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Dissipative Quantum Dynamics with Many Coupled Molecular States: Photodesorption from Metal Surfaces†

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A general density matrix treatment is presented for the localized dynamics of a molecular system strongly coupled to a medium, and leading to dissipation and fluctuation phenomena. A self-consistent field description allows for the response of the medium when this is driven away from equilibrium. The dynamics of the primary region is described with a dissipative potential within an atomic model, whereas the medium is described in a statistical manner in terms of dissipative rates. This treatment is applied to the femtosecond photodesorption of CO from the Cu(001) surface, in a model which includes several vibrational modes of the adsorbate, and the nonlinear response of the substrate metal treated with a modified optical Bloch equation. A computational procedure based on the split operator propagator and fast Fourier transform is applied to several studies with an increasing number of adsorbate degrees of freedom. It introduces a combination of discretization on a grid and expansions in basis sets of vibrational adsorbate states, to obtain results on yields of desorbed CO versus the fluence of the light pulse, in very good agreement with experimental results.

1. Introduction

The dynamics of a many-atom system in contact with a medium involves special challenges because it requires a description of fluctuation and dissipation phenomena. This contribution presents a density operator treatment of dissipative quantum dynamics, suitable for phenomena where the system and its surroundings are strongly interacting, and where the system contains many atoms or alternatively many degrees of freedom. It describes two different approaches that account for dissipation. One of them, based on dissipative potentials, is suitable for a detailed treatment within a molecular model, and the other one describes dissipation in terms of rate coefficients that can be obtained semiempirically or from kinetics models. A numerical procedure is given to solve the coupled differential equations arising from our treatment, and an application is presented for the photodesorption of CO from the Cu(001) metal surface resulting from absorption of a femtosecond pulse of visible light.

The study of the quantum dynamics of a molecule M in a medium or bath B requires a combination of quantum and statistical mechanics to incorporate thermal effects and non-equilibrium initial conditions. The density operator, satisfying the Liouville−von Neumann (L−vN) equation,[1−3] provides a general tool for such studies. This presentation expands previous treatments[4−8] to allow for the strong coupling of molecule and bath, when both undergo fluctuation and dissipation processes. Starting with the equations for the whole system, a partition into primary and secondary regions (p- and s-regions for short) is introduced to derive an equation for the primary region where a localized dynamics occurs. It contains the molecule and its immediate surroundings, while the secondary region contains the rest of the extended system, as pictorially shown in Figure 1. The present treatment is developed for phenomena involving active media, excited by the absorption of light. Aspects of this formulation within a density matrix theory have recently been published.[9−11]

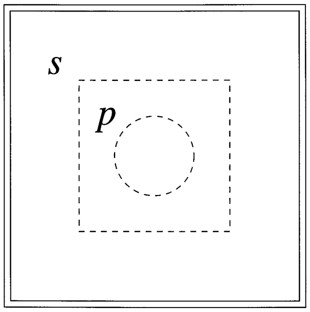

Figure 1. Schematic partition of the whole system into p- and s-regions, with the p-region containing the molecule of interest and the surrounding bonded atoms.

The treatment of quantum dynamics in the primary region has many aspects in common with the treatment of isolated molecular systems, particularly when time-dependent methods are used.[12−20] Numerical methods developed for isolated systems[21−26] can be extended to systems undergoing dissipative dynamics, as we shall mention.

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.[27−31] 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.[32−36] It has provided results for yields of CO desorbed from the ground and excited 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,[37] and has also been used to predict the effect of chirped pulses on desorption yields.[38,39]

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2. Equations of Motion for Coupled Primary and Secondary Regions

The total system, made up of a molecule M and a medium or bath B, interacting with light L, is described in a quantum treatment by means of a Hamiltonian containing the energy operators for the free molecule, the medium, the coupling between the molecule and medium, the coupling between the molecule and light field, and the coupling between the medium and the light field. However, in cases where the molecule is strongly interacting with its environment, 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 medium atoms, and a secondary (s) region including the remaining medium, both interacting with light, the Hamiltonian operator terms are regrouped into the form

$$\hat{H}(t) = \hat{H}^{(0)}(t) + \hat{H}^{(1)}(t) \tag{1}$$

where

$$\hat{H}^{(0)}(t) = \hat{H}_{\mathrm{p}}\left(\vec{X},\frac{\partial}{\partial X}\right) + \hat{H}_{\mathrm{s}}(\{\hat{B}\}) + \hat{H}_{\mathrm{ps}}\left(\vec{X},\frac{\partial}{\partial X},\{\hat{B}\}\right)$$
$$\hat{H}^{(1)}(t) = \hat{H}_{\mathrm{pl}}(\vec{X}, t) + \hat{H}_{\mathrm{sl}}(\{\hat{B}\},t) \tag{2}$$

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.

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

$$\partial\hat{\Gamma}/\partial t = -(\mathrm{i}/\hbar)[\hat{H}\hat{\Gamma}(t) - \hat{\Gamma}(t)\hat{H}] \tag{3}$$

This equation can be rewritten to display energy fluctuation and dissipative terms,[5] and to incorporate assumptions about the interaction of p- and s-regions. Strong couplings must be expected between p- and s-regions, and in our approach we have introduced a self-consistent field (or mean field) that allows it, in a statistical approximation that factors the total density operator into p- and s-reduced density operators $\hat{\Gamma}^{\mathrm{p}} = \mathrm{tr}_{\mathrm{s}}(\hat{\Gamma})$ and $\hat{\Gamma}^{\mathrm{s}} = \mathrm{tr}_{\mathrm{p}}(\hat{\Gamma})$, where the trace has been taken to sum over s- and p-region variables, respectively.[32−36] The p-density operator is to be obtained from a detailed molecular model, whereas the s-density operator must be known only within a statistical description. This involves a statistical distribution for a given macroscopic properties such as the initial temperature T and number density N of the s-region and for initial values of dynamical properties. The factorization can be justified by introducing an averaging of the total density operator over a distribution of initial values of the properties of the s-region, shown in what follows by an overline, so that in particular $\overline{\hat{\Gamma}^{\mathrm{p}}(t)} = \hat{\rho}(t)$. Those properties can be positions and momenta in the medium, or the initial amplitudes of its collective density fluctuations. The starting assumption is then that

$$\overline{\hat{\Gamma}}(t) = \hat{\rho}(t) \otimes \hat{\Gamma}^{\mathrm{s}}(t) \tag{4}$$

at all times. This factorization is less restrictive than the assumption of a factorized wave function in other treatments, insofar as the present choice is equivalent to a statistical superposition of factorized density amplitudes. A treatment can be developed to go formally beyond the selfconsistent density operators, to include the statistical correlation of p- and s-region dynamics by means of projection operators.[9]

