  eV, FWHM is 3.4 eV, and  $\Delta^2 = 2.085$  eV<sup>2</sup>. (b) Plot of  $P(E) = \exp(A/E^{1/2})$ , where  $A = 10.5$  eV<sup>1/2</sup>. (c) Plot of  $P(E) = \exp(-A/E^{1/2})$  and  $Q(E) = \exp[-(E - E_i)^2/2\Delta^2]$ , where  $A = 10.5$  eV<sup>1/2</sup>,  $E_i = 4.0$  eV, and  $\Delta^2 = 4.2$  eV<sup>2</sup>. (d) Comparison of the experimental data (+) to the theoretical (—) IED cross section which includes reneutralization.  $Y = \exp[-(E - E_i)^2/2\Delta^2] \exp(-A/E^{1/2})$ , where  $\Delta^2 = 4.2$  eV<sup>2</sup>,  $A = 10.5$  eV<sup>1/2</sup>, and  $E_i = 4.0$  eV.

ic well of characteristic frequency determined from spectroscopic studies. The final-state wave function  $\phi_{e_f v_f}(\mathbf{R})$  can be obtained if the ion-surface final-state interaction potential is known. A simple choice of  $\phi_{e_f v_f}(\mathbf{R})$  would be a stationary-state WKB solution. Since a WKB wave function has its predominant peak close to the classical turning point (see the Appendix), numerical integration shows that  $I_{FC}$  is approximately equal to  $\phi_{e_i v_i}(\mathbf{R}_C)$  where  $\mathbf{R}_C$  is the classical turning point. This is equivalent to saying that at  $t = 0$  when electronic transitions occur, the final-state wave function is a  $\delta$  function at  $\mathbf{R}_C$ . This is the essence of the reflection approximation. The final-state ion-surface interaction potential, therefore, acts as a mirror reflecting the ground-state function  $\phi_{e_i v_i}(\mathbf{R})$  into the

observed ion energy and ion angle distribution patterns. Further justification of the reflection approximation is discussed in the Appendix Sec. 1. The results of the RA calculation of IED were the subject of Ref. 1.

### C. Evaluation of $I_{FC}$ using WKB final state with a real potential

The Franck-Condon overlap integral  $I_{FC}(E)$  was calculated for normal desorption using a final-state WKB wave function calculated as described in Ref. 12. A potential is composed of a repulsive Born-Mayer (exponential) term and an attractive image term initially using the same parameters as in Ref. 1. If the overlap integral is expressed as

$$I_{\text{FC}}(E) = \int dZ \phi_{e_f v_f}^*(E, Z) \phi_{e_i v_i}(Z), \quad (6)$$

then each point of a theoretical IED is given by

$$D(E) = D_0 |I_{\text{FC}}(E)|^2,$$

where  $D_0$  is independent of ion energy. In Fig. 4 plots of the ground vibrational and WKB functions for W-O are shown as a function of  $Z$  for various energies. One sees that a cancellation occurs, causing the IED found by calculation of the overlap integral to be equivalent to the IED found by use of the RA. That is, only the principal WKB peak is effective in computing  $I_{\text{FC}}$  even though the width of the ground vibrational state and the WKB state ( $\lambda_{\text{deb}}$ ) are comparable.

In Fig. 1 we show theoretical IED (circles) as calculated by a Franck-Condon overlap integral where the final state is represented by a corrected WKB wave function

