Desorption by Femtosecond Laser Pulses:
An Electron-Hole Effect?

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Desorption of molecules from metal surfaces induced by femtosecond visible laser pulses has been reported. Since the lattice temperature rise is insufficient to explain desorption, an electronic mechanism is clearly responsible. It is shown that a theory based on direct coupling between the center-of-mass degree of freedom of the adsorbate and the electron-hole excitations of the substrate provides a satisfactory explanation of the various experimental findings.

§ 1. Introduction

The energy transfer mechanism between an atom or molecule at thermal energy and a metal surface is usually considered to be phononic. However, for a long time an alternative energy channel\(^1\) has received some attention from theorists, the direct coupling between the adsorbate degrees of freedom and electron-hole pairs excited in the metal Fermi distribution. As an energy sink in sticking, electron-hole pairs have been considered by various authors,\(^3\)-\(^5\) and coupling to them can be related to the scattering phase shift of the adsorbate valence orbitals.\(^3\)-\(^5\) A formulation of such a dissipative process in terms of an electronic friction coefficient has been thought of.\(^1\),\(^6\),\(^7\)

An example where electron hole dissipation has a good deal of experimental support is in vibrational linewidth of adsorbate normal modes. In many cases, most extremely in that of intramolecular vibrations such as that of NO at \(\approx 230\) meV, the adsorbate vibrational frequency greatly exceeds the substrate Debye cutoff frequency. Hence relaxation of the singly excited normal mode into the phonon bath requires a multi-phonon process whose strength is too weak to explain the observed homogeneous linewidths of up to a few cm\(^{-1}\). Therefore the electron-hole mechanism has been invoked and discussed in detail by Persson and Persson.\(^8\) In a related development, vibrational excitation of a molecule, such as NO\(^9\) scattered at a hot metal surface can be attributed to\(^10\),\(^11\) absorption of energy from hot electron-hole pairs. As in the vibrational de-excitation case, the adsorption of a quantum of energy from phonons is too difficult.

But as regards the mechanisms of adsorption and desorption, the lack of conclusive evidence for the electron-hole channel has hindered wide acceptance of its significance. What would be most desirable is to be able to control, in a desorption
experiment, the electronic and phononic temperatures independently, these temperatures driving the electron-hole mediated and phonon-mediated desorption channels respectively. Recent femtosecond-pulse laser experiments indeed come close to being able to realize this independent temperature control, and to provide rather convincing evidence for the electron-hole channel.

In these experiments\textsuperscript{10,11} the laser light at 620 nm\textsuperscript{12} is formed into infrequent pulses of \( \sim 200 \) fs width. The radiation energy of a pulse is absorbed by the substrate electron system over a penetration depth, and rapidly creates a distribution of thermalized electrons and holes. Given the low specific heat of the electron system, high peak electron temperatures of several thousand K are achieved. Decay of the electron system's energy into phonons proceeds primarily via electron-phonon coupling\textsuperscript{14} (which can thereby be measured), and is relatively slow, of order several ps. Because the phonon system has a much higher specific heat, its temperature rises only a few hundred K when full equilibrium is reached.

In the experiment of Ref. 12), each laser pulse could typically desorb a fraction \( P_{\text{des}} \approx 10^{-3} - 10^{-4} \) of NO adsorbed on Pd (111). It is found that the phonon heating of a few hundred K is far too small to explain the desorption yield of this chemisorbed system.\textsuperscript{12a} Moreover an autocorrelation time \( \tau \) can be measured from the variation of \( P_{\text{des}} \) when excitation is by means of two laser pulses separated by a known time interval.\textsuperscript{12b} The measured time \( \tau \) is much too short to be compatible with the known slow growth of the phonon bath temperature.