The differential equation for $\hat{\rho}(t)$ can be derived introducing Liouville superoperators shown as caligraphic symbols, such that $\hat{\mathscr{H}} = [\hat{H},\hat{A}]$ and starting with

$$\mathrm{i}\hbar\partial\hat{\Gamma}/\partial t = \hat{\mathscr{H}}\hat{\Gamma}(t) \tag{5}$$

This can be transformed into an integrodifferential equation to display correlations in the s-region,[5] and we summarize the derivation first without an external field. Decomposing the Hamiltonian as $\hat{H} = \hat{F} + \hat{H}'$, where $\hat{F}$ is a convenient, possibly time-dependent, effective Hamiltonian to be defined, chosen here as

$$F = \hat{F}_{\mathrm{p}} + \hat{F}_{\mathrm{s}} - \langle\langle\hat{H}_{\mathrm{ps}}\rangle\rangle$$
$$\hat{F}_{\mathrm{p}} = \hat{H}_{\mathrm{p}} + \hat{G}_{\mathrm{p}} \tag{6}$$

with $\hat{G}_{\mathrm{p}} = \overline{\mathrm{tr}_{\mathrm{s}}[\hat{H}_{\mathrm{ps}}\hat{\Gamma}^{\mathrm{s}}]}$ and $\langle\langle\hat{H}_{\mathrm{ps}}\rangle\rangle = \overline{\mathrm{tr}_{\mathrm{ps}}[\hat{H}_{\mathrm{ps}}\hat{\Gamma}^{\mathrm{p}}\hat{\Gamma}^{\mathrm{s}}]}$, and similarly for the s-operators, so that $\hat{F}$ is a SCF Hamiltonian with an average equal to the instantaneous energy of the total system, involving the SCF potentials $\hat{G}_{\mathrm{p}}(t)$ and $\hat{G}_{\mathrm{s}}(t)$. This definition leads to $\hat{H}' = \hat{H}_{\mathrm{ps}} - (\hat{G}_{\mathrm{p}} + \hat{G}_{\mathrm{s}}) + \langle\langle\hat{H}_{\mathrm{ps}}\rangle\rangle$, a residual coupling due to the non-SCF correlation of motions in the p- and s-regions which averages to zero at all times.

Solving formally for the full density operator, $\hat{\Gamma}(t)$, and replacing it in the L−vN equation display the fluctuation and dissipation terms.[9] An equation for $\hat{\rho}$ follows by taking the trace over s-states and averaging over s- initial conditions to obtain

$$\mathrm{i}\hbar\partial\hat{\rho}/\partial t = \hat{\mathscr{F}}_{\mathrm{p}}\hat{\rho}(t) + \hat{\mathscr{R}}_{\mathrm{p}}(t)\,\hat{\rho}(0) - (\mathrm{i}/\hbar)\int_0^t \mathrm{d}t'\,\hat{\mathscr{M}}_{\mathrm{p}}(t,t')\,\hat{\rho}(t')$$
$$\hat{\mathscr{R}}_{\mathrm{p}}(t) = \overline{\mathrm{tr}_{\mathrm{s}}[\hat{\mathscr{H}}'\,\hat{\mathscr{U}}_0(t,0)\,\hat{\Gamma}^{\mathrm{s}}(0)]}$$
$$\hat{\mathscr{M}}_{\mathrm{p}}(t,t') = \overline{\mathrm{tr}_{\mathrm{s}}[\hat{\mathscr{R}}(t)\,\hat{\mathscr{R}}(t')^{\dagger}\hat{\Gamma}^{\mathrm{s}}(t')]} \tag{7}$$

where $\hat{\mathscr{U}}_0(t,t') = \exp_{\mathrm{T}}[-\mathrm{i}\int_{t'}^{t} \mathrm{d}t''\,\hat{\mathscr{F}}(t'')/\hbar]$ is a time-evolution superoperator written as a time-ordered exponential, and $\hat{\mathscr{R}}_{\mathrm{p}}$ and $\hat{\mathscr{M}}_{\mathrm{p}}$ are energy fluctuation and energy dissipation rate superoperators, respectively. A similar procedure can be followed by reversing the roles of p- and s-regions to derive the equation for $\hat{\Gamma}^{\mathrm{s}}(t)$. The secondary region, however, evolves in time much more rapidly than the primary region, because its energy is spread over many more degrees of freedom, so that the dissipation of energy in the p- and s-regions can best be treated separately.

