

Density Matrix Treatment of Optical Response with Combined Instantaneous and Delayed Dissipation: Adsorbates on Solid Surfaces

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1 Introduction

The interaction of light with a localized (primary) region in a many-atom system undergoing electronic and vibrational transitions leads to energy dissipation and fluctuations through both nearly instantaneous and delayed processes in the medium (the secondary region). A fast dissipation typically occurs due to electronic energy relaxation, while a delayed dissipation arises from vibrational energy relaxation. A theoretical and computational treatment of these phenomena has been done in terms of a reduced density operator (RDO) satisfying a generalized Liouville-von Neumann equation.[1] Instantaneous dissipation is described by a Lindblad term containing electronic transition rates,[2] while the delayed dissipation is given by a memory term constructed from the time-correlation function (TCF) of atomic displacements in the medium.[4] We consider cases where the TCF decays exponentially (fast) or as an inverse power (slowly). An initial thermal equilibrium can not be assumed when there are long lasting interactions between the primary region and the medium. We describe a general procedure that provides the optical response in this case by calculating the difference between solutions for the RDM with and without excitation by a light pulse.

We present examples for relaxation of optical excitation including dissipation in CO/Cu(001) and Ag₃/Si(111).[5] Numerical results for state populations and quantum coherences have been obtained with an extended Runge-Kutta algorithm for integro-differential equations.[7]

2 Density Operator Theory

2.1 Dissipative Dynamics from the Reduced Density Operator

Starting with a hamiltonian $\hat{H} = \hat{H}_F + \hat{H}_I$, where \hat{H}_F stands for an effective Hamiltonian for non-interacting primary (p-) and secondary (s-) regions of a many-atom system, and \hat{H}_I is a residual (ps) interaction energy operator, the equation of motion for the density operator $\hat{\Gamma}^{(I)}$ of the whole system in the interaction picture is given by the Liouville-von Neumann (L-vN) equation $i\hbar \partial \hat{\Gamma}^{(I)} / \partial t = [\hat{H}_F^{(I)}, \hat{\Gamma}^{(I)}]$. For strongly coupled p- and s-regions we seek special solutions factorized after averaging over initial conditions (shown by overlines), so that $\hat{\Gamma}^{(I)}(t) = \hat{\rho}^{(I)}(t) \otimes \hat{\gamma}^{(I)}(t)$, where $\hat{\rho}^{(I)}(t) = \text{tr}_s[\hat{\Gamma}^{(I)}(t)]$ and $\hat{\gamma}^{(I)}(t) = \text{tr}_p[\hat{\Gamma}^{(I)}(t)]$. The integrodifferential equation for the RDM of the p-region is then

$$i\hbar \partial \hat{\rho}^{(I)} / \partial t = -(i/\hbar) \int_0^t dt' \text{tr}_s([\hat{H}_F^{(I)}(t), [\hat{H}_F^{(I)}(t'), \hat{\rho}^{(I)}(t') \hat{\gamma}^{(I)}(t')])$$

with a memory kernel that can be expressed in terms of time correlation functions (TCFs) of the s-region.

2.2 Competing Instantaneous and Delayed Dissipation

For a molecular system in a medium, electronic state transitions lead to almost instantaneous dissipation, while vibrational state transitions give delayed dissipation. Returning to the Schroedinger picture, this gives

$$\partial \hat{\rho} / \partial t = -(i/\hbar) [\hat{H}_p, \hat{\rho}(t)] + (\partial \hat{\rho} / \partial t)_D^{(el)} + (\partial \hat{\rho} / \partial t)_D^{(at)}$$

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The electronic dissipation involves almost instantaneous decorrelation and can be described by a Markovian rate in the Lindblad form,

$$\left(\frac{\partial \hat{\rho}}{\partial t}\right)_D^{(el)} = -\frac{1}{2} \sum_k [\hat{L}_p^{(k)\dagger} \hat{L}_p^{(k)} \hat{\rho}(t)]_+ - 2 \hat{L}_p^{(k)} \hat{\rho}(t) \hat{L}_p^{(k)\dagger}$$

and the $\hat{L}_p^{(k)}$ operators in the p-region can be constructed from relaxation and decoherence rates of each transition $k = (\beta \leftarrow \alpha)$ between states of the p-region induced by couplings to the electronic motions in the s-region.