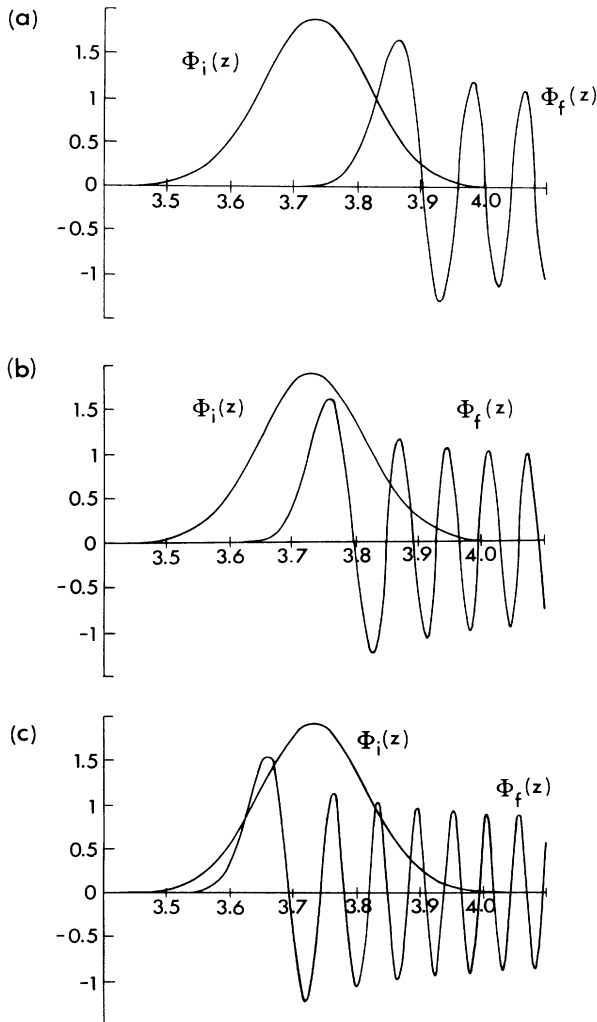


FIG. 4. Initial- and final-state adatom (ion) wave functions for three different ion kinetic energies. (a) 7 eV, (b) 9 eV, and (c) 11 eV.

(i.e., properly joined at the classical turning points). Experimental IED data are also displayed (crosses). A representative number of systems considered in Ref. 1 are shown.

Thus we have shown by direct calculation that the usual approximation involved in calculating IED, namely the reflection approximation, is valid under circumstances beyond those usually stated. Using WKB final-state wave functions in the Franck-Condon model, the IED are in substantial agreement with those calculated previously.<sup>1</sup> We conclude that the usual statement about the RA, that the final state is essentially classical, i.e.,  $\delta$  function is too narrow and the IED can be assumed to be proportional to the initial-state probability distribution function under more general circumstances due to cancellation effects.

A complete description of IED, however, requires a reneutralization factor which we will consider next. In this connection the similar efforts by Brenig and co-workers<sup>13</sup> should be mentioned.

### III. A SIMPLE TREATMENT OF RENEUTRALIZATION: $I_{\text{FC}}$ USING A FINAL-STATE WKB WITH AN OPTICAL POTENTIAL

In Sec. II we discussed in detail how the ion (neutral) desorption cross section can be factored into three parts, i.e., the initial electronic excitation, the FC factor leading to desorption, and the effect of reneutralization. The initial electronic excitation was categorized as strictly an initial-state effect, and reneutralization a final-state effect whereas the FC factor involves both initial and final states. In this section we attempt to show that with an appropriate choice of potential (optical potential) describing the ion (neutral) trajectory, the FC integral naturally factors into the usual  $I_{\text{FC}}$  and a reneutralization probability.

#### A. Time-independent theory

The transition matrix element for the desorption of an ion in a one-dimensional model is given by

$$T_{fi} = T_{e_f e_i}(Z_e) \int dZ \phi_{e_f v_f}^*(Z) \phi_{e_i v_i}(Z). \quad (7)$$

For simplicity the one-dimensional model is chosen but can be extended very easily to three dimensions. In the case of normal desorption, if the all-final-state surface potential is only  $Z$  dependent then the particular choice of the one-dimensional problem requires no modification.

As already discussed in a previous section,  $T_{e_f e_i}(Z_e)$  is the electronic contribution to the transition matrix element and the remaining integral over ion coordinates is the Franck-Condon overlap integral. The reneutralization of the ion along its trajectory can be modeled by a complex potential that acts on the adsorbate along with a real conservative potential. The specifics of this potential can be shown to be related to a number of other theoretical quantities such as drag or viscous forces and electronic level broadening.<sup>14</sup> The total Hamiltonian of the ion can be written as

$$H = H_R(Z) - iW(Z), \quad (8)$$

where  $H_R = T_i + V(Z)$  denotes the real part of  $H$  and  $T_i$  is the kinetic energy operator of the ion. Since the Hamiltonian is non-Hermitian, its eigenvalue is no longer real. For a very small dissipative potential  $W(Z)$  a quasiclassical, quasistationary wave function may be chosen. Thus the eigenvalue problem becomes

$$[H_R(Z) + iW(Z)]\phi_{e_f v_f} = (E - i\Gamma)\phi_{e_f v_f}. \quad (9)$$

Noting the fact that the expectation value of the real part of the Hamiltonian has to be real, the expectation value of  $W(Z)$  can be written as

$$T_{fi} = T_{e_f e_i}(Z_e) \int dZ \phi_{e_i v_i}(Z) \exp\left[\frac{-M}{\hbar} \int_{Z_c}^Z \frac{W(Z')}{p(Z')} dZ'\right] \exp\left[\frac{M}{\hbar} \int_{Z_c}^Z \frac{\Gamma dZ'}{p(Z')}\right] \exp\left[\frac{-i}{\hbar} \int_{Z_c}^Z p(Z') dZ'\right] / [p_{\text{com}}(Z)]^{1/2}, \quad (13)$$