Therefore some kind of electronic mechanism seems to be responsible for desorption in these experiments. Conventional photodesorption mechanisms, either directly or through the excitation of substrate electrons, would be expected to show a linear dependence of desorption yield on the fluence of the laser pulses. In fact, a yield varying in a strongly nonlinear manner with laser fluence is observed.\textsuperscript{12} This behaviour suggests that the desorption process may be closely linked to the electronic temperature of the substrate. Such a model, to be developed in this work represents a different limit from a DIET process arising from a single highly nonequilibrium excitation. The DIET limit has been considered for desorption of NO/Pt by nanosecond pulses by Gadzuk and coworkers.\textsuperscript{15}

Other features of the experiment\textsuperscript{12a} are a low outgoing center-of-mass kinetic energy and a high NO vibrational temperature in excess of 2000 K. A high vibrational temperature could indeed result from adsorbate motion near the surface given its high electron temperature, in the electron-hole mechanism described in Refs. 10) and 11). A low outgoing kinetic energy suggests a model based on a frictional coupling mechanism rather than a transition between potential energy curves, as is characteristic of photon and electron stimulated desorption processes.

In short, a mechanism based on coupling of the NO center-of-mass to electron-hole pairs seems promising on a preliminary view of the data in this experiment. A more quantitative approach based on a Langevin equation will be published elsewhere,\textsuperscript{16} in the following we consider a simple analytic approach which gives quite similar results to those of Ref. 16).
§ 2. Model

In this paper we are interested in a conceptual approach, rather than a fully quantitative approach. We shall assume a truncated harmonic oscillator well for the NO center-of-mass (CM) degree of freedom, and ignore NO internal degrees of freedom. The dynamics of the NO center-of-mass in the well will be described by the harmonic oscillator master equation

$$\frac{dW_n}{dt} = \frac{\eta_e}{e^{\beta \omega_0 t} - 1} ([n + 1] e^{\beta \omega_0 t} W_{n+1} - W_n [n + 1 + n e^{\beta \omega_0 t}] + n W_{n-1}),$$  \(1\)

where \(W_n\) is the probability of being in the \(n\)th harmonic oscillator level at time \(t\), \(\omega_0\) is the vibration frequency of the NO center-of-mass against the surface, \(\beta = 1/T_e\), with \(T_e\) the electron temperature.

In a classical picture, we can think of \(\eta_e\) as the electronic friction coefficient, producing a force \(F_e\) proportional to the NO center-of-mass velocity \(v\), \(F_e = -\eta_e M v\), where \(M\) is the NO mass. The friction coefficient can be related to the phase shift \(\delta\) at the Fermi energy, and in the simplest approximation is given by

$$\eta_e = \frac{1}{\pi M} \left( \frac{\partial \delta(x)}{\partial x} \right)^2,$$

where \(x\) is coordinate of the NO CM.

At zero temperature, the decay of \(W_n\) is described by \(dW_n/dt = -\eta_e W_n\), so we can also identify \(\eta_e\) as the vibrational linewidth (FWHM) of the NO-surface normal mode of frequency \(\omega_0\).

Multiplying (1) by \(n\), and summing over \(n\), we get an equation for the mean oscillator quantum number \(\bar{n}\)

$$\frac{d\bar{n}}{dt} + \eta_e \frac{\partial \bar{n}}{\partial \bar{n}} = \frac{\eta_e}{e^{\beta \omega_0 t} - 1},$$  \(2\)

which one of us used earlier in describing vibrational excitation of NO.\(^{10}\) We are interested in very high electron temperatures, much greater than \(\omega_0\), hence it is appropriate to take the classical limit of (1), to obtain a one-variable Fokker-Planck equation for the energy distribution function \(W(\epsilon, t)\)

$$\frac{\partial W}{\partial t} = \eta_e \frac{\partial}{\partial \epsilon} \left\{ \epsilon \left[ 1 + T_e(t) \frac{\partial}{\partial \epsilon} \right] W \right\}.$$

\((3a)\)