An equation for the p-region density operator can be derived using the assumptions that fluctuation forces average to zero on the primary time scale, and that the dissipation is instantaneous, so that $\overline{\hat{\mathscr{R}}_{\mathrm{p}}(t)\hat{\rho}(0)} = 0$, and $\hbar^{-1}\overline{\hat{\mathscr{M}}_{\mathrm{p}}(t,t')\hat{\rho}(t')} = \delta(t-t')\,\hat{\mathscr{W}}_{\mathrm{p}}(t)\hat{\rho}(t)$, which defines a time-dependent dissipative potential superoperator $\hat{\mathscr{W}}_{\mathrm{p}}(t)$, to the right. These will be called here the stochastic medium assumptions. The equation for $\hat{\rho}(t)$ is then

$$\partial\hat{\rho}/\partial t = -(\mathrm{i}/\hbar)[\hat{\mathscr{F}}_{\mathrm{p}} - (\mathrm{i}/2)\,\hat{\mathscr{W}}_{\mathrm{p}}]\hat{\rho}(t) \tag{8}$$

In our previous work,[32−36] we have implemented this approach in a computationally convenient way, starting instead with a total density operator expressed in terms of density amplitudes $\Psi_\mu(t)$ with statistical weights w_μ, as $\hat{\Gamma} = \underline{\Sigma_\mu} w_\mu|\Psi_\mu\rangle \times \langle\Psi_\mu|$ and factorized forms $w_\mu = w_\alpha^{\mathrm{p}}\,w_\beta^{\mathrm{s}}$ and $\Psi_\mu(t) = \Psi_\alpha^{\mathrm{p}}(t)\,\Psi_\beta^{\mathrm{s}}(t)$, and constructing as above an integrodifferential equation for the p-region amplitude. The p-density operator is

$$\hat{\rho}(t) = \sum_{\alpha} w_{\alpha} |\Psi^{\mathrm{p}}_{\alpha}\rangle\langle\Psi^{\mathrm{p}}_{\alpha}| \tag{9}$$

and the stochastic medium assumptions give then p-amplitude equations

$$\mathrm{i}\hbar\frac{\partial}{\partial t}|\psi^{\mathrm{p}}_{\alpha}\rangle = (\hat{F}_{\mathrm{p}} - \mathrm{i}\hat{W}_{\mathrm{p}}/2)|\psi^{\mathrm{p}}_{\alpha}(t)\rangle \tag{10}$$

where now $\hat{W}_{\mathrm{p}}$ is a positive dissipative operator quadratic in the residual coupling $\hat{H}'$,[32] given by

$$\hat{W}_{\mathrm{p}}(t) = (2/\hbar)\int_0^t \mathrm{d}t'\, \overline{\mathrm{tr}_{\mathrm{s}}[\hat{H}'\hat{U}_0(t,t')\, \hat{H}'\hat{\Gamma}^{\mathrm{s}}(t')]} \tag{11}$$

and the normalized p-amplitudes are $|\Psi^{\mathrm{p}}_{\alpha}\rangle = |\psi^{\mathrm{p}}_{\alpha}\rangle/\langle\psi^{\mathrm{p}}_{\alpha}|\psi^{\mathrm{p}}_{\alpha}\rangle$. This explicit form for the dissipative potential allows for its calculation or parametrization starting with an atomic model of the p-region. Additional details may be found in refs 9 and 32.

Dissipation in the s-region can be treated similarly, making the same stochastic medium assumptions to obtain the equation of motion

$$\partial\hat{\Gamma}^{\mathrm{s}}/\partial t = -(\mathrm{i}/\hbar)\hat{\mathscr{F}}_{\mathrm{s}}\hat{\Gamma}^{\mathrm{s}}(t) + \hat{\mathscr{L}}^{(\mathrm{D})}_{\mathrm{s}}\hat{\Gamma}^{\mathrm{s}}(t) \tag{12}$$

where $\hat{\mathscr{L}}^{(\mathrm{D})}_{\mathrm{s}}$ is the dissipative rate superoperator in the s-region.[9] To proceed, one must note that the s-density operator can be obtained only as a statistical property, insofar as it describes a medium subject to thermodynamical constraints. At the initial time it is prepared at a certain temperature T_0 and with a chemical potential μ_0, or equivalently an average number density $\bar{N}_0$. The s-region is further found in stationary states $\Psi^{\mathrm{s}}_{\beta}$. As the total system is perturbed and coupling with the p-region takes effect, the s-region undergoes changes in temperature and density and transitions between states.

Instead of trying to describe the s-region in full detail, it is enough to follow its dynamics only to the extent needed to model the phenomena of interest in the p-region. This can be achieved by using a description of the s-region in terms of its time-dependent macroscopic temperature $T(t)$ and number density $\bar{N}(t)$, and of its reduced density operator $\hat{\gamma}(t)$, obtained from a subset $\{\Phi^{\mathrm{s}}_{\underline{\lambda}}\}$ of s-region states. Equations for the time evolution of $T(t)$, $\bar{N}(t)$, and $\hat{\gamma}(t)$ can be derived from $\hat{\Gamma}^{\mathrm{s}}(t)$.[36]

Writing the (ps)-coupling Hamiltonian in the form $\hat{H}_{\mathrm{ps}} = \Sigma_k \hat{A}^{(k)}_{\mathrm{p}}\hat{B}^{(k)}_{\mathrm{s}}$, the s-dissipative rate superoperator takes the form

$$\hat{\mathscr{L}}^{(\mathrm{D})}_{\mathrm{s}}\hat{\Gamma}^{\mathrm{s}}(t) = \sum_{L}\{\hat{C}^{(\mathrm{L})}_{\mathrm{s}}\hat{\Gamma}^{\mathrm{s}}(t)\hat{C}^{(\mathrm{L})\dagger}_{\mathrm{s}} - [\hat{C}^{(\mathrm{L})\dagger}_{\mathrm{s}}\hat{C}^{(\mathrm{L})}_{\mathrm{s}}, \hat{\Gamma}^{\mathrm{s}}(t)]_{+}/2\} \tag{13}$$

where the last term is an anti-commutator. This expression is of the Lindblad form,[40] and it is known to give a density operator that is positive definite over time. One way to implement this in applications, already used in studies of photodesorption,[36,41] is to make the choice $\hat{C}^{(\mathrm{L})}_{\mathrm{s}} = \sqrt{\kappa_{\lambda\to\lambda'}}|\Phi^{\mathrm{s}}_{\lambda'}\rangle\langle\Phi^{\mathrm{s}}_{\lambda}|$, where the transition rates $\kappa_{\lambda\to\lambda'}$, obtained from separate calculations or from experiment, can be used to construct the dissipative rate operator. This leads to an equation of motion for the reduced matrix $\boldsymbol{\gamma}^{\mathrm{s}}(t)$ with elements $\gamma_{\lambda'\lambda}{}^{\mathrm{s}}(t)$ in a basis of stationary s-states.