where  $p_R(Z) = \{2M[E - V(Z)]\}^{1/2}$  and  $Z_c$  is the classical turning point. Since  $W(Z)$  is assumed very small, the argument of the exponential varies very slowly compared to the rest of the integrand; therefore, factoring it out yields

$$T_{fi} = T_{e_f e_i}(Z_e) \exp\left[-\int_{Z_c}^{\infty} \frac{W(Z') dZ'}{\hbar V(Z')}\right] \int dZ \phi_{e_i v_i}(Z) \exp\left[\int_{Z_c}^Z \frac{\Gamma dZ'}{\hbar v(Z')}\right] \exp\left[\frac{-i}{\hbar} \int^Z p(Z') dZ'\right] / [p_{\text{com}}(Z)]^{1/2}, \quad (14)$$

$v(Z)$  being the local velocity. Again  $[E - V(Z)]$  in the denominator of the integral is much greater than  $[W(Z) - \Gamma]$  (which is very close to zero), except at the classical turning point. Therefore one can again evaluate the integral at the classical turning point where  $[E - V(Z)] = 0$  and

$$\left[\exp\left(\frac{i}{\hbar} \int dZ' p(Z')\right)\right] / p^{1/2}(Z)$$

becomes a  $\delta$  function, therefore,

$$T_{e_f} = T_{e_f e_i}(Z_e) \exp\left[-\int_{Z_c}^{\infty} \frac{W(Z')}{\hbar v(Z')} dZ'\right] \phi_{e_i v_i}(Z_c). \quad (15)$$

The exponential term can be identified as the ion survival probability amplitude or the reneutralization reduction factor. Since the desorption cross section is proportional to  $|T_{fi}|^2$ , the ion yield reduction factor would be

$$P = \exp\left[-2 \int_{Z_c}^{\infty} dZ' W(Z') / \hbar v(Z')\right]. \quad (16)$$

From the above calculation it is seen that with a simple choice of wave function, namely a WKB, the reduction factor comes out automatically from the Franck-Condon overlap factor provided one uses an optical potential. Thus this treatment accomplishes a number of things: first it allows the reneutralization factor to come in a natural way without just appending it as is often done, second it establishes the exponential form, and finally it establishes the precise quantities occurring in  $P$ . For example, the imaginary part of the potential defines the reneutralization rate and later we will also see how it is related to the energy-level broadening of the one-electron state of the adsorbate. The particular choice of the quasistationary wave function implies probability drain

$$\langle \phi_{e_f v_f} | W | \phi_{e_f v_f} \rangle = \Gamma. \quad (10)$$

We choose a quasiclassical form for the wave function

$$\phi_{e_f v_f}(Z) = \frac{1}{[p_{\text{com}}(Z)]^{1/2}} \exp\left[\frac{i}{\hbar} \int^Z p_{\text{com}}(Z') dZ'\right], \quad (11)$$

where  $p_{\text{com}}(Z)$  is a complex momentum, namely

$$p_{\text{com}}(Z) = (2M\{E - V(Z) + i[W(Z) - \Gamma]\})^{1/2}. \quad (12)$$

Substituting Eq. (12) into Eq. (7), we obtain

which can be associated with the reneutralization of the ions.

## B. Time-dependent theory

The previous approach was the quasistationary approximation. Here we derive the result more generally. The Hamiltonian for complex potential can be written as the sum of the Hermitian and the anti-Hermitian part namely

$$H = H_H + H_A, \quad (17)$$

where  $H_H = (H + H^\dagger)/2$  and  $H = (H - H^\dagger)/2$ . Using the Schrödinger equation,

$$i\hbar \frac{\partial \phi}{\partial t} \phi_{e_f v_f}(Z, t) = H \phi_{e_f v_f}(Z, t), \quad (18)$$

the time rate of change of the expectation value of any operator  $O$  can be written as<sup>15,16</sup>

$$\begin{aligned} \frac{d}{dt} \int \phi_{e_f v_f}^* O \phi_{e_f v_f} dZ \\ = \int \phi_{e_f v_f}^* \left[ \frac{i}{\hbar} (H^\dagger O - O H) + \frac{\partial O}{\partial t} \right] \phi_{e_f v_f} dZ. \end{aligned} \quad (19)$$

Since  $H_A^\dagger = -H_A$ , Eq. (19) can be written as

$$\begin{aligned} \frac{d}{dt} \int \phi_{e_f v_f}^* O \phi_{e_f v_f} dZ \\ = \int \phi_{e_f v_f}^* \left[ \frac{i}{\hbar} [H_h, O]_- + \frac{\partial O}{\partial t} - \frac{i}{\hbar} [H_A, O]_+ \right] \phi_{e_f v_f} dZ. \end{aligned} \quad (20)$$