In \((3a)\), \(\epsilon\) is the energy of the NO CM measured from the bottom of the harmonic well. Note that the generalization of \((3a)\) to arbitrary potentials can be derived on the basis of classical local frictional coupling.\(^{18}\)

Our problem is to solve \((3a)\) for a time-varying electron temperature \(T_e(t)\), with appropriate boundary conditions. The boundary condition\(^{18}\)

$$W(V_B, t) = 0; \quad \eta_e < \omega_0 T_e/V_B,$$

\((3b)\)

where the well depth \(V_B\) is the chemisorption energy of NO, is appropriate for the low
friction limit\textsuperscript{13} indicated in (3b), which is satisfied in the present situation (even if $T$ is used instead of $T_e$). An initially thermal distribution for $W$, \begin{equation}
abla W_{0} = \frac{1}{T_0} e^{-\frac{\varepsilon}{\tau_s}}, \tag{3c} \end{equation}
usually with $T_0 = 0$, may be assumed. We shall first consider various kinds of solutions to (3a), before trying to achieve satisfaction of both the boundary conditions.

\section{3. Solutions}

In the special case where $T_e = 0$, Eq. (3a) has a general solution \begin{equation}
abla W = \frac{1}{\varepsilon} f(\eta_\varepsilon \varepsilon + \log \varepsilon), \tag{4} \end{equation}
in which the arbitrary function $f$ can be related to the initial condition via $f(\log(\varepsilon))/\varepsilon = W(\varepsilon, 0)$.

In general, solutions to (3a) involve a function $T(t)$, which is the effective temperature of the NO degree of freedom. $T(t)$ obeys the classical version of (2) \begin{equation}\frac{dT}{dt} + \eta_\varepsilon T = \eta_\varepsilon T_e(t). \tag{5} \end{equation}

We immediately spot that a normalized solution to (3a) is the time-dependent Boltzmann distribution \begin{equation} W(\varepsilon, t) = \frac{1}{T(t)} e^{-\varepsilon T(t)}. \tag{6} \end{equation}

It is useful to rewrite (3a) in terms of the (towards smaller $\varepsilon$) current $j$ \begin{equation} \frac{\partial W}{\partial t} = \frac{\partial}{\partial \varepsilon}, \tag{7a} \end{equation}
where \begin{equation} j = \eta_\varepsilon \left( 1 + T_e(t) \frac{\partial}{\partial \varepsilon} \right) W. \tag{7b} \end{equation}

Finally, it is useful to recall the stationary state solution\textsuperscript{18} to (3a) (for $T_e(t) = T(t) = T_0$), with constant current $j$, which is \begin{equation} W = \frac{i j}{\eta_\varepsilon T_0} e^{-\varepsilon T_0} \int^t e^{x \varepsilon T_0} \frac{dx}{x} - dx + \frac{A}{T_0 e^{-\varepsilon T_0}}, \tag{8} \end{equation}
where $A$ is a constant.

We can choose $A$ so as to satisfy the boundary condition (3b). If we do this in the asymptotic regime $T_0 \ll V_0$ we get an expression for the current\textsuperscript{18} \begin{equation} j \approx -\eta_\varepsilon \frac{V_0}{T_0} e^{-\varepsilon V_0/T_0}. \tag{9} \end{equation}

In this low-current regime, the Kramers desorption rate\textsuperscript{13} in the low-friction limit
(3b) is retrieved.

§ 4. Desorption probability

To get the desorption probability, we need a solution satisfying both boundary conditions (3b) and (3c). We shall initially assume $T_0=0$ for simplicity. It is possible to satisfy (3b) by introducing an 'image' solution $W_i$, and writing

$$W = W_0 + W_i.$$  \hfill (10)

$W_0$ has the initial condition $W_0(\epsilon,0) = \delta(\epsilon)$, while $W_i(\epsilon,0) = g_i(\epsilon)$, where $g_i(\epsilon)$ is a function defined to be nonzero only in the unphysical region $\epsilon > V_\beta$. By suitable choice of $g_i(\epsilon)$, (3b) can be satisfied. $g(\epsilon)$ will be negative, and its area equals the quantity desorbed $P_{des}$. We shall content ourselves here with getting a result in the relevant asymptotic region $T_\epsilon \ll V_\beta$.