To summarize, the description of coupled p- and s-regions requires the solution of the following set of coupled differential equations.

$$\frac{\partial}{\partial t}\psi^{\mathrm{p}}_{\alpha}(\vec{X},t) = -\frac{\mathrm{i}}{\hbar}[\hat{F}_{\mathrm{p}}(t) - \mathrm{i}\hat{W}_{\mathrm{p}}(t)/2]\psi^{\mathrm{p}}_{\alpha}(\vec{X},t) \qquad \text{(A)}$$

$$\mathrm{d}T/\mathrm{d}t = F[T(t),N(t)] \qquad \mathrm{d}N/\mathrm{d}t = G[T(t),N(t)] \qquad \text{(B)}$$

$$\mathrm{d}\gamma^{\mathrm{s}}/\mathrm{d}t = -(\mathrm{i}/\hbar)[\mathbf{F}_{\mathrm{s}}(t),\gamma^{\mathrm{s}}(t)] + \mathscr{L}^{(\mathrm{D})}_{\mathrm{s}}\gamma^{\mathrm{s}}(t) \qquad \text{(C)} \tag{14}$$

Here the functions F and G can be obtained from treatments of near equilibrium processes[42,43] and contain macroscopic parameters such as heat capacities, excitation rates, and relaxation rates. The Hamiltonian operator $\hat{F}_{\mathrm{p}}(t)$ and the matrix $\mathbf{F}_{\mathrm{s}}(t)$ of the effective Hamiltonian in the s-region are shown to be time dependent, to allow for inclusion of couplings with an external light pulse of electric field $\mathscr{E}(t)$. The set of coupled equations in eqs 14A−C must be solved coupled to each other.

In the application that follows, the external field first excites the s-region by coupling to its polarizability operator, giving a density operator $\hat{\Gamma}^{\mathrm{s}} = \hat{\Gamma}^{\mathrm{s}}_0 + \hat{\Gamma}^{\mathrm{s}}_{\mathrm{l}}$, where the second term results from the response of the s-region to the field. This then shows as an indirect excitation of the p-region, through the SCF potential $\hat{G}_{\mathrm{p}} = \hat{G}^0_{\mathrm{p}} + \hat{G}^{\mathrm{l}}_{\mathrm{p}}$. The second term here is expressed as the field coupled to an effective p-dipole operator, which can be parametrized from experiment[32,34] or alternatively by the coupling of the p-dipole operator to an effective field in the p-region, as has been more recently derived from a theory of the nonlinear response of the s-region to a pulse of light.[36,39]

To implement a numerical solution of these equations, it is further necessary to transform the partial differential equation of the p-density amplitudes into coupled ordinary differential equations in time. This can be done expanding the amplitudes in a basis of electronic states $\{|\psi^{(\mathrm{el})}_{\mathrm{J}}(\vec{X})\rangle\}$, to obtain

$$|\psi^{\mathrm{p}}_{\alpha}(\vec{X},t)\rangle = \sum_{\mathrm{J}}|\psi^{(\mathrm{el})}_{\mathrm{J}}(\vec{X})\rangle\psi^{(\mathrm{nu})}_{\mathrm{J},\alpha}(\vec{X},t) \tag{15}$$

where the bracket notation refers to states of the electronic system, and using either discretization of the atomic position variables $\vec{X}$ on a grid or expansions of the states $\psi^{(\mathrm{nu})}_{\mathrm{J},\alpha}$ in basis sets, or a combination of discretization and basis set expansion. This transforms the partial differential equation for $\psi^{\mathrm{p}}_{\alpha}(\vec{X},t)$ into a set of coupled ordinary differential equations for amplitudes in a matrix representation $\boldsymbol{\psi}^{(\mathrm{nu})}(t)$ of $\psi^{\mathrm{p}}(t)$ for given initial state α,

$$\frac{\mathrm{d}}{\mathrm{d}t}\psi^{(\mathrm{nu})}(t) = -\frac{\mathrm{i}}{\hbar}[\mathbf{F}_{\mathrm{p}}(t) - \mathrm{i}\mathbf{W}_{\mathrm{p}}(t)/2]\psi^{(\mathrm{nu})}(t) \qquad (\mathrm{A}') \tag{16}$$

The equations in sets (18A′), (14B), and (14C) are all coupled, but sets (14B) and (14C) can first be integrated over time to obtain the response of the s-region, and their results can be interpolated over time as needed to integrate the set (18A′), where the effective field must be obtained from that response. For a basis set in the s-region of dimension $N^{\mathrm{s}}_{\mathrm{B}}$, sets (14B) and (14C) contain $(N^{\mathrm{s}}_{\mathrm{B}})^2 + 2$ coupled equations, which must be solved with a numerical procedure suitable for the fast density oscillations in that region. The total number of p-region amplitudes that are coupled over time depends on the number $N^{\mathrm{p}}_{\mathrm{el}}$ of electronic basis functions there, the number of grid points $N^{\mathrm{p}}_{\mathrm{G}}$ for atomic position variables, and the number $N^{\mathrm{p}}_{\mathrm{B}}$ of atomic basis functions, which give a total of $N^{\mathrm{p}}_{\mathrm{el}}\, N^{\mathrm{p}}_{\mathrm{G}}\, N^{\mathrm{p}}_{\mathrm{B}}$ coupled differential equations in time. These contain the effective field

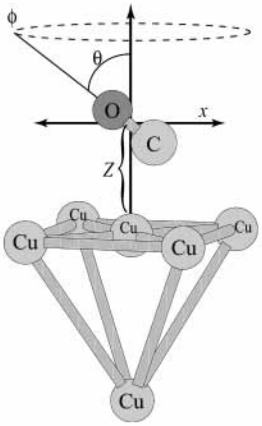

Figure 2. The CO/Cu$_6$ cluster model of CO/Cu(001) for the adsorbate region. Here Z is the position of the center of mass of CO above the surface, x is the frustrated translation variable, and θ and ϕ are frustrated rotation variables.

in the p-region and can be solved with an extension of the split-operator propagator that includes a dissipative potential matrix.