The probability  $I(t)$  is defined as

$$\int \phi_{e_f v_f}^*(\mathbf{Z}, t) \phi_{e_f v_f}(\mathbf{Z}, t) d\mathbf{Z} . \quad (21)$$

Then from Eq. (20) replacing  $O$  by the unit operator gives

$$\frac{dI(t)}{dt} = -\frac{2i}{\hbar} \int \phi_{e_f v_f}^*(\mathbf{Z}, t) H_A \phi_{e_f v_f}(\mathbf{Z}, t) d\mathbf{Z} . \quad (22)$$

In the problem of reneutralization  $H_H = T_i + V(\mathbf{Z})$  and  $H_A = -iW(\langle \mathbf{Z} \rangle_{cl})$ . This choice makes  $W$  an explicit function of time and in the classical limit  $\langle \mathbf{Z} \rangle_{cl}$  is the classical path, which is consistent with MGR model. Thus

$$\langle H_A(t) \rangle = \left[ \int \phi_{e_f v_f}(\mathbf{Z}, t) H_A \phi_{e_f v_f}(\mathbf{Z}, t) d\mathbf{Z} \right] / I(t) , \quad (23)$$

and

$$\int d\mathbf{Z} \phi_{e_f v_f}^*(\mathbf{Z}, t) \phi_{e_f v_f}(\mathbf{Z}, t) = \int d\mathbf{Z} \phi_{e_f v_f}^*(\mathbf{Z}, 0) \phi_{e_f v_f}(\mathbf{Z}, 0) \exp \left[ -\frac{2i}{\hbar} \int_0^t H_A(\langle \mathbf{Z} \rangle_{cl}) dt' \right] . \quad (27)$$

Since the above equation is true for all values of time and all volume elements, without loss of generality one can write

$$\begin{aligned} \phi_{e_f v_f}(\mathbf{Z}, t) &= \phi_{e_f v_f}(\mathbf{Z}, 0) \exp \left[ -\frac{i}{\hbar} \int_0^t H_A(\langle \mathbf{Z} \rangle_{cl}) dt' \right] \\ &\times \exp[if(\mathbf{Z}, t)] , \end{aligned} \quad (28)$$

where  $\exp[if(\mathbf{Z}, t)]$  is some arbitrary phase factor with the restriction  $f(\mathbf{Z}, 0) = 0$ . It can be noted that the argument of the exponential is real since  $H_A = iW(\langle \mathbf{Z} \rangle_{cl})$  and  $\mathbf{Z}$  is Hermitian. Thus

$$T_{fi}(t) = T_{e_f e_i}(Z_e) \int d\mathbf{Z} \exp \left[ -\frac{i}{\hbar} \int_0^t W(\langle \mathbf{Z} \rangle_{cl}) dt \right] e^{if(\mathbf{Z}, t)} \phi_{e_f v_f}^*(\mathbf{Z}, 0) \phi_{e_i v_i}(\mathbf{Z}) . \quad (31)$$

Under the reflection approximation,  $\phi_{e_f v_f}(\mathbf{Z}, 0)$  is a  $\delta$  function around the classical turning point namely where  $E(0) = V(Z_c)$ . The desorption cross section at  $t = \infty$  or at the detector is proportional to  $|T_{fi}(t = \infty)|^2$  or,

$$|T_{fi}(\infty)|^2 = \exp \left[ -\frac{2}{\hbar} \int_0^\infty W(\langle \mathbf{Z} \rangle_{cl}) dt \right] |\phi_{e_i v_i}(Z_c)|^2 . \quad (32)$$

Therefore it is seen that this particular choice of the complex potential, the desorption cross section again factorizes into a product of two terms—the Franck-Condon factor evaluated at  $t = 0$  and a reduction factor which is a measure of the ion survival probability.

#### IV. CALCULATION OF THE EFFECTS OF RENEUTRALIZATION ON IED

In Sec. II we saw how a WKB final state could be used to represent a large variety of experimental curves using

$$\frac{dI(t)}{dt} = -\frac{2i}{\hbar} \langle H_A(t) \rangle I(t) . \quad (24)$$