Now the function $W_i$ has, in the region $\epsilon \gg V_\beta$, a high internal temperature $\sim V_\beta$. When $T_\epsilon \ll V_\beta$, we may hope to ignore $T_\epsilon$, and calculate $W_i$ as if $T_\epsilon=0$. When $\epsilon \ll V_\beta$, $W_i$ is only a very small fraction of the total solution and its behavior does not matter. Therefore from (4),

$$W_i \approx \frac{1}{\epsilon} f(\eta_e t + \log \epsilon),$$ \hfill (11)

where

$$f(\log \epsilon) / \epsilon = g_i(\epsilon).$$ \hfill (12)

We take $W_0$ as being given by (5 + 6), with $T(0)=0$. Hence our solution satisfies (3c) in $\epsilon < V_\beta$ (the physical region).

Now to satisfy (3b), we require

$$f(\eta_e t + \log V_\beta) = -\frac{V_\beta}{T} e^{-\nu_\beta T},$$ \hfill (13)

which implies

$$f(x) = -\frac{V_\beta}{\bar{T}} e^{-\nu_\beta \bar{T}},$$ \hfill (14)

where $\bar{T} = T((x - \log V_\beta)/\eta_e)$.

Now

$$g(\epsilon) = -\frac{V_\beta}{\epsilon \bar{T}} e^{-\nu_\beta \bar{T}},$$ \hfill (15)

where $\bar{T} = T(\log(\epsilon/V_\beta)/\eta_e)$. Equation (15) is seen to have the required property that it is zero for $\epsilon < V_\beta$ (since $T(t)=0$ for $t \leq 0$).

The current at any time is now from (7b), (10), (6), (11) and (14)

$$j(t) = -\eta_e V_\beta \frac{T^2(t)}{T^3} e^{-\nu_\beta T(t)}.$$ \hfill (16)
We may obtain the desorption probability $P_{\text{des}}$ from integrating (15) on time, or integrating the initial distribution $g(\varepsilon)$, given by (15), over energy. Asymptotically we get the same result, namely

$$P_{\text{des}} \approx \eta_e V_B \int_0^\infty \frac{dt}{T(t)} e^{-\frac{\varepsilon}{k_{\text{B}} T(t)}},$$

(17)

because the stationary point $t = t^*$ of the exponential is defined by $T' = 0$, which is where $T = T_e = T^*$, from (5). The result (17) has a clear physical interpretation as the time integral of the low-friction Kramers rate (9) using the time-dependent adsorbate temperature defined by (5).

Asymptotic evaluation of (17) yields

$$P_{\text{des}} \approx \sqrt{\frac{2\pi \tau_e V_B}{T^*}} e^{-\frac{\varepsilon}{k_{\text{B}} T^*}},$$

(18)

where $\tau_e = -T_e/T_e|^z=\tau$. These results can evidently be extended to the case where $T$ is calculated with the boundary condition $T_0$ nonzero, provided $T_0 \ll V_B$.