3. An Application to Femtosecond Photodesorption in CO/Cu(001)

The main steps in the femtosecond photodesorption of CO from Cu(001) are excitation by the substrate, followed by energy transfer to the adsorbate region and break-up of the Cu−C bond.[27,44,45] The desorption dynamics is fast compared with vibrational motions in the substrate metal, so that only electronic excitation and de-excitation of its electrons must be considered. The steps are as follows.

$$\mathrm{CO}(\mathbf{v})/\mathrm{Cu}(001) \xrightarrow{\text{light}} \mathrm{CO}(\mathbf{v})/\mathrm{Cu}(001)^* \text{ (light absorption)}$$
$$\mathrm{CO}(\mathbf{v})/\mathrm{Cu}(001)^* \rightarrow \mathrm{CO}(\mathbf{v}') + \mathrm{Cu}(001)^* \text{ (breakup)}$$

corresponding to an indirect photodesorption, where $\mathbf{v}$ indicates the collection of vibrational quantum numbers for the normal modes of the adsorbate. The modes with the lowest excitation energy, and most likely to be excited during desorption, are the so-called frustrated translation and frustrated rotations.[46] The position of the center of mass of the CO above the surface is called Z, the frustrated translation coordinate parallel to the surface is x, and the frustrated rotation angles are (θ, ϕ), as shown in Figure 2, in a cluster model CO/Cu$_6$ for the adsorbate site.

In our model, the transfer of energy from the substrate metal to the adsorbate region is mediated by the dipole−dipole interaction

$$\hat{H}_{\mathrm{ps}} = \int \mathrm{d}^3 r_{\mathrm{s}} \frac{\hat{\vec{D}}_{\mathrm{p}}(\vec{r}_{\mathrm{p}})\cdot\hat{\vec{P}}_{\mathrm{s}}(\vec{r}_{\mathrm{s}}) - 3[\hat{\vec{D}}_{\mathrm{p}}(\vec{r}_{\mathrm{p}})\cdot\vec{n}_{\mathrm{p}}]\hat{\vec{P}}_{\mathrm{s}}(\vec{r}_{\mathrm{s}})\cdot\vec{n}_{s}}{|\vec{r}_{\mathrm{s}} - \vec{r}_{\mathrm{p}}|^3} \tag{17}$$

from which the SCF potential $\hat{G}_{\mathrm{p}}$, the dissipative potential $\hat{W}_{\mathrm{p}}$, and dissipative rates in the s-region can be derived. Here $\hat{\vec{D}}_{\mathrm{p}}$ is the dipole operator of the p-region, $\hat{\vec{P}}_{\mathrm{s}}$ is the dipole operator per unit volume in the s-region, and $\vec{n}_{\mathrm{i}} = \vec{r}_{\mathrm{i}}/r_{\mathrm{i}}$, i = p, s, denotes a unit vector in the p- or s-region. This simplifies for an electric field of long wavelength polarized parallel to the surface, to give for the SCF potential[36]

$$\hat{G}_{\mathrm{p}}(\vec{r}_{\mathrm{p}},t) = \hat{D}_{\mathrm{p}}(z_{\mathrm{p}})\, D_{\mathrm{s}}(t;Z_{\mathrm{s}})|Z_{\mathrm{s}} - z_{\mathrm{p}}|^{-3} \tag{18}$$

where $D_{\mathrm{s}}(t;Z_{\mathrm{s}})$ is the average substrate dipole induced by the applied field inside the metal at distance Z_{s}.

Expanding the amplitudes in a basis set of vibronic states

$$|\Phi_{\mathrm{J}\mathbf{v}}(Z,x,\theta,\phi)\rangle = |\phi_{\mathrm{J}}^{(\mathrm{el})}(Z,x,\theta,\phi)\rangle \phi_{\mathrm{vx}}^{\mathrm{T}}(x)\, U_{\mathrm{r}}(\theta)\, V_{\mathrm{s}}(\phi) \tag{19}$$

where the ket indicates an electronic state for fixed nuclear positions, and $\phi_{\mathrm{vx}}^{\mathrm{T}}$, U_{r}, and V_{s} are basis functions suitable for the surface vibrational modes with quantum numbers $\mathbf{v} = (\upsilon_x, r, s)$, the p-amplitude $\Psi_{\mathrm{g}\mathbf{v}}$, starting in the ground electronic and vibrational state $\mathbf{v}$ of the adsorbate, is

$$|\Psi_{\mathrm{g}\mathbf{v}}(Z,x,\theta,\phi,t)\rangle = \sum_{\mathrm{J},\mathbf{v}'} |\Phi_{\mathrm{J}\mathbf{v}'}(Z,x,\theta,\phi)\rangle \psi_{\mathrm{J}\mathbf{v}',\mathrm{g}\mathbf{v}}^{(\mathrm{nu})}(Z,t) \tag{20}$$

with J = g, e electronic states, and the equation for the matrix $\boldsymbol{\psi}^{(\mathrm{nu})}(Z,t)$ of coefficient functions is

$$\frac{\partial \boldsymbol{\psi}^{(\mathrm{nu})}}{\partial t} = -\frac{\mathrm{i}}{\hbar}[\hat{\mathbf{F}}_{\mathrm{p}} - \mathrm{i}\mathbf{W}_{\mathrm{p}}/2 - \mathscr{E}_{\mathrm{p}}(t)\mathbf{D}_{\mathrm{p}}]\boldsymbol{\psi}^{(\mathrm{nu})} \tag{21}$$

to be solved with a split-operator propagator[22] modified to include the dissipative potential term, and using a fast Fourier transform on a Z-grid of $N_{\mathrm{G}}^{(\mathrm{p})}$ values. The effective electric field in the p-region, $\mathscr{E}_{\mathrm{p}}(t)$ is obtained from the nonlinear response of the metal substrate as explained below.

