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Laser-Induced Electron-Phonon Processes on Metal Surfaces

by William C. Murphy and Thomas F. George

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Journal of Chemical Physics, in press

LASER-INDUCED ELECTRON-PHONON PROCESSES ON METAL SURFACES

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Electronic charge transfer from bulk to surface states in metals induced by laser radiation is examined. Due to the position of the Fermi energy, it is necessary to also include phonon excitations. Cross sections for this second-order process are presented. Comparison with the surface excitation in semiconductors is made. It is seen that for metals the required laser frequencies are larger and the cross sections substantially less than for semiconductors.

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I. Introduction

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In a previous paper [1], we examined the effects of laser radiation on the surface states of a semiconductor. Within a one-dimensional model, the optical cross section was calculated for the excitation of electrons from the bulk valence band to various surface states. For surface states with charge densities confined to the first few lattice layers, a large cross section on the order of 1 or 2 $Å^2$ was discovered. This indicated that a low-power laser (1-10 W/cm²) could be used effectively to transfer charge from the bulk of the crystal to the surface region. Furthermore, this surface charge was shown to have a significant influence on the interaction with a charged adspecies [2]. Consequently, we suggested that this effect could be used to enhance the desorption or adsorption of charged or polar atoms and molecules.

In the above studies, we confined our efforts to examining wideband semiconductors. However, metals have a band structure that is qualitatively similar to the energy levels of these semiconductors. Consequently, we would expect that laser radiation could also be used to transfer charge to metal surfaces and thus influence surface dynamics.

In Section II we shall show that our one-dimensional model developed for semiconductors can easily be extended to the case of metals. In Section III we shall use time-dependent perturbation theory to examine surface excitations. This theory involves electron-phonon coupling, which will be evaluated in Section IV. In Section V the optical cross sections at various laser frequencies for the metals will be presented. Finally, in Section VI we shall discuss the differences with our previous works and suggest possible ways to enhance the laser-stimulated surface dynamics in metals.

II. The Model

As with wide-band semiconductors, the valence electron wave functions of a metal of infinite extent can be written as a sum of plane waves [3]. Consequently, if we model a metal as a truncated one-dimensional chain, the bulk wave function, $\psi_k(z)$ obtained via the nearly-free-electron approximation will be functionally the same for a metal and a semiconductor:

1

$$\psi_{k}(z) = \left\{ 1 + \left[\frac{E_{k} - \frac{k^{2}}{2}}{V_{g}} \right]^{2} \right\}^{-\frac{1}{2}} \left\{ \phi_{k}(z) + \frac{E_{k} - \frac{k^{2}}{2}}{V_{g}} \phi_{k-g}(z) \right\}, \quad (1)$$

where for z < a/2

$$\phi_{k}(z) = \left(\frac{2}{L}\right)^{1/2} \sin[k(z-\frac{a}{2}) + \theta_{k}], \qquad (2A)$$

and for z > a/2

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$$\phi_k(z) = (\frac{2}{L})^{1/2} \sin_{\theta_k} e^{-q_k(z-\frac{a}{2})}$$
 (28)

L is the length of the chain, a is the lattice constant, g is the reciprocal lattice vector, k is the electron wave vector, and V_g is the lattice interaction matrix. The phase factor and the exponential constant are given elsewhere [4]. This wave function has the corresponding energy

$$E_{k} = \frac{1}{4} \{ [k^{2} + (k-g)^{2}] \pm \sqrt{[k^{2} - (k-g)^{2}]^{2} + 4E_{g}^{2} \}}, \qquad (3)$$

where E_{g} is the band gap.

To obtain the wave function for the surface states, we assume the wave vectors to be complex,

$$k = \frac{q}{2} + i\kappa \tag{4}$$

but the energies to be real [5]. Consequently, some algebra [4] leads to the surface wave functions

$$\psi_{\kappa}(z) = C_{s} \sin[(\frac{q}{2})(z - \frac{a}{2}) + \theta_{\kappa}]e^{-\kappa(z - \frac{a}{2})}$$
 (5A)

for z < a/2 and

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$$\psi_{\kappa}(z) = C_{s} \sin_{\theta_{\kappa}} e^{-q_{\kappa}(z - \frac{a}{2})}$$
(5B)

for z > a/2, where the normalization constant, the phase factor and the exponential constant are found elsewhere [4]. The corresponding energy is

$$E_{\kappa} = \frac{1}{2} \left[\left(\frac{g}{2} \right)^2 - \kappa^2 \pm \sqrt{E_g^2 - \kappa^2 g^2} \right].$$
 (6)