The solution of the above equation is

$$I(t) = I(0) \exp \left[ -\frac{2i}{\hbar} \int_0^t H_A(\langle \mathbf{Z} \rangle_{cl}) dt' \right] , \quad (25)$$

where

$$I(0) = \int \phi_{e_f v_f}^*(\mathbf{Z}, 0) \phi_{e_f v_f}(\mathbf{Z}, 0) d\mathbf{Z} ,$$

and  $\phi_{e_f v_f}(\mathbf{Z}, 0)$  satisfies the time-dependent Schrödinger equation

$$[T_i + V(\mathbf{z})] \phi_{e_f v_f}(\mathbf{Z}, 0) = E(0) \phi_{e_f v_f}(\mathbf{Z}, 0) , \quad (26)$$

and can be modeled to have a simple WKB-like form. Equation (25) can be rewritten as

$$\begin{aligned} &\exp \left[ -\frac{i}{\hbar} \int_0^t \langle H_A(t') \rangle dt' \right] \\ &= \exp \left[ -\frac{i}{\hbar} \int_0^t W(\langle \mathbf{Z} \rangle_{cl}) dt' \right] . \end{aligned} \quad (29)$$

Also  $\langle \mathbf{Z} \rangle_{cl}$  defined below is the classical expectation value and is an explicitly time-dependent real quantity,

$$\langle \mathbf{Z} \rangle_{cl} = \int \phi_{e_f v_f}^*(\mathbf{Z}, t) \mathbf{Z} \phi_{e_f v_f}(\mathbf{Z}, t) dt . \quad (30)$$

The transition matrix element can then be written as

$$T_{fi}(t) = T_{e_f v_f}(Z_e) \int d\mathbf{Z} \phi_{e_f v_f}^*(\mathbf{Z}, t) \phi_{e_i v_i}(\mathbf{Z}) .$$

Substituting for  $\phi_{e_f v_f}(\mathbf{Z}, t)$ ,

only a real potential. Some of the data, however, showed asymmetries that could not be accounted for in that simple theory. We will now address this problem using the full  $I_{FC}$  derived in Sec. III. The level width function in the case of the time-dependent perturbation theory<sup>17</sup> is defined as

$$\Delta(t) = \frac{\pi}{\hbar} \sum_k |V_{dk}(t)|^2 \delta(\epsilon - \epsilon_k) , \quad (33)$$

whereas the reneutralization rate in the case of the MGR



model is defined as (the golden rule)

$$W(t) = R(t) = \frac{2\pi}{\hbar} \sum_{\hbar} |V_{dk}(t)|^2 \delta(\epsilon - \epsilon_k). \quad (34)$$

This difference in the factor of 2 results because

$$\exp\left[-\int^t \Delta(t') dt'\right]$$

$$n(\infty) = \frac{1}{2}(1 - e^{-2\Lambda p}) \pm (1 - e^{-2\Lambda p}) \left[ \frac{1}{2} - \frac{2}{\pi} \exp\left[-\frac{\pi |\epsilon_F - \epsilon_d|}{\hbar \gamma v_{\perp}}\right] \right], \quad \epsilon_F > \epsilon_d, \quad \epsilon_F < \epsilon_d. \quad (35)$$

where  $\Lambda = \Delta_0 / \hbar \gamma v_{\perp}$  and  $p = e^{-\gamma Z_0}$  with  $v_{\perp}$  the normal component of the velocity and  $\epsilon_F$  the Fermi level. The above result is obtained by assuming an exponential time dependence for  $\Delta(t)$ , namely  $\Delta(t) = \Delta_0 \exp[-\gamma(Z_0 + v_{\perp} t)]$ . The MGR model, on the other hand, under the same approximation, yields

$$P(\infty) = \exp(-2\Lambda p). \quad (36)$$

For the case of reneutralization of positive ions (in which case the adiabatic limit is often used) the time-dependent approach yields  $P(\infty) = 1 - n(\infty)$ . For most cases of interest it is seen that  $\pi |\epsilon_F - \epsilon_d|$  is of the order of a few eV whereas  $\Delta_0$  is of the order of 1 or 2 eV. Under these circumstances the leading contribution to  $P(\infty)$  for the case of  $\epsilon_F > \epsilon_d$  and small  $v_{\perp}$  is the same as Eq. (36). Similar results can be obtained for more realistic time dependence of the affinity level.<sup>7</sup> Thus one can conclude that the adiabatic limit is a small velocity limit of the more rigorous time-dependent theory, especially in the cases of resonant charge transfer where the resonance width is much smaller than the difference of the work function and affinity level.

In this section we use the MGR model for the reduction factor  $P$  in obtaining further corrections to the IED curves of hydrogen from tungsten and oxygen from molybdenum. From Figs. 2 and 3 it is seen that augmenting the Franck-Condon factor (which is essentially a Gaussian around the peak energy) with a factor representing the ion survival probability is capable of explaining observed right and left skewing of the observed IED. Another interesting result of the energy dependence of  $P$  is that it can cause significant shifts in the peak of the IED making it apparent that one must take care in interpreting the empirical parameters that come from fitting of experimental data.

