Adsorbate Vibrational Effects on the Photodesorption of CO from Cu(001)[†]

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We have studied the desorption dynamics of vibrationally excited CO on Cu(001), induced by femtosecond pulses of visible light. The theory is based on a density matrix approach and the propagation of wave packets using a basis of two electronic states and a model which includes the distance from CO to the surface, and the displacement corresponding to a frustrated-translation mode of the adsorbate vibration. The model incorporates potential energy surfaces from electronic structure calculations and contains dissipation effects represented by complex potentials. Equations for density amplitudes are solved nonperturbatively with a propagation procedure valid for large light fluence values. The population of vibrational states of the adsorbed CO were calculated versus time as it desorbs. Desorption yields are found to be more pronounced for initially excited vibrational states. Temperature effects are considered for several initial thermal equilibrium distributions before the arrival of the light pulse.

1. Introduction

Accurate quantum mechanical studies of chemical reaction dynamics[1] show that vibrational energy initially stored in chemical bonds has a large effect on probabilities of reactions and bond dissociation. This contribution describes the photodesorption of CO from the vibrationally excited CO/Cu(001) adsorbate, following absorption of a femtosecond pulse of visible light. The subject of femtosecond desorption of molecules from solid surfaces has been actively studied experimentally and theoretically in recent years, and several reviews have been published.[2−6] Our treatment is based on a model we have recently developed to account for the dissipative dynamics of these phenomena, making use of density matrix methods.[7−9] It has provided results for yields of CO desorbed from the ground vibrational state of the system, versus the fluence of the pulse and for the delay between arrival of the pulse and desorption, both in good agreement with experiments,[10] and has been used to predict the effect of chirped pulses on desorption yields.[11] The approach has been generalized to account for related phenomena where bond breaking results from activation of a medium.[12,13]

The CO adsorbate sits, at low surface coverage, on top of a Cu atom, with its axis perpendicular to the surface. The vibrational motions of such adsorbates have been extensively studied experimentally for the ground electronic states of several systems, and involve analysis of the normal modes of the adsorbate.[14,15] Theoretical studies have also clarified the role of dissipation in the relaxation of vibrationally excited adsorbates,[16,17] and have been the subject of dynamics studies based on ab initio electronic structure calculations.[18−20] Recent theoretical work has dealt with the effect of initial vibrational excitation of a metal−carbon bond,[21] vibrational energy dissipation using a density matrix treatment,[22] and the role of excitation of the N−O stretch mode in photodesorption.[23] For the CO/Cu(001) system, it is known from experimental work[24,25] that the softest vibrational normal mode is a frustrated translation of CO parallel to the metal surface, called the T-mode, with a vibrational energy quantum of 32 cm^{-1}. This mode is excited at the low temperatures, around 100 K, used in measurements of photodesorption yields. The light pulses are known to be absorbed by the metal, inducing excitations between electronic band states, which are then transferred to the adsorbate location and lead to bond breaking. For CO/Cu(001), the result of this indirect mechanism is that CO desorbs most probably in its ground electronic state, while the surface is left electronically excited, and later on relaxes by electron−phonon coupling.[6,26]

We are presently concerned with the effect of initial vibrational excitations on the desorption yields. These excitations could result from heating of the surface, or from preparation of the adsorbate in a specific vibrational state. We assume here that the states of interest are the frustrated translations, with vibrational states labeled by the quantum number v.

The sequence of events triggered by absorption of a light pulse is as follows, with the * and † symbols signifying electronically or vibrationally excited substrates, respectively.