The dispersion relation, given by eqs. (3) and (6), is illustrated in Fig. 1. As can be seen the band structure is similar to that of the semiconductor previously calculated [1]. However, whereas in the semiconductor the lower band was populated to the top, in a metal the Fermi energy, E_F , lies somewhat below. For example, in the case of sodium the

Fermi energy is 0.7 eV below the band edge and, thus, the surface states. This immediately implies that our laser frequency must be higher in metals than in semiconductors in order to excite electrons to the surface states. To calculate this laser-induced transition rate between the bulk states, eq. (1), and the surface states, eq. (5), we proceed as previously by examining the coupling between these states via timedependent perturbation theory.

III. Perturbation Theory

If the metal is now exposed to laser radiation in order to excite bulk states to surface states, it will be seen that the transitions that conserve the real part of the crystal momentum are favored. This selection rule was previously developed for semiconductors [1,4] and is still valid for metals since our wavefunctions, eqs. (1) and (5), are essentially the same. However, there are no occupied bulk states with real momentum at or near g/2 which is the real momentum of the surface states [eq. (4)]. To overcome this problem, the electrons can be excited not only with a laser but also with the vibrational momentum of the crystal. Thus, photons would supply the energy needed for the transition and phonons would supply the needed crystal momentum. A suggested pathway for this combined photon and phonon excitations is illustrated in Fig. 1

For the one-dimensional model, the electronic Schrodinger equation is

$$i \frac{\partial \Psi(z,t)}{\partial t} = H(t) \Psi(z,t)$$
(7)

where

$$H(t) = H^{0} + H^{f} e^{-i\omega} f + H^{p} e^{-i\omega} p^{t}.$$
 (8)

 H^0 is the electronic Hamiltonian of the system in the ground state, H^f is the coupling of electrons to the laser field of frequency ω_f , and H^p is the coupling of the electrons to a phonon of frequency ω_p . Our wave function is expanded in terms of the stationary states:

$$\Psi(z,t) = \{k'';n_{K}^{>} e^{-iE_{k}''t} + \sum_{k} C_{k} | k;n_{K}^{-1>} e^{-iE_{k}t}$$
(9)

where k in the ket notation refers to the stationary electronic states, eq. (1) and (5), and n_{K} refers to the phonon number state with crystal momentum K. The double prime refers to an electronic state below the Fermi energy, and no prime labels a surface state.

If first-order perturbation theory is now applied, we obtain

$$i \dot{C}_{k}^{(1)} = \langle k; n_{K}^{-1} | H^{f} | k''; n_{K}^{>} e^{i[E_{k} - E_{k}'' - \omega_{f}]t} + \langle k; n_{K}^{-1} | H^{p} | k''; n_{K}^{>} e^{i[E_{k} - E_{k}'' - \omega_{p}]t}.$$
(10)

However, the first term will vanish since the laser field is not coupled to the phonons, and thus crystal momentum is not conserved. The second term is also zero since one phonon term cannot supply sufficient energy for the excitation. Consequently, higher-order perturbation theory must be used [6].

In second-order perturbation theory, the electron is first excited to an intermediate state and then to the final state:

$$|\mathbf{k}^{"};\mathbf{n}_{\mathsf{K}}^{\mathsf{b}} \xrightarrow{\omega_{\mathsf{p}}} |\mathbf{k}^{\mathsf{b}};\mathbf{n}_{\mathsf{K}}^{-1\mathsf{b}} \xrightarrow{\omega_{\mathsf{f}}} |\mathbf{k}^{\mathsf{b}};\mathbf{n}_{\mathsf{K}}^{-1\mathsf{b}}, \qquad (11)$$

where the initial state k" below the Fermi energy is excited by absorption of a phonon to intermediate state k' in the same band and from there excited to the final surface state k by a photon. This pathway is illustrated in Fig. 1. Another possible pathway is

$$|\mathbf{k}'';\mathbf{n}_{\mathsf{K}}\rangle \xrightarrow{\omega_{\mathsf{f}}} |\mathbf{k}';\mathbf{n}_{\mathsf{K}}\rangle \xrightarrow{\omega_{\mathsf{p}}} |\mathbf{k};\mathbf{n}_{\mathsf{K}}^{-1}\rangle.$$
 (12)

Here the first excitation is done by the photon, and the intermediate state k' will lie in an upper conduction band. Because of the large energy mismatch in each step, however, this pathway would contribute only a small part to the transition rate. Consequently, only the first pathway, eq. (11), is considered.