## V. CONCLUSION

We have shown how ion energy distributions for a broad class of metal-adsorbate systems are well represented by a final-state wave function in the quasiclassical limit using a complex potential. The latter leads to a reneutralization reduction factor which accounts for a number of anomalous effects left unexplained by our previous treatment using only a Franck-Condon factor calculated in the reflection approximation. The imaginary part of the optical potential experienced by the ion is simply related to

represents the instantaneous probability amplitude rather than the probability itself. In general, the results of the time-dependent perturbation theory are more complete than those of the MGR approach but there are limiting cases where both methods yield the same result. As shown in Ref. 17 the result of the constant affinity level  $E_d(t)$  and a constant velocity of the desorbing atom, one obtains

the reneutralization rate and hence the electron tunneling probability from metal to adsorbate. We have also shown how the reflection approximation is valid under circumstances beyond those usually stated. Thus, using WKB final-state wave functions in the Franck-Condon model, the IED were in substantial agreement with those calculated previously.<sup>1</sup> This appears to be due to canceling effects in the final quasiclassical state beyond the principal maximum that occurs near the classical turning point.

Finally, we have shown how the classical and quasiclassical approximations are related using both time-independent WKB wave function as well as time-dependent Gaussian wave packet. We thus have seen the technical details as well as the real meaning of the reflection approximation corresponding to the classical trajectory as a final-state representation of the ion. In addition, the Appendix, Sec. 1, in particular, points the direction to other potentially useful approximations as a formal series in  $\hbar$ .

## APPENDIX

### 1. Connection between the classical limit and the RA approximation

It is often stated that the reflection approximation is a result of replacing the final-state wave function by a  $\delta$  function.<sup>18,19</sup> Since the momentum of the desorbing particle is large compared to the electronic momentum, for most purposes the final-state ion trajectory is justifiably treated classically. The notion of trajectory therefore implies a dynamical system and thus one ought to deal with a time-dependent wave function. The Franck-Condon overlap integral is then evaluated at the time  $t=0$ . In this section we show how the  $\delta$  function results from the usual  $\hbar \rightarrow 0$  limit of a quantum wave function. For simplicity of notation we will drop subscripts; i.e.,  $\phi_{e_f v_f}(\mathbf{X}, t) \equiv \phi(X, t)$  and treat the problem in one dimension. The formal generalization to three dimensions is not very difficult.

Quantum mechanics is generally said to reduce to classical mechanics in the  $\hbar \rightarrow 0$  limit. According to Yaffe<sup>20</sup> this statement needs justifying. In order to obtain the classical limit, the quantum system has to be prepared in such a way that ensures a state whose uncertainty in both position and momentum vanishes as  $\hbar$  tends to zero. Fol-

lowing Heller<sup>21</sup> we choose a wave function as a Gaussian about the classical path  $X_t = \langle X \rangle / \langle \phi | \phi \rangle$ . A Gaussian wave function is the solution to the Schrödinger equation for a harmonic potential. For a smoothly varying  $V(X)$  one can always expand the potential about the classical path and retain up to the quadratic term, namely

$$V(X) = V(X_t) + \partial V(X) / \partial X |_{X=X_t} (X - X_t) + \frac{1}{2} \frac{\partial^2 V(X)}{\partial X^2} \Big|_{X=X_t} (X - X_t)^2. \quad (\text{A1})$$

A Gaussian wave function of the form

$$\phi(x, t) = \frac{1}{(2\pi\hbar)^{1/2}} \exp \left[ \frac{i}{\hbar} \alpha_t (X - X_t)^2 + \left[ \frac{i}{\hbar} \right] p_t (X - X_t) + \left[ \frac{i}{\hbar} \right] \beta_t \right] \quad (\text{A2})$$

may be chosen as the solution to the Schrödinger equation where  $p_t = \langle p \rangle / \langle \phi | \phi \rangle$  and  $\beta_t$  are chosen such that  $\langle \phi | \phi \rangle = 1$ . In general  $\alpha_t$  and  $\beta_t$  are complex and  $p_t$  and  $X_t$  are real quantities. (Here  $\beta_t$  takes care of any time-dependent normalizing constants.) The Hamiltonian for the particle is

$$H = -\frac{\hbar^2}{2M} \frac{\partial^2}{\partial X^2} + V(X_t) + V_X(X - X_t) + \frac{1}{2} V_{XX}(X - X_t)^2, \quad (\text{A3})$$

where  $V_X = \partial V(X) / \partial X |_{X_t}$  and  $V_{XX} = \partial^2 V(X) / \partial X^2 |_{X_t}$ .