$$\mathrm{CO}(v)/\mathrm{Cu}(001) \xrightarrow{\text{light}} \mathrm{CO}(v)/\mathrm{Cu}(001)^* \text{ (light absorption)}$$

$$\mathrm{CO}(v)/\mathrm{Cu}(001)^* \rightarrow \mathrm{CO}(v') + \mathrm{Cu}(001)^* \text{ (break-up)}$$

$$\mathrm{CO}(v)/\mathrm{Cu}(001)^* \rightarrow \mathrm{CO}(v')/\mathrm{Cu}(001)^\dagger \text{ (electr.-vib. en. transfer)}$$

$$\mathrm{CO}(v')/\mathrm{Cu}(001)^\dagger \rightarrow \mathrm{CO}(v'')/\mathrm{Cu}(001) \text{ (vibr. relaxation)}$$

$$\mathrm{CO}(v')/\mathrm{Cu}(001)^\dagger \rightarrow \mathrm{CO}(v'') + \mathrm{Cu}(001) \text{ (break-up)}$$

corresponding, respectively, to absorption of light, break-up in the electronically excited state, electronic-vibrational energy transfer into the ground electronic state, vibrational relaxation there, and break-up in the ground electronic state, with the second step being the most probable.

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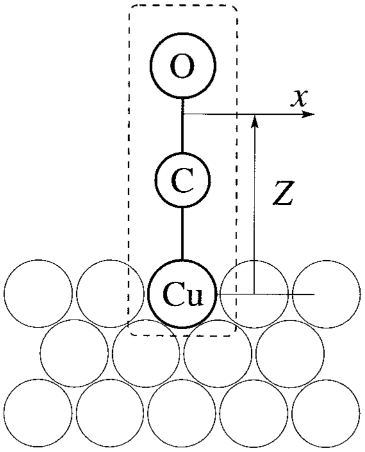

Figure 1. Partition of the CO/Cu(001) system into primary and secondary regions, and coordinates for the model.

Our model for photodesorption starts with a partitioning of the physical system into a primary region including the adsorbed molecule and nearby metal atoms, and a secondary region with the remaining metal atoms. The system is described by means of a density operator and a self-consistent field treatment of the interacting regions, which we had previously also applied to photodissociation of polyatomics.[27,28] In the case of desorption, where the metal substrate involves many rapidly decaying excited states, it is acceptable in addition to introduce a stochastic description of the secondary region with an assumed fast response. The model leads to a time-dependent Liouville-von Neumann (L-vN) equation for the density operator with an effective Hamiltonian for the primary region, including a dissipative potential term.[7,9,11] An alternative more recent derivation using superoperators in Liouville space leads to a more general description of dissipation.[12]

The effective Hamiltonian can be expanded in a basis set of two electronic states, and expressed in terms of two potential energy surfaces and their couplings, and the mentioned dissipative potential functions. The potentials were previously obtained from a combination of electronic structure calculations within a semiempirical (ZINDO-CI) approximation,[29] which have provided the electronically excited states and transition dipoles for our model of CO adsorbed on a cluster of Cu atoms, and of measured bond distances and energies for the ground state, and were parametrized for our recent study of the dynamics induced by an intense laser pulse.[9] Two degrees of freedom are included in our treatment, one for the distance Z between the center of mass of the adsorbate and the substrate, the other for the displacement due to parallel vibrations, x. These are shown in Figure 1, which also displays an illustration of the primary region.

The resulting density matrix differential equations involve 2×2 matrixes whose elements are functions of the time and two space variables. They have been solved using a time-dependent split-operator propagator (SOP) in time,[30] and a fast Fourier transformation (FFT) between space domain and momentum domain for the space variables. The SOP procedure was modified to include an additional unitary transformation factor to account for the dissipation terms in the effective Hamiltonian. This procedure has provided state populations versus time and distances from which we could extract the yield dependencies on initial vibrational state of the frustrated-translation (T) mode, and on the initial temperature of the substrate.

In the sections that follow we briefly describe our physical model for CO/Cu(001) interacting with a femtosecond light pulse, but refer to recent publications for detailed derivations[12,13] of the theory. We describe the potential energy surfaces and couplings between electronic states, and the numerical procedure, and finally results on photodesorption yields. The Conclusion section points out some of the implications of this study for the treatment of metal surface coverage, and for fundamental studies of chemical bond breaking at metal surfaces.