Second-order perturbation theory will now yield

$$C_{k}^{(2)} = \sum_{k'} \frac{H_{kk'}^{f} H_{k'k''}^{p}}{\omega_{k'k''} - \omega_{p}} \left[\frac{e^{i(\omega_{kk''} - \omega_{p} - \omega_{f})t}}{\omega_{kk''} - \omega_{p} - \omega_{f}} \right]$$
(13)

where

$$H_{kk'}^{f} = \langle k; n_{K}^{-1} | H^{f} | k'; n_{K}^{-1} \rangle, \qquad (14)$$

$$H^{p}_{k'k''} = \langle k'; n_{K} - 1 | H^{p} | k''; n_{K} \rangle, \qquad (15)$$

and

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$$\omega_{kk''} = E_k - E_{k''}.$$
 (16)

We have only considered the conservative term and disregarded that due to the sudden turning on of the perturbation [7]. Taking the modulus squared of eq. (13) at large times, we obtain the transition rate from state k'':

$$\lim_{\mathbf{t}\to\infty} \frac{\mathbf{C}_{\mathbf{k}}\mathbf{C}_{\mathbf{k}}^{\star}}{\mathbf{t}} = 2\pi \left[\sum_{\mathbf{k}'} \frac{\mathbf{H}_{\mathbf{k}\mathbf{k}'}^{\mathsf{f}}\mathbf{H}_{\mathbf{k}'\mathbf{k}''}^{\mathsf{p}}}{\omega_{\mathbf{k}'\mathbf{k}''}^{\omega_{\mathbf{p}}} \mathbf{e}} \right]^{2} \delta(\omega_{\mathbf{k}\mathbf{k}''}^{\omega_{\mathbf{p}}} \omega_{\mathbf{f}}), \qquad (17)$$

where $\delta(...)$ is the Dirac delta function. To proceed further and calculate the total transition rate, we must first determine an expression for H^p , as done below.

IV. Electron-Phonon Coupling

The total lattice potential, V(z), can be written as a sum of ionic potentials

$$V(z) = \sum_{\ell} v(z - Z_{\ell}), \qquad (18)$$

where $v(z-Z_{\ell})$ is the for all end potential caused by the lattice ion at position Z_{ℓ} . If a single phonon is present we, can write

$$Z_{\ell} = Z_{\ell}^{0} + U_{\ell} e^{-i\omega pt}, \qquad (19)$$

where Z_{ℓ}^{0} is the ionic equilibrium position and U_{ℓ} is the displacement amplitude.

Using a Taylor series, we obtain

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$$V(z) = V^{0}(z) + \sum_{\ell} v'(z - Z_{\ell}^{0}) U_{\ell} e^{-i\omega pt}, \qquad (20)$$

where $v'(z-Z_{\ell}^{0})$ is the gradient of the screened potential evaluated at equilibrium. $V^{0}(z)$ is the equilibrium potential that is contained in H^{0} [eq. (8)]. The second term is due to the electron-phonon coupling, and thus

$$H_{k'k''}^{p} = \langle k'; n_{k} - 1 | v'(z - Z_{\ell}^{0}) U_{\ell} | k''; n_{k}^{>}.$$
(21)

It is convenient to express the displacement in terms of the phonon annihilation, a(K), and creation $a^{\dagger}(K)$, operators [8]:

$$U_{\ell} = [2NM \omega_{p}]^{-\frac{1}{2}} [e^{iKZ_{\ell}}a(K) + e^{-iKZ_{\ell}}a^{\dagger}(K)], \qquad (22)$$

where M is the mass of the lattice atoms and N is the total number of these atoms. Using eq. (22) in eq. (21), we obtain

$$H_{k'k''}^{p} = \sum_{\ell} [2NM \omega_{p}]^{-\frac{1}{2}} e^{iKZ_{\ell}} n_{K}^{1/2} < k' |v'(z-Z_{\ell}^{0})|k''>.$$
(23)

To evaluate the integral in this expression, we note that the bulk stationary states in a metal can be roughly approximated by a plane wave:

$$|k\rangle \sim \frac{1}{L^{1/2}} e^{ikz}$$
 (24)

Consequently, eq. (23) becomes

$$H_{k'k''}^{p} = -i(NM)^{-1/2} \frac{(k'-k'')v(k'-k'')}{[2\omega_{n}]^{1/2}} n_{k'-k''}^{1/2} \delta_{k'-k''}$$
(25)

where v(k'-k'') is the Fourier transform of v(z) and $\delta_{K,k'-k''}$ is the Kronecker delta function. Eq. (25) constitutes the electron-phonon coupling in our transition, which will now be combined with the field coupling to yield the optical cross section below.