Desorption yields Y_α from initial vibrational-electronic state $\alpha = (\mathrm{g}, \mathrm{v}_Z, \mathbf{v})$, are obtained integrating the probabilities from a desorption distance Z_{D} to infinity,

$$Y_\alpha(t) = \sum_{I\mathbf{v}'} \int_{Z_{\mathrm{D}}}^{\infty} \mathrm{d}Z\, |\psi_{I\mathbf{v}',\alpha}^{(\mathrm{nu})}(Z,t)|^2 \tag{22}$$

which also provides the time evolution of the desorption yield as a pulse of light is applied.

The potential energy functions in the p-region were previously obtained from information about measured bond distances and energies for the ground state and from electronic structure calculations within a semiempirical approximation for ground and excited states. Electronic states were obtained from ZINDO−CI calculations,[47,48] which provided potential energy surfaces and transition dipoles for adiabatic states for our model of CO adsorbed on a cluster Cu$_6$ of surface atoms. The excited state with the largest transition dipole in the region of relevant photon energies (around 2 eV), and the ground electronic state, form a two-state basis set, so that J = g, e, giving an adiabatic electronic representation of operators in terms of 2 × 2 matrices. The matrices were then transformed into a diabatic representation, to eliminate momentum couplings and numerically solve the matrix differential equations. The potentials and couplings were parametrized as shown in our recent study of the dynamics induced by an intense laser pulse.[34,36,39] Further expansion in vibrational states and on a grid for Z transforms the partial differential equations into coupled ordinary differential equations. In matrix form, the equation for the nuclear density amplitudes is in detail

$$\frac{\mathrm{d}}{\mathrm{d}t}\boldsymbol{\psi}(t) = -\frac{\mathrm{i}}{\hbar}\left(\hat{\mathbf{K}} + \mathbf{V} + \mathbf{G} - \frac{\mathrm{i}}{2}\mathbf{W}\right)\boldsymbol{\psi}(t) \tag{23}$$

The propagation of the density amplitudes has been done specifying initial states at $t = 0$ with vibrational quantum numbers $\upsilon_Z = \upsilon_x = \upsilon_\theta = \upsilon_\phi = 0$, corresponding to ground vibrational states of frustrated translations and rotations.

The integration over time in the p-region was done with a split-operator propagation (SOP) scheme[21,49] and a fast Fourier transformation (FFT) between space domain and momentum domain for the space variables, repeatedly used at time intervals $t_n = t_0 + n\Delta t$, $n = 1$ to N_t, and modified to include a dissipative potential.[33,34] The SOP factorization can be used repeatedly, first for the dissipative potential and then for the SCF Hamiltonian including the field, to obtain the time evolution of the wave function from t to $t + \Delta t$ as

$$\begin{gathered}\boldsymbol{\psi}(t+\Delta t) = \mathbf{U}(t+\Delta t,t)\ \boldsymbol{\psi}(t)\\ \mathbf{U}(t+\Delta t,t) = \mathbf{U}_{\mathrm{W}}(\Delta t/2)\ \mathbf{U}'(t+\Delta t,t)\ \mathbf{U}_{\mathrm{W}}(\Delta t/2)\\ \mathbf{U}_{\mathrm{W}}(\Delta t/2) = \exp[-\mathbf{W}\Delta t/(4\hbar)]\\ \mathbf{U}'(t+\Delta t,t) = \exp\{-\mathrm{i}[\hat{\mathbf{K}} + \mathbf{V} + \mathbf{G}^{\mathrm{l}}(t)]\Delta t/\hbar\}\end{gathered} \tag{24}$$

with $\hat{\mathbf{V}}'(t) = \hat{\mathbf{V}} + \hat{\mathbf{G}}(t)$ so that

$$\mathbf{U}'(t+\Delta t,t) = \exp[-\mathrm{i}\mathbf{V}'(t)\Delta t/(2\hbar)]\ \exp[-\mathrm{i}\hat{\mathbf{K}}\Delta t/\hbar]\ \exp[-\mathrm{i}\mathbf{V}'(t)\Delta t/(2\hbar)] \tag{25}$$

which is accurate to order Δt^3. Exponentials of 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 with a grid of points in the Z variable, with vibrational basis sets of increasing size, and with sufficient time steps to converge to desired accuracies.

In the s-region, the nonlinear optical response of the metal substrate results from electronic excitations between band states that can be described as vertical transitions of fixed wavevector $\vec{k}$, between conduction and occupied bands, b = c, u. It is sufficient for our model to assume that electronic transitions occur between one-electron band states and to describe them in terms of the one-electron density matrix in the s-region. The one-electron density operator $\hat{\gamma}_{\mathrm{s}}^{\mathrm{el}}(t)$ in the s-region becomes therefore a 2 × 2 matrix, and the average value of the total electric dipole in the s-region, $D_{\mathrm{s}}(t)$, can be obtained from the one-electron dipole $\hat{d}_{\mathrm{s}}^{\mathrm{el}}$ and a knowledge of the number of electrons $\bar{N}_{\mathrm{el}}(t)$ in the s-region, by means of

$$\bar{D}_{\mathrm{s}}(t) = \bar{N}_{\mathrm{el}}(t)\frac{\mathrm{tr}_{\mathrm{s}}[\hat{\gamma}_{\mathrm{s}}^{\mathrm{el}}(t)\hat{d}_{\mathrm{s}}^{\mathrm{el}}]}{\mathrm{tr}_{\mathrm{s}}[\hat{\gamma}_{\mathrm{s}}^{\mathrm{el}}(t)]} = \bar{N}_{\mathrm{el}}(t)\frac{\Sigma_{\mathrm{b,b'}}\,\gamma_{\mathrm{b,b'}}^{\mathrm{el}}(t)\ d_{\mathrm{b',b}}^{\mathrm{el}}}{\Sigma_{\mathrm{b,b'}}\,\gamma_{\mathrm{b,b'}}^{\mathrm{el}}} \tag{26}$$

The p- and s-regions are coupled through the dissipative potential $\mathbf{W}(Z,t)$ and an effective electric field $\mathcal{E}_{\mathrm{p}}(t)$ generated by the s-dipole $\bar{D}_{\mathrm{s}}(t)$, which couples to $\mathbf{D}_{\mathrm{p}}$.