2. Physical Model for CO/Cu(001) Interacting with a Short Light Pulse

The Hamiltonian operator for the total system made up of a molecule M and substrate S, interacting with light L, is

$$\hat{H}(t) = \hat{H}_M + \hat{H}_S + \hat{H}_{MS} + \hat{H}_{ML}(t) + \hat{H}_{SL}(t) \qquad (1)$$

where $\hat{H}_M$, $\hat{H}_S$, $\hat{H}_{MS}$, $\hat{H}_{ML}(t)$, and $\hat{H}_{SL}(t)$ are, respectively, the Hamiltonians for the free molecule, the substrate, the coupling between the molecule and substrate, the coupling between the molecule and light field, and between the substrate and the light field. However, in cases where the molecule is strongly interacting with the medium, as in chemisorption, it is more convenient to redefine the region where a localized dynamics of interest occurs. Introducing a primary (p) region containing the molecule M and adjacent bath atoms, and a secondary (s) region including the remaining bath and interacting with light, the Hamiltonian operator terms are regrouped into the form

$$\hat{H}(t) = \hat{H}^0(t) + \hat{H}_{sl}(t) \qquad (2)$$

where

$$\hat{H}^0(t) = \hat{H}_p\left(\vec{X}, \frac{\partial}{\partial \vec{X}}\right) + \hat{H}_s(\{\hat{B}\}) + \hat{H}_{ps}\left(\vec{X}, \frac{\partial}{\partial \vec{X}}, \{\hat{B}\}\right) \qquad (3)$$

with $\vec{X}$ a set of primary degrees of freedom, and $\{\hat{B}\}$ a collection of boson-like operators (electron−hole pairs or phonons) describing excitations of the s-region, and the interactions of the s-region with light given in the dipole approximation by

$$\hat{H}_{sl}(t) = -\int d^3r\, \epsilon_{loc}(\vec{r},t)\hat{D}_s(\vec{r}) \qquad (4)$$

in terms of the dipole per unit volume $\hat{D}_s$ in the s-region, projected on the direction of the external electric field with local value ϵ_{loc} inside the s-region.

Our treatment starts with with the density operator $\hat{\Gamma}(t)$ for the whole system, satisfying the L-vN equation

$$\partial\hat{\Gamma}/\partial t = (i\hbar)^{-1}[\hat{H}\hat{\Gamma}(t) - \hat{\Gamma}(t)\hat{H}] \qquad (5)$$

This equation can be rewritten to display energy fluctuation and dissipative terms,[31] and to incorporate assumptions about the interaction of p- and s-regions. Strong couplings must be expected between p- and s-regions when the latter is activated by light absorption. Therefore a perturbative treatment for their interaction would not suffice; our approach has been to instead look for a self-consistent field (or mean field) molecular approximation, justified by the introduction of a stochastic medium and averaging over a distribution of initial values of the substrate electronic density amplitudes, shown here by a bar, so that

$$\bar{\hat{\Gamma}}(t) = \hat{\Gamma}^p(t) \otimes \hat{\Gamma}^s(t) \qquad (6)$$

at all times. An equation for the p-region density operator can then be derived using the assumptions that fluctuation forces average to zero on the primary time scale, and that the dissipation is instantaneous, to obtain

$$\partial\hat{\Gamma}^p/\partial t = (i\hbar)^{-1}[\hat{F}_p, \hat{\Gamma}^p(t)] + (\mathrm{d}\hat{\Gamma}^p/\mathrm{d}t)_{diss}$$

$$\hat{F}_p = \hat{H}_p + \hat{G}_p \tag{7}$$

with $\hat{G}_p = tr_s[\hat{H}_{ps}\hat{\Gamma}^s]$, and where we have included a dissipative rate term which follows from the formalism,[9] to be specified.