V. Cross Sections

Using eq. (25), we can readily simplify eq. (17) to give

$$\lim_{t \to \infty} \frac{C_{k}C_{k}^{\star}}{t} = (\frac{\pi}{NM})\delta(\omega_{kk''} - \omega_{p} - \omega_{f})$$

$$\sum_{k'} \frac{H_{kk'}^{f^{2}}(k'-k'')^{2}v(k'-k'')^{2}n_{k'-k''}\delta_{k,k'-k''}}{(\omega_{k'k''} - \omega_{p})^{2}\omega_{p}}.$$
(26)

To find the total transition rate, T, we must sum over all possible initial, k", final, k, and phonon, K, states:

$$T = \sum_{k} \sum_{k'' K} \frac{\lim_{t \to \infty} \frac{C_k C_k^*}{t}}{t}.$$
 (27)

To simplify the transition rate, we make use of our previously determined field coupling [1,4]:

$$(H_{\kappa k'}^{f})^{2} = (\frac{2\pi I}{137}) \frac{g}{\omega_{f}^{2}} \delta(k' - \frac{g}{2}) \frac{|\langle \kappa| \frac{d}{dz} |k' \rangle|_{0}^{2}}{1 - e^{2\kappa a}} ,$$
 (28)

where I is the intensity of the laser and the subscript zero implies integration over the first unit cell. Furthermore, since only the imaginery part of the surface state wave vector changes [see eq. 4], we have replaced the index k with κ .

Defining the optical cross section by

$$\sigma \equiv \frac{\omega T}{I}$$
 (29)

and using eqs. (26), (27) and (28), we obtain

$$\sigma = \frac{1}{N} \sum_{K} \frac{\kappa^2 v^2(K) n_{K}}{2M(\omega_g/2, g/2 - K^{-\omega_p})^2 \omega_p} \sigma^{(1)}(\kappa), \qquad (30)$$

where $\sigma^{(1)}(\kappa)$ has the same functional form as the cross section previously obtained from first-order perturbation theory [1,4]. The phonon wave vector, κ , and the complex part of the surface wave vector, κ , are related by the resonance condition

$$\omega_{f} + \omega_{p} = E_{\kappa} - E_{g/2-K}.$$
(31)

The first-order cross section term multiplied by the field frequency is plotted in Fig. 2 using parameters characterized of sodium [9].

The zero near the center of the plot is due to the branch point in the energy, eq. (6), at which there is no surface state. The cross section diverges at the high-energy side, because at this point one should be considering absorption coefficients for transitions between bulk bands. It should also be notes that $\omega_{f}\sigma^{(1)}(\kappa)$ is independent of field frequency.

In view of eq. (30), all phonon effects can be grouped into a scaling factor:

$$S(K) = \frac{K^2 v^2(K) n_K}{2M \omega_p (\omega_g/2, g/2 - K - \omega_p)^2}$$
(32)

The phonon states in this one-dimensional system are given by the dispersion relation [3]

$$\omega_{\rm p} = \omega_{\rm max} \sin(\frac{ka}{2}), \qquad (33)$$

where ω_{max} is the maximum frequency of the acoustic phonons. The population of the phonon states is assumed to be thermal and thus given by the Bose-Einstein statistics,

$$n_{K} = \frac{1}{e^{\beta \omega p} - 1} , \qquad (34)$$

where β is the Boltzmann factor. Using eqs. (33) and (34) in eq. (32) along with the potential v(K) given by Appapillari and Williams [10], we have obtained the scaling factor for sodium at room temperature and show our results in Fig. 3. The exponential shape of the curve

is due to the domination of the population term, eq. (34), in the scaling expression. This curve is also independent of any laser present or any initial or final states. It depends only on the phonon wave vector K.