The time evolution of the electronic density matrix can be obtained from the optical Bloch equations,[5] for a femtosecond light pulse chosen of the form

$$\mathcal{E}(t) = \mathcal{E}_0 \exp[-4(t - t_0)^2/\tau_{\mathrm{p}}^{\ 2}] \cos(\omega_0 t) \tag{27}$$

and introducing the rotating wave approximation, which keeps only terms that satisfy the resonance condition $\epsilon_{\mathrm{u}\vec{k}} - \epsilon_{\mathrm{c}\vec{k}} = \hbar\omega$. Dissipative effects due to energy transport away from the surface into the metal, and due to energy transfer to the adsorbate bond that breaks up, can be described with the dissipative superoperator $\hat{\mathcal{L}}_{\mathrm{s}}^{(\mathrm{D})}$ in those equations. As in our previous treatment,[36] dissipation in the s-region is described in a semiempirical way using the Lindblad form $\hat{\mathcal{L}}_{\mathrm{s}}^{(\mathrm{D})}\hat{\gamma}_{\mathrm{s}} = \Sigma_{\mathrm{J}}(\hat{C}_{\mathrm{J}}\hat{\gamma}_{\mathrm{s}}\hat{C}_{\mathrm{J}}^{\dagger} - 1/2[\hat{C}_{\mathrm{J}}^{\dagger}\hat{C}_{\mathrm{J}}, \hat{\gamma}_{\mathrm{s}}]_{+})$, where now the operators $\hat{C}_{\mathrm{J}} = \sqrt{\kappa_{\mathrm{bb'}}}|\mathrm{b}\rangle\langle\mathrm{b'}|$ are obtained from relaxation rates $\kappa_{\mathrm{bb'}}$ due to electron−electron collisions and interband transitions.[36] The density matrix can be conveniently propagated in time using its Pauli components from $\boldsymbol{\gamma} = \gamma_0\mathbf{I} + \Sigma_j\boldsymbol{\sigma}_j\gamma_j$, where $\boldsymbol{\sigma}_j$, $j = 1, 2, 3$, are the Pauli matrices, and $\gamma_0 = {}^1/_2$ by normalization. It is obtained by solving the modified optical Bloch equations containing dissipative rates and a femtosecond light pulse,

$$\begin{gathered}\dot{\gamma}_1 = \Omega_2 f(t)\gamma_3 - \frac{\gamma_1}{\tau_{\mathrm{coh}}}\\ \dot{\gamma}_2 = -\Omega_1 f(t)\gamma_3 - \frac{\gamma_2}{\tau_{\mathrm{coh}}}\\ \dot{\gamma}_3 = (\Omega_1\gamma_2 - \Omega_2\gamma_1)f(t) - \frac{1}{\tau_{\mathrm{pop}}}(\gamma_3 - \tilde{\gamma}_3)\end{gathered} \tag{28}$$

Here $\Omega_1 = -2\mathrm{Re}(d_{\mathrm{cu}}^{\mathrm{el}})\mathcal{E}_0/\hbar$ and $\Omega_2 = -2\mathrm{Im}(d_{\mathrm{cu}}^{\mathrm{el}})\mathcal{E}_0/\hbar$ are Rabi frequencies containing the one-electron transition dipole d_{cu}, τ_{pop} is the decay time of the population difference, and τ_{coh} is the coherence relaxation time, both derived from the electronic relaxation rates.[36]

Calculation of the nonlinear response also requires solutions of the rate equations for the time-dependent excited electron density and temperature in the metal substrate,[36,50,51]

$$\begin{gathered}\frac{\mathrm{d}\bar{N}_{\mathrm{el}}^{*}}{\mathrm{d}t} = J(t)\bar{N}_{\mathrm{el}}^{0} - K_{\mathrm{d}}\bar{N}_{\mathrm{el}}^{*}(t)\\ \frac{\mathrm{d}T_{\mathrm{el}}}{\mathrm{d}t} = \frac{g_{\mathrm{ep}}(T_{\mathrm{in}} - T_{\mathrm{el}}) + \bar{S}(t)}{\gamma_{\mathrm{el}}\ T_{\mathrm{el}}}\end{gathered} \tag{29}$$

where $J(t) = \bar{S}(t)B_{\mathrm{s}}$, $\bar{S}(t)$ is the pumping rate, g_{ep} is the electron−phonon coupling constant, γ_{el} is the electron specific heat constant, and K_{d} is a rate of decay due to electron−electron and electron−phonon collisions.