$$\phi(X, t) = \frac{(1/a_t)^{1/2}}{(2\pi\hbar/a_t)^{1/2}} \exp \left\{ -\frac{a_t}{\hbar} (X - X_t)^2 + (i/\hbar) p_t (X - X_t) + (i/\hbar) \int_0^t dt' \left[ -E + \frac{p_t^2}{M} - \frac{\hbar^2}{2} \left[ \frac{V_{XX}}{M} \right]^{1/2} \right] \right\}, \quad (\text{A8})$$

with  $a_t = (MV_{XX})^{1/2}/2$ . The Gaussian representation of a  $\delta$  function

$$\delta(X) = \frac{1}{\sqrt{\pi}} \lim_{\epsilon \rightarrow 0} \frac{1}{\sqrt{\epsilon}} \exp(-X^2/\epsilon),$$

automatically implies that in the limit  $\hbar \rightarrow 0$ ,  $\phi \rightarrow \delta(X - X_t)$ . Thus in the classical limit the particle is at its instantaneous classical location  $X_t$ . It is easily verified that the Fourier transform of  $\phi(X, t)$  is a Gaussian around  $p_t$  which again in the  $\hbar \rightarrow 0$  limit results in a  $\delta$  function at  $p_t$ , i.e.,

$$\begin{aligned} \phi(p, t) &= \frac{1}{(2\pi\hbar)^{1/2}} \int_{-\infty}^{\infty} dX \exp(-ipX/\hbar) \phi(X) \\ &= \frac{(-2i\alpha_t)^{1/2}}{\sqrt{2\pi\hbar}} \exp \left[ -i \frac{(p - p_t)^2}{4\hbar\alpha_t} - \frac{ip}{\hbar} X_t - i\gamma_t/\hbar \right]. \end{aligned} \quad (\text{A9})$$

The Franck-Condon overlap integral can also be evaluated in the momentum space where  $\phi_{e, v_i}(p, 0)$  will now be

Substituting Eq. (A2) into the Schrödinger equation  $i\hbar d\phi/dt = H\phi$  and collecting coefficients of  $(X - X_t)^n$ , where  $n=0, 1, 2, \dots$ , the following equations are obtained:

$$\dot{\alpha}_t = - \left[ \frac{2}{M} \right] \alpha_t^2 - V_{XX}/2; \quad -\dot{p}_t = V_X, \quad (\text{A4})$$

$$\dot{\beta}_t = \frac{i\hbar}{M} \alpha_t + p_t^2/M - V(X_t) - p_t^2/2M. \quad (\text{A5})$$

In deriving Eqs. (A4) and (A5) the fact that  $X_t = p_t/M$  has been used. If  $H(p_t, X_t) = p_t^2/2M + V(X_t) = E$  then the equation of motions are

$$\begin{aligned} \dot{X}_t &= \partial H / \partial p_t, \quad \dot{p}_t = -\partial H / \partial X_t \\ \dot{\alpha}_t &= -(2/M)\alpha_t^2 - V_{XX}/2, \end{aligned} \quad (\text{A6})$$

$$\dot{\beta}_t = i\hbar\alpha_t/M + p_t^2/M - E.$$

In order to write  $\phi(X, t)$  as a Gaussian coherent state,<sup>20,22</sup> we let  $\alpha_t$  be purely imaginary and equal to  $i(MV_{XX})^{1/2}/2$  such that  $\dot{\alpha}_t = 0$ . This choice makes

$$\dot{\beta}_t = -\frac{\hbar}{2} \left[ \frac{V_{XX}}{M} \right]^{1/2} + p_t^2/M - E, \quad (\text{A7})$$

$$\beta_t = -Et + \int_0^t dt' \left[ \frac{p_t^2}{M} - \frac{\hbar}{2} \left[ \frac{V_{XX}}{M} \right]^{1/2} \right],$$

Equation (A7) implies that in addition to the ordinary phase factor  $-iEt/\hbar$  we have another time-dependent contribution arising mainly due to the normalization.

evaluated at classical momentum  $p_t = 0$ . Since most of the information regarding bond length and bond direction can be easily inferred in coordinate representation, it is most common to use coordinate space wave functions. Assuming that  $V_{XX}(t=0)$  is a mild energy-dependent quantity [energy dependence coming from the classical turning point where  $V(X_c) = E$ ] one can write  $|I_{FC}|^2$  as

$$|I_{FC}|^2 \propto |\phi_{e, v_i}(X_c)|^2, \quad (\text{A10})$$

where  $X_c$  represents the location of the particle at  $t=0$ , namely the turning point.

Another approach to the reflection approximation is to show how the quasiclassical WKB wave function when treated in the linearized potential approximation, valid near the turning point, leads formally not to a  $\delta$  function but to an infinite series of correction terms in successively higher orders of  $\hbar$ . The Airy function solution to the Schrödinger equation for linearized potential at large distances goes over to the WKB. Therefore near the turning point where the potential can be effectively linearized, the integral representation of the Airy function gives a formal

series of derivatives of the  $\delta$  function. This is discussed next.