The procedure we have followed to construct the dissipative rate is based on the decomposition of the p-density operator in terms of amplitudes. Using here normalized amplitudes $\Psi^p_\alpha(t)$ and statistical weights w_α for p-states α, the normalized density operator is

$$\hat{\Gamma}^p(t) = \sum_\alpha w_\alpha |\Psi^p_\alpha(t)\rangle\langle\Psi^p_\alpha(t)| \tag{8}$$

which can be constructed from amplitudes $\psi^p_\alpha(t)$ satisfying

$$i\hbar\frac{\partial}{\partial t}\left|\psi^p_\alpha\right\rangle = (\hat{F}_p - i\hat{W}_p/2)|\psi^p_\alpha(t)\rangle \tag{9}$$

where $\hat{W}_p$ is a positive dissipative operator derived from the residual coupling $\hat{H}'$ describing the correlation of motions between p- and s-regions.[7,12] In terms of the amplitudes $|\Psi^p_\alpha(t)\rangle = |\psi^p_\alpha(t)\rangle/[\langle\psi^p_\alpha(t)|\psi^p_\alpha(t)\rangle]^{1/2}$, the reduced L-vN equation becomes

$$i\frac{\partial\hat{\Gamma}^p}{\partial t} = (\hat{F}_p - i\hat{W}_p/2)\hat{\Gamma}^p(t) - \hat{\Gamma}^p(t)(\hat{F}_p + i\hat{W}_p/2) + i\hat{K}_p\hat{\Gamma}^p \tag{10}$$

with

$$\hat{K}_p\hat{\Gamma}^p = \sum_\alpha w^p_\alpha k^p_\alpha |\Psi^p_\alpha(t)\rangle\langle\Psi^p_\alpha(t)|$$

$$k^p_\alpha = \langle\Psi^p_\alpha|\hat{W}_p|\Psi^p_\alpha\rangle \tag{11}$$

This displays the effect of dissipation and gives a primary density operator with a time-independent normalization.

A similar equation applies for the s-region. It includes the interaction with the external electric field of the light pulse, and leads to a sum $\hat{\Gamma}^s(t) = \hat{\Gamma}^s_0(t) + \hat{\Gamma}^s_l(t)$ of a term appearing in the absence of light plus a term due to the interaction with the light field. This in turn gives $\hat{G}_p(t) = \hat{G}^0_p + \hat{G}^l_p(t)$, where the last term describes the indirect coupling of light to the p-region. In more detail,[9,12]

$$\hat{G}^l_p(t) = -\int \mathrm{d}z \int_0^t \mathrm{d}t'\hat{\Delta}_p(t, t'; z)E_{loc}(z, t') \tag{12}$$

where $\hat{\Delta}_p$ is the effective dipole density per unit time describing a nonlinear response to the local field at a depth z inside the metal. For a stochastic s-region, the response is instantaneous and we have that $\hat{\Delta}_p(t, t'; z) = 2\delta(t - t')\hat{\Delta}_p(z, t)$, which simplifies the expression for the indirect coupling. A more explicit form for the effective dipole operator may be found in ref 12.

3. Computational Procedure

The dynamics of the primary region can be obtained from the solutions of the operator differential equation

$$i\hbar\frac{\partial}{\partial t}\left|\psi^p_\alpha(Z, x, t)\right\rangle = (\hat{K}_p + \hat{V}_p + \hat{G}^l_p - i\hat{W}_p/2)|\psi^p_\alpha(Z, x, t)\rangle \tag{13}$$

which must yet be expanded in a basis of N_{el} p-electronic states $|\Phi_J(Z, x)\rangle$ as

$$|\psi^p_\alpha(Z, x, t)\rangle = \sum_{J=1}^{N_{el}} \psi_{J\alpha}(Z, x, t)|\Phi_J(Z, x)\rangle \tag{14}$$

where the coefficients are nuclear wave functions which satisfy a matrix equation.

Electronic states were obtained from ZINDO-CI calculations, which provided potential energy surfaces and transition dipoles for adiabatic states.[9] The excited state with the largest transition dipole in the region of relevant photon energies (around 2 eV) was selected to form with the ground electronic state a two-state basis set, so that $J = g, e$, giving an adiabatic representation of operators in terms of 2 × 2 matrixes. The matrixes were then transformed into a diabatic representation with nuclear wave functions $\{\psi^d_{J\alpha}\}$, to eliminate momentum couplings and numerically solve the matrix differential equations. The upper index d will be dropped in what follows.