The two sets of equations above provide the SCF potential energy operator and effective electric field at the p-region, and in particular, their components lead to energy transfer, from

$$\begin{gathered}\hat{G}_{\mathrm{p}}^{*}(t) = -\hat{D}_{\mathrm{p}}(z_{\mathrm{p}})\ \mathcal{E}_{\mathrm{p}}(t)\sin(\omega_0 t)\\ \mathcal{E}_{\mathrm{p}}(t) = -\bar{N}_{\mathrm{el}}^{*}(t)|d_{\mathrm{cu}}^{(\mathrm{el})}|2\gamma_2(t)|Z - z_{\mathrm{p}}|^{-3}\end{gathered} \tag{30}$$

as follows from energy transfer from s- to p-regions through a dipole−dipole interaction.[36]

The physical parameters needed in the potential functions and dipole of the p-region, and the optical Bloch and transport equations for the s-region, have been obtained from our previous electronic structure calculations and from experiment, as tabulated in refs 34 and 36 for the Z and x dependencies, and as recently calculated[52,53] for the θ and ϕ dependencies. The pulse parameters were a light wavelength $\lambda_0 = 620$ nm, pulse width $\tau_{\mathrm{p}} = 100$ fs, and field strength in the range 0−6 mJ/cm^2. The s-region equations (28) and (29) were integrated with a Runge−Kutta algorithm and time step δt determined by a relative error tolerance $\eta = 10^{-5}$ and provide the effective field $\mathcal{E}_{\mathrm{p}}(t)$. With a basis set of dimension $N_{\mathrm{B}}^{(\mathrm{s})} = 2$ for the reduced density matrix, the number of coupled s-equations is $N^{(\mathrm{s})} = 5$.

The p-region equations (23) are solved with an expansion in a basis set of $N_{\mathrm{el}}^{(\mathrm{p})} = 2$ electronic states, $N_{\mathrm{B}}^{(\mathrm{p})}$ vibrational functions and discretization on a grid of $N_{\mathrm{G}}^{(\mathrm{p})} = 512$ points for Z, giving matrices of dimension $N^{(\mathrm{p})} = 2N_{\mathrm{B}}^{(\mathrm{p})}\cdot N_{\mathrm{G}}^{(\mathrm{p})}$. The time propagation is done with a split-operator and a time step $\Delta t = 5.0$ au taken $N_{\mathrm{t}} = 3000$ times, with the effective electric field obtained at each time step by interpolation. The nonlinear dependence of yields versus the fluence F was considered within

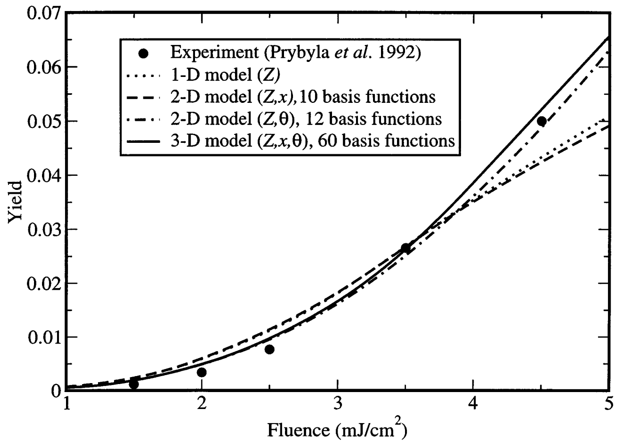

Figure 3. Yield of desorbed CO versus light pulse fluence for models with several degrees of freedom as shown in the inset.

four models. The simplest one involves only the *Z* position above the surface and is called here the 1-D model. Two 2-D models were studied, one including the space variables (*Z*, *x*), with $N_{\mathrm{vib}} = 5$ harmonic oscillator functions, to account for coupling to the frustrated translation parallel to the surface, and the other including only (Z,θ), with $N_{\mathrm{rot}} = 6$ Legendre polynomials combined to account for frustrated rotation states $u_\rho(\theta)$. A more elaborate 3-D model involves the three space variables, (Z, x, θ), in addition to time, all treated quantum mechanically with a basis set of dimension $N_{\mathrm{B}}^{(\mathrm{p})} = 2 \times 5 \times 6 = 60$ at each of the 512 grid points. Harmonic oscillator basis functions were used for the frustrated translation, and spherical harmonics for the frustrated rotations. The initial vibrational state for a bound *CO* was chosen to be the ground state $v_{\mathrm{Z}} = v_x = \rho = s = 0$, suitable for surface temperatures around 100 K. In the calculations, it was found that the dependence of potentials and couplings on the ϕ variable was quite small, because the *Cu*(001) surface has small corrugation. The sizes of vibrational basis sets required for convergence were found increasing them for the *x*-variable to a maximum of 20 basis functions, and for θ to a maximum of 10 functions. The finally chosen sizes were found to give the desired accuracy for the present properties, which are sums over vibrational states.

We verified that results for variables (*Z*, *x*) agreed numerically with previous calculations using grids in *Z* and *x*.[36] Comparisons of the four models with experimental data[37] are shown in Figure 3. A single value of the yield was fit to experiment at a fluence of 3.5 mJ/cm^2 by choosing the value of B_{s} in the rate equations. This comparison establishes that the treatment is realistic and that the 1-D model is useful for studies at low fluence. The models also display a delay between pulse arrival and photodesorption, as observed in the experiments, calculated here to be about 250 fs, and provide insight on the time evolution of desorption, not shown here. Also calculated but not shown here are $T_{\mathrm{el}}(t)$ and $\bar{N}_{\mathrm{el}}(t)$, which were previously published[36] and agree with model results[37,50,51] used to interpret experiments.

The 2-D models give similar results for the smaller fluence values and are very close to the 1-D model. However, as the fluence increases, the model including the frustrated rotation gives better agreement with experiment. The 3-D model is of course more realistic, and Figure 3 shows a widening difference with the 1-D model at high fluence values with the 3-D model giving larger yields, which can be expected because the 3-D model allows for desorption through more states insofar as it includes both the frustrated translation and rotation modes of adsorbate vibrations. Calculations at even higher fluence show that the 3-D model also gives a flatter graph, due to increased de-excitation rates.

4. Conclusions

The present paper describes a general density matrix approach for the treatment of dissipative dynamics of a primary region with many coupled quantum states, strongly interacting with an active medium or secondary region. This approach leads to sets of coupled differential equations (14A)−(14C) in the text, obtained from an atomic model of the p-region, and a statistical model of the s-region.

The treatment was applied to the photodesorption of CO from Cu(001), a case where four space variables have been treated quantum mechanically, and up to 60 coupled states on a grid were included in density matrix calculations of models with an increasing number of degrees of freedom in the p-region.

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