If we now wished to obtain the total cross section, eq. (30) would be written in the form

$$\sigma = \frac{1}{N} \sum_{K} S(K) \sigma^{(1)}(\kappa).$$
(35)

However, it is not clear over which states the sum should be performed. If one sums over over all possible phonon states, for instance, surface states near the band edge would be included. Since these states have a great deal of bulk character, they are of little interest in surface dynamics but they would dominate the total cross section. Furthermore, to understand how charge is transfered to the surface, it is more instructive to look at the "cross sections", σ_{κ} , for individual surface states:

$$\sigma_{\kappa} \equiv S(K)\sigma^{(1)}(\kappa), \qquad (36)$$

where again K and κ are related by eq. (31). Again, using parameters for sodium, σ_{κ} is plotted in Fig. 4 for a variety of laser frequencies from the infrared (0.925 eV) to the ultraviolet (4.213 eV). Laser frequencies which are less than the difference between the band edge and the Fermi energy, Δ , are too small to excite surface states. On the other hand, if the laser frequency is greater than $E_F + \Delta + E_g$, the photons will be too large to excite surface states. Results for other laser frequencies can readily be obtained by combining

values of $\sigma^{(1)}(\kappa)$, Fig. 2, and S(K), Fig. 3, under the appropriate resonance condition, eq. (31).

VI. Discussion

The second-order cross section, Fig. 4, is readily comparable with the cross sections previously obtained for a semiconductor [1]. However, whereas the scale for the semiconductor cross section was in A^2 , the results for surface excitations in metals are smaller by a factor of 10^{-4} . This means that a larger laser power (10-100 KW/cm², in contrast to 1-10 W/cm²) would be needed in the metal to achieve a similar surface excitation.

In silicon, the laser frequency needed to achieve surface excitation is between 0.0 eV and 1.2 eV. In sodium the frequency is between 0.7 eV and 4.4 eV. Hence, the metal requires a much higher frequency for surface excitation, but offers a broader range of frequencies from which to choose.

Furthermore, in a semiconductor one could be selective in the surface state excited: one laser frequency would only excite one surface state. However, in a metal, any given laser frequency would excite a number of surface states, and the total cross section would be a sum of these excitations, eq. (30). Certain groups of surface states nonetheless would be more favored than others in a metal for a given laser frequency (see Fig. 4).

Since our goal is to increase surface charge in order to effect surface dynamics, as in the semiconductor, the main surface states of interest lie near the center of the gap, roughly between 0.4 E_g and 0.6 E_q . This confines the surface charge to the first 5 or 6 layers

of the lattice. Because one laser frequency in a metal excites several surface states, this would tend to enhance the surface charge more than in a semiconductor where only one state is excited. The surface charge could be further increased by heating the surface and thus increasing the supply of phonons [see eq. (32)].

In the foregoing discussion, the laser was used to excite the electrons while the phonons were thermally excited. A more detailed model of surface excitation should consider the possible coupling of the same laser or a different laser to the surface phonons. Such phonon excitations would increase the optical cross section and would improve the selectivity of the electronic excitation. Furthermore, the presence of adspecies on the surface can alter both the electron and phonon dispersion relation. Such alterations could enhance the surface charge excitation. Finally, the effects of higher dimensionality must be considered for a more realistic description of the laser surface excitation. These and other problems associated with laser-stimulated surface dynamics are the subject of continuing research.

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Figure Captions

Fig. 1. Dispersion relation for a metal and an excitation pathway to the surface states. The vertical arrow represents a photon of frequency ω ; the horizontal arrow, a phonon of momentum K. UC is an upper conduction band. The dot-dash line is the projection of the surface states on the (E versus real k)-plane.

<u>Fig. 2</u>. Laser field frequency multiplied by the first-order cross section in units of 10^{-2} ha²₀ versus the energy of the surface state measured from the band edge.

Fig. 3. Phonon scaling factor versus the phonon wave vector.

Fig. 4. Cross sections for surface state κ in units of pm² versus the energy of the surface state measured from the band edge. Curve (1) has $\omega_f = \Delta + \frac{E_g}{2}$ (0.925 eV); (2) $\omega_f = \Delta + E_g$ (1.150 eV); (3) $\omega_f = \frac{E_f + E_g + 2\Delta}{2}$ (2.569 eV); (4) $\omega_f = E_F + \Delta$ (3.988 eV); and (5) $\omega_f = E_F + \Delta + \frac{E_g}{2}$.

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