Ground and excited PESs $V_g(Z, x)$ and $V_e(Z, x)$, the diagonal elements of a matrix $\mathbf{V}$, can be written in terms of the C−Cu distance $r = (z^2 + x^2)^{1/2}$, where $z = Z - \gamma d_{CO}$ is the distance from the Cu atom at the origin of coordinates to the C atom, in terms of $\gamma = M_O/(M_C + M_O)$ and the equilibrium distance d_{CO} between C and O. Letting r_g and r_e be the values of r for equilibrium values z_g and z_e in ground and excited states, we write

$$V_J(Z, x) = V^0_J\{exp[-2\alpha_J(r - r_J)] - 2exp[-\alpha_J(r - r_J)]\} + M_{CO}\Omega_J(Z)^2/2 + \Delta V_J$$

$$\Omega_J(Z) = \Omega^T_J(Z)[1 - tanh(2\alpha_J(Z - Z_J)]/2 \tag{15}$$

with $\Delta V_g = 0$ and other parameters found in ref 9 for $J = g, e$. Dissipative potentials were given a dependence on atomic positions consistent with the overlap of substrate and adsorbate atomic orbitals, of the form

$$W_J(Z, x) = W^0_J\, exp[-2\alpha_J(r - r_J)] \tag{16}$$

with exponential parameters from ZINDO and preexponential factors from experimental values of electronic state lifetimes τ_g and τ_e, with $W^0_g = \hbar/\tau_g$ and $W^0_e = \hbar/\tau_e$, that form the diagonal elements of a matrix $\mathbf{W}$.[9]

Diabatic couplings, the off-diagonal elements of the $\mathbf{V}$ and $\mathbf{W}$ matrixes, followed, respectively, from the electronic structure calculations and from the requirement that the dissipative potential should have nonnegative eigenvalues, and were parametrized as

$$V_c(Z, x) = (V^0_c/2)\{1 - tanh[\alpha_c(r - r_c)]\}$$

$$r_c = Z_c - \gamma d_{CO} \tag{17}$$

and

$$W_c(Z, x) = [W_g(Z, x)W_e(Z, x)]^{1/2} \tag{18}$$

with parameters tabulated in ref 9. Finally the calculated off-diagonal element of the dipole matrix $\mathbf{D_p}$ was fit with the functional form

$$D_c(Z, x) = D_0 Z^2\{1 - tanh[\eta(Z - Z_g)]\} \qquad (19)$$

with parameters also listed in ref 9.

Using these matrixes for the potentials, the matrix equation for the nuclear motion amplitudes in the diabatic basis $\{\Phi_J^d(Z, x)\}$ is

$$i\frac{\partial}{\partial t}\psi(Z, x, t) = \left(\hat{\mathbf{K}} + \mathbf{V} - \frac{i}{2}\mathbf{W} + \mathbf{G}^l\right)\psi(Z, x, t) \qquad (20)$$

where ψ is a column 2×1 matrix and $\hat{\mathbf{K}}$, $\mathbf{V}$, $\mathbf{W}$ and $\mathbf{G}^l = -\Delta\epsilon_{loc}(t)$, with Δ the matrix of the $\hat{\Delta}$ effective p-dipole, are 2×2 matrixes.

The propagation of the density amplitudes is done specifying first the initial states at $t = 0$ with vibrational quantum numbers $v_Z = 0$ and v_x, so that only the T normal mode is excited, and the initial state is $\alpha = (g, 0, v_x)$,

$$|\Psi_\alpha(Z, x, 0)\rangle = \psi_{g0v_x}(Z, x)|\Phi_g(Z, x)\rangle$$

$$\psi_{g0v_x}(Z, x) = N_{v_x} \exp[-\alpha_Z^2(Z - Z_g)^2] \exp[-\alpha_x^2 x^2]\, H_{v_x}(\sqrt{2}\alpha_x\, x)$$

$$\alpha_Z^2 = 40.31 \text{ au } \alpha_x^2 = 3.78 \text{ au} \qquad (21)$$

where $\psi_{g0v_x}(Z, x)$ is an eigenfunction of H_g, the ground-state Hamiltonian, and $H_{v_x}(y)$ is the v_xth order Hermite polynomial, generated from the first two polynomials $H_0(y) = 1$ and $H_1(y) = 2y$ and the recursion formula $H_{v+1}(y) = 2yH_v(y) - 2vH_{v-1}(y)$.