§ 5. Results and discussion

Some approximate parameters for the NO/Pd(111) system are detailed in Table I. The well depth of 1.4 eV is assumed in the model to provide the appropriate steady-state desorption rate for desorption under conventional equilibrium conditions. For the variation of the electron temperature $T_e(t)$, we chose the model variation

$$T_e(t) \propto e^{-t/\tau_e}/(e^{-t/\tau_e} + 1).$$

(19)

Equation (19) is parametrized by the values of peak electron temperature $T_{e,\text{m}}$, the characteristic variation time $\tau_e$ and the much shorter laser pulse time $t_p$, derived from simulations of heat flow in the coupled substrate electron and phonon systems.12,14

<table>
<thead>
<tr>
<th>$V_B$ (eV)</th>
<th>$T_{e,\text{m}}$ (K)</th>
<th>$\tau_e$ (psec)</th>
<th>$T^*$ (K)</th>
<th>$\eta_e$ (cm$^{-1}$)</th>
<th>$t_p$ (psec)</th>
<th>$P_{\text{des}}$</th>
<th>$r$ (psec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.4</td>
<td>3650</td>
<td>0.60</td>
<td>1590</td>
<td>5</td>
<td>.945</td>
<td>$2.3 \times 10^{-4}$</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Table I.

Fig. 1. Plot of $T_e$, $T$, $j$ and $P_{\text{des}}$ integrated up to $t$ from (16), using parameters of Table I, with an initial temperature $T_0 = 400$ K. $T_e$ and $T$ are in K (left-hand scale), while $j$ is in arbitrary units.

Fig. 2. Plot of desorption probability in two pulse experiment vs time delay between pulses.
The value of $\eta_e$ is not known; it is selected to bring $P_{des}$ in line with experimental data. Finally we obtained the results illustrated in Fig. 1 from (5), (16) and the time integral of the current (16).

We get (Table I) a desorption probability in the experimental range ($10^{-3}-10^{-4}$ per pulse) for $\eta_e=5\ \text{cm}^{-1}$. The reasonableness of this value is discussed below. In the low friction Kramers limit, the energy of the outgoing species is usually considered\textsuperscript{10} to be zero.

Further revealing experimental information comes from measuring $P_{des}$ in an experiment involving two pulses separated by a known time interval, yielding an autocorrelation function with a characteristic time $\tau$. We calculate this function in Fig. 2; the autocorrelation time (HWHM of the function in Fig. 2) is 0.8 psec (Table I), which compares with an estimate from the numerical approach of Ref. 16) of 0.6 psec. In fact, the experimental result (analysed by excluding a central coherence peak) is even shorter,\textsuperscript{15} at 0.4 psec.

§ 6. Conclusion

It seems clear from the magnitude of the adsorbed fraction relative to the low phonon temperature, and from the shortness of the desorption autocorrelation time $\tau$, that the desorption mechanism for NO on Pt (111) in the pulsed laser experiment of Ref. 12) is not phononic.

The present theory involves coupling of the NO center-of-mass to the electron-hole excitations of the metallic substrate, whose temperature reaches several thousand K in the experiment. It is then possible to explain the desorbed fraction in a manner consistent with the observed high vibrational temperature and low translational energy of the split adsorbed species. The electronic friction $\eta_e$ needs to be of order 5 cm$^{-1}$ which is rather high relative to vibrational linewidths,\textsuperscript{8} but this might be explained by a spatially non-uniform $\eta_e$. The correlation time $\tau$ comes out considerably longer than that measured experimentally.

The present simple-minded theory using a harmonic well and a spatially homogeneous $\eta_e$ yield results substantially in agreement with a more sophisticated treatment based on a Langevin equation approach,\textsuperscript{14} using numerical solution with a large number of trajectories. The Langevin treatment involves a realistic well shape, non-uniform $\eta_e$ and inclusion of phonons (which absorb energy from the desorbing species, inhibiting desorption).

It may be that consideration of other phenomena is needed to resolve fully the issues of magnitude of $\eta_e$ and shortness of correlation time $\tau$ discussed above. One problem ignored here is the presence of the Kondo effect,\textsuperscript{7} inevitable at some point in the trajectory, which will make the implicit assumption that electronic times are short compared with center-of-mass times break down. Perhaps still more significant, the present analysis permits motion only along a single potential energy surface. For the high electronic temperatures relevant in these experiments, motion on excited potential energy surfaces may need to be included.
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References