## 2. $\delta$ function representation of the Airy function

We will show here how the quasiclassical wave function when treated in the linearized potential approximation, valid near the turning point, leads formally not only to a  $\delta$  function but to an infinite series of correction terms in successively higher orders of  $\hbar$ .

We begin with the one-dimensional Schrödinger equation,

$$\left[ -\frac{\hbar^2}{2M} \frac{d^2}{dZ^2} + K^2(Z) \right] \phi(Z) = 0, \quad (\text{A11})$$

where  $k^2(Z) = (2m/\hbar^2)[E - V(Z)]$ . Let  $Z_c = Z$  be the classical turning point. We expand  $k^2(Z)$  about  $Z_c$  and since  $E = V(Z_c)$ ,  $k^2(Z_c) = 0$ . Thus  $k^2(Z) = a(Z - Z_c) + \dots$ , where

$$a = -\left( 2m/\hbar^2 \right) \left[ \frac{\partial V(Z)}{\partial Z} \right]_{Z=Z_c} = 2mF(Z_c)\hbar^2.$$

Equation (A11) now becomes

$$\left[ \frac{d^2}{dZ^2} + a(Z - Z_c) \right] \phi(Z) = 0. \quad (\text{A12})$$

Defining  $y = -a^{1/3}(Z - Z_c)$ , Eq. (A12) can be written as

$$\left[ \frac{d^2}{dy^2} - y \right] \phi(y) = 0, \quad (\text{A13})$$

which is the differential equation satisfied by the Airy functions  $\text{Ai}(y)$  and  $\text{Bi}(y)$ . The scale factor  $a$  determines the period of the Airy function, that is the narrower function results from increasing the scale factor  $a$  and thus corresponds to approaching the classical limit  $\hbar \rightarrow 0$ . Using the integral representation for  $\text{Ai}(y)$ , we find

$$\begin{aligned} \text{Ai}(\pm y) &= \left[ \frac{1}{\pi} \right] \int_0^\infty \cos \left[ \frac{t^3}{3} \pm yt \right] dt \\ &= \left[ \frac{1}{2\pi} \right] \int_{-\infty}^\infty \cos \left[ \frac{t^3}{3} \pm yt \right] dt. \end{aligned} \quad (\text{A14})$$

Since the integrand is an even function of  $t$ ,

$$\text{Ai}(\pm y) = \frac{\text{Re}}{2\pi} \int_{-\infty}^\infty \exp \left[ i \left[ \pm yt + \frac{t^3}{3} \right] \right] dt, \quad (\text{A15})$$

$$\text{Ai}(\pm y) = \frac{\text{Re}}{2\pi} \int_{-\infty}^\infty e^{\pm iyt} \left[ \sum_{n=0}^\infty \frac{1}{n!} \left[ \frac{it^3}{3} \right]^n \right] dt. \quad (\text{A16})$$

But

$$\mp \frac{1}{3} \frac{d^3}{dy^3} e^{\pm iyt} = \left[ \frac{it^3}{3} \right] \exp(\pm iyt)$$

whence,

$$(it^3/3)^n = \left[ \mp \frac{1}{3} \frac{d^3}{dy^3} \right]^n \exp(\pm iyt).$$

Thus we have a formal representation of  $\text{Ai}(\pm y)$ ;

$$\begin{aligned} \text{Ai}(\pm y) &= \left[ \frac{1}{2\pi} \right] \int_{-\infty}^\infty \sum_{n=0}^\infty \left[ \mp \frac{1}{3} \frac{d^3}{dy^3} \right]^n \exp \frac{(\pm iyt)}{n!} dt \\ &= \sum_{n=0}^\infty \frac{(\mp 1)^n}{n!} \left[ \frac{1}{3} \frac{d^3}{dy^3} \right]^n \delta(y). \end{aligned} \quad (\text{A17})$$

Since

$$\delta(y) = \frac{1}{2\pi} \int_{-\infty}^\infty \exp(\pm iyt) dt.$$

This of course means, in the usual way, that the right-hand side of Eq. (A17) is equivalent to  $\text{Ai}(\pm y)$  when used in an integral. For  $n=0$  the Franck-Condon overlap integral is,

$$I_{\text{FC}} \propto dy \phi_{e_i, v_i}(y) \text{Ai}(y),$$

$$I_{\text{FC}} \propto \phi_{e_i, v_i}(y=0),$$

with  $\phi_{e_i, v_i}(y)$  being the vibrational ground state of the adsorbate.

\*Present address: Natural Sciences and Mathematics, Stockton State College, Pomona, New Jersey 08240.

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