The propagation over time was done within a split-operator (SOP) scheme[32] repeatedly used at time intervals $t_n = t_0 + n\Delta t$, $n = 1$ to N_s, modified to include a dissipative potential.[8,9] The time evolution of the wave function from t to $t + \Delta t$ is

$$\psi(t + \Delta t) = \mathbf{U}(t + \Delta t, t)\psi(t)$$

$$\mathbf{U}(t + \Delta t, t) = exp\{-i[\hat{\mathbf{K}} + \mathbf{V} + \mathbf{G}^l(t) - i\mathbf{W}/2]\Delta t/\hbar\} \qquad (22)$$

in terms of the time-evolution operator for a small time increment Δt.

The SOP factorization can be used repeatedly, first for the dissipative potential to obtain

$$\mathbf{U}(t + \Delta t, t) = \mathbf{U}_W(\Delta t/2)\mathbf{U}'(t + \Delta t, t)\mathbf{U}_W(\Delta t/2)$$

$$\mathbf{U}_W(\Delta t/2) = exp[-\mathbf{W}\Delta t/(4\hbar)]$$

$$\mathbf{U}'(t + \Delta t, t) = exp\{-i[\hat{\mathbf{K}} + \mathbf{V} + \mathbf{G}^l(t)]\Delta t/\hbar\} \qquad (23)$$

and next for the time-dependent potential $\hat{\mathbf{V}}'(t) = \hat{\mathbf{V}} + \hat{\mathbf{G}}^l(t)$ so that

$$\mathbf{U}'(t + \Delta t, t) = exp[-i\mathbf{V}'(t)\Delta t/(2\hbar)]\, exp[-i\hat{\mathbf{K}}\Delta t/\hbar]\, exp[-i\mathbf{V}'(t)\Delta t/(2\hbar)] \qquad (24)$$

which are accurate to order Δt^3. Exponentials of 2×2 matrices are easily obtained by diagonalization of the exponents, and the exponential with the kinetic energy operator follows from a fast Fourier transform to momentum variables. The propagation was done for a grid of points in the Z and x variables, and with sufficient time steps to converge to desired accuracies. Typical propagation parameters are given in ref 9.

Populations of the electronic states $J = e$, g evolved from the initial vibrational states $\alpha = I$, v_Z, v_x were obtained from

$$P_{J\alpha}(t) = \langle\psi_{J\alpha}(t)|\psi_{J\alpha}(t)\rangle \qquad (25)$$

while photodesorption yields followed from

$$Y_{J\alpha}(t) = \int_{Z_D}^{\infty}\int_{x_{min}}^{x_{max}}|\psi_{J\alpha}(Z, x, t)|^2 \mathrm{d}Z\, \mathrm{d}x \qquad (26)$$

where $Z_D = 9.2$ au, is the distance past which desorption occurs. These populations satisfy the relation $P_g + P_e = 1 - P_{diss}$, where P_{diss} is the dissipation probability relating to energy loss into the substrate; this is small in our case, so that using instead normalized wave functions gives the same calculated yields to our accuracy.

Thermal averages at surface temperatures T are given by

$$\bar{Y}_J(t; T) = \sum_\alpha w_\alpha(T) Y_{J\alpha}(t)$$

$$w_\alpha = exp(-E_\alpha/k_B T)/Q_{vib}(T) \qquad (27)$$

in terms of the Boltzmann distribution and partition function Q_{vib} for the vibrational modes.

4. Results for Desorption Yields

Calculations were done for an electric field pulse with a Gaussian envelope peaking at a time t_0, and a carrying wave with a central wavelength $\lambda_0 = 620$ nm,

$$\epsilon(t) = 2\bar{F}^{1/2}\left(\frac{2}{\pi\Delta^2}\right)^{1/4} exp\left[-\frac{4(t - t_0)^2}{\Delta^2}\right] cos(\omega_0 t) \qquad (28)$$

with $\omega_0 = 2\pi c/\lambda_0$, Δ the pulse width, and $\bar{F}$ its fluence averaged over frequency oscillations. We have set $\Delta = t_0$ for convenience. For the effective transition dipole operator, we chose the following form suggested by the theoretical model,

$$\bar{\hat{\Delta}}_p = \hat{D}_p\left[\alpha + \beta\left(\frac{\bar{F}}{\bar{F}_0}\right)^2\right] \qquad (29)$$

with $\bar{F}_0 = 1.0$ mJ/cm^2, and $\alpha = 0.40$ and $\beta = 0.28$ obtained fitting the experimental values for yields at $F = 1.5$ mJ/cm^2 and $F = 4.5$ mJ/cm^2.[10]

Results were obtained for each initial vibrational quantum number $v_x = 0$ to 6 and for $v_Z = 0$, starting the calculations at $t = 0$ from the ground electronic state $I = g$ before arrival of a pulse with fluence $\bar{F} = 3.0$ mJ/cm^2. Thermal averages were generated for surface temperatures $T = 75$, 100, 125, and 150 K. Figure 2 shows results for the yields $Y_\alpha(t) = \sum_J Y_{J\alpha}(t)$ versus time up to final times of 17 000 au (with 1 fs = 41.342 au), after which the desorption can be considered as complete. It also shows for comparison the shape of the Gaussian pulse, which illustrates the delay between arrival of the pulse and completion of desorption, with a delay time in agreement with experiment.[10] The asymptotic values of the yield increase with v_x, except for a slight decrease at $v_x = 1$, 2. Figure 3 provides again yields for each vibrational state, but now weighted by the Boltzmann probability at a temperature of 100 K, or $w_\alpha Y_\alpha(t)$, and shows that now the vibrational states contribute to the yield in the same order as their population values, with the ground vibrational state the most populated and also the one giving the largest yield. Finally Figure 4 shows cumulative

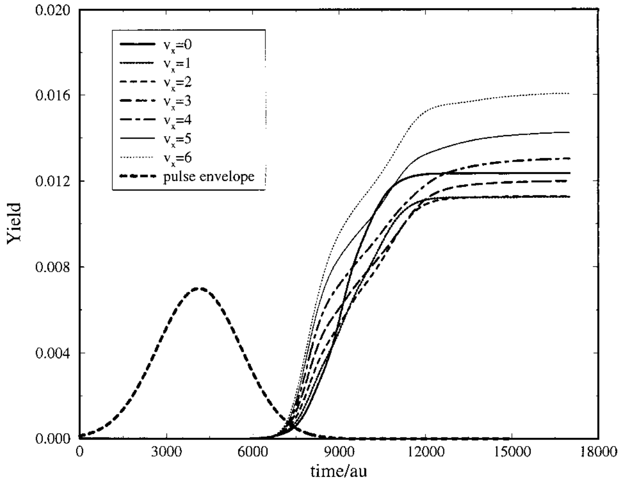

Figure 2. Time evolution of the yields for the individual initial vibrational states of the frustrated-translation mode.

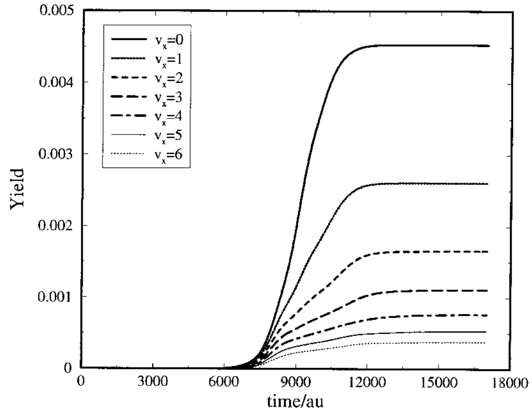

Figure 3. Yields for initial vibrational states with populations weighted by the Boltzmann distribution for a surface temperature of 100 K.

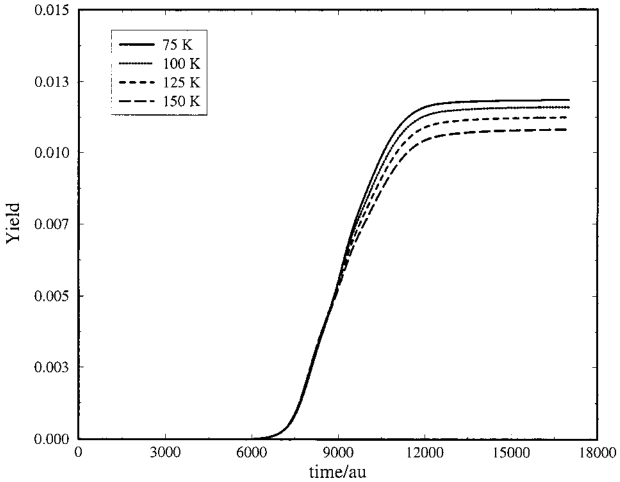

Figure 4. Cumulative yields versus time for several surface temperatures.

yields for v_x = 0 to 6 $\bar{Y} = \bar{Y}_g + \bar{Y}_e$ versus time for several temperatures, and indicates that temperature effects are small.

5. Conclusions

The main result of the present study is the observation that photodesorption yields of CO from individual initial vibrational states of the frustrated-translation mode increase with increasing values of v_x, except for a slight decrease at $v_x = 1, 2$. Therefore photodesorption is promoted by initially exciting the frustrated-translation vibrational mode.

Thermal weighting of the initial vibrational states brings the dependence of yields on initial vibrational states back to the expected order from an initial Boltzmann distribution, but the higher efficiency of energy stored in excited vibrational states means that a deviation from the Boltzmann distribution arises during the dynamics of photodesorption. Adding over our initial states and varying the initial surface temperature around 100 K, typical of experiments, gives theoretical results indicating a slight change in yields as initial temperatures are lowered.

The model employed in the present calculations was previously used to calculate the nonlinear dependence of photodesorbed CO versus laser pulse fluence, and the time dependence of the desorption process, which showed a delay time between arrival of the pulse and completion of desorption,[9] both in good agreement with experiment. The model has been based on calculated potential energy surfaces and parametrized dissipative potentials. The potential energy surfaces were obtained for variable parallel displacements from equilibrium of the adsorbed CO, from which it was possible to estimate the displacement force constants for the ground and excited electronic states in the model. The present results made use of the same model potentials to predict the effect of initial vibrational excitation of the T-mode of the adsorbed CO on the photodesorption yields. These depend on the shape of the potentials, which are only approximately known, and could change if potentials were more accurately calculated. The present results nevertheless indicate that measurements of yields versus initial vibrational states could provide a valuable probe of interaction potentials which are little known, particularly for electronically excited states.

Our model is compatible with the assumption that hot electrons are responsible for the fast response of the metal substrate to the light pulse.[5,6] In our case the primary region, which contains both the adsorbate molecule and neighboring metal atoms, undergoes an electronic rearrangement and electron transfer consistent with that picture, but more specifically due to the interaction of this p-region with the electrons of the excited substrate or s-region. Because of the fast response of these electrons, our stochastic description leads to the indirect coupling potential of eq 12, of the form $\hat{G}^{l}_{p}(t) = \hat{\Delta}_{p}(t)E_{loc}(t)$, with the same shape as the initial pulse. This assumption can be investigated by considering the nonlinear optical response of the metal substrate, and some preliminary work[33] on this (without electronic relaxation) indeed shows a fast response. More recent ongoing work[34] including relaxation due to electron−electron collisions, indicates that the response shape is similar to the incoming pulse shape, but delayed as shown in ref 9 and first found experimentally.[10] Electron relaxation due to the electron−phonon interaction is too slow (on the scale of several picoseconds) to affect the desorption which occurs in about 100 fs.

The optical control of desorption of adsorbates is also of great interest, and our model has previously predicted a large effect of chirping of the laser pulse, which could be used to enhance or suppress desorption of CO from Cu(001).[11] The present results add to this the possibility of altering the extent of desorption by preparing the adsorbate in specific vibrational states, for example by preliminary photoinduced or collision-induced vibrational excitation of its frustrated-translation mode.

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