For delayed dissipation due to atomic vibrations, the dissipative kernel can be constructed to second order in the ps-coupling from TCFs of atomic displacements. Here we only consider an adsorbate vibrational mode A coupled to a reservoir of harmonic oscillators R , with coupling energy

$$H_{AR} = \hbar \sum_j \kappa_j (a^\dagger b_j^\dagger + a^\dagger b_j + ab_j^\dagger + ab_j)$$

where a and a^\dagger are the creation and annihilation operators for the vibrations of the adsorbate, and b_j and b_j^\dagger are the operators for the bath. In terms of the displacement $\hat{q} = (a^\dagger + a)/2$ and a basis set of vibronic states (r, s, \dots) the delayed dissipation rates are [6]

$$\left(\frac{d\rho_{rs}}{dt}\right)_D^{(at)} = -\sum_{cd} \int_0^t d\tau [M_{cd,ds}(-\tau) e^{i\omega_{dr}\tau} \rho_{rc}(t-\tau) + M_{rc,cd}(\tau) e^{i\omega_{sc}\tau} \rho_{ds}(t-\tau) - M_{ds,rc}(-\tau) e^{i\omega_{sc}\tau} \rho_{cd}(t-\tau) - M_{ds,rc}(\tau) e^{i\omega_{dr}\tau} \rho_{cd}(t-\tau)] \quad (4)$$

where $\omega_{rs} = (E_r - E_s)/\hbar$, $H_A \phi_r = E_r \phi_r$, $q_{rs} = \langle \phi_r | \hat{q} | \phi_s \rangle$, and $M_{rs,cd}(\tau) = C(\tau) q_{rs} q_{cd} / \hbar^2$, with a TCF at temperature T

$$C(t) = \hbar^2 \int_0^\infty \left[\cos(\omega t) \coth\left(\frac{\hbar\omega}{2k_B T}\right) - i \sin(\omega t) \right] \omega^2 J(\omega) d\omega$$

where $J(\omega)$ is the spectral density of s-vibrational modes.

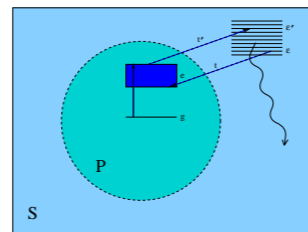


Figure 1: Pictorial representation of delayed dissipation from the primary region to the secondary region over times t and t' . Both ground and excited electronic p-states undergo dissipation.

The excitation energy operator is given by the coupling of the dipole operator of the p-region \hat{D}_p to the effective electric field $\mathcal{E}(t)$ in this region.[8, 9]

2.3 Initial Conditions

Before an electric field is turned on at an initial time t_{in} , the total system is at thermal equilibrium with DOP $\hat{\Gamma}_{eq}(T) = \hat{\rho}_{in} \hat{\gamma}_{eq}(T)$. It can be shown that $\hat{\rho}_{in} = \hat{\rho}_{eq}(T)$ is the correct form of the p-RDO in the presence of instantaneous and delayed dissipative rates, provided the Lindblad rate operator is constructed from transition rates that satisfy detailed balance and provided a long time has elapsed so that the delayed dissipation has disappeared [6]. As we show in what follows, one can not assume that an initial thermal p-RDO will remain time-independent when the medium TCFs are large and decay slowly. It is then necessary to numerically generate the p-RDO for a long time before the external field is applied, and to calculate the response of the p-region when the field is introduced by subtracting the background unperturbed solution $\hat{\rho}^{(0)}(t)$ from a perturbed $\hat{\rho}'(t)$, so that

$$\hat{\rho}(t) = \hat{\rho}_{eq}(T) + \Delta \hat{\rho}(t), \quad \Delta \hat{\rho}(t) = \hat{\rho}'(t) - \hat{\rho}^{(0)}(t)$$

3 Energy Dissipation in Adsorbates

3.1 The CO/Cu(001) and Ag₃/Si(111):H Models

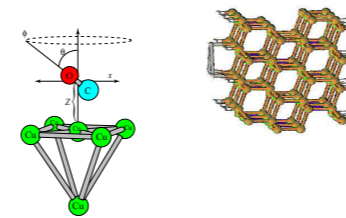


Figure 2: The CO/Cu₆ model of CO/Cu(001).[2] Here x is the frustrated translation displacement of present interest (left). The Ag₃Si(111):H slab model for the metal cluster adsorbate (right).[3]

3.2 Fast and Slow Delayed Dissipation

In the case of CO/Cu(001), we use a Debye model for the vibrations of the medium, with the couplings to the primary region taken from a parameterization of $\kappa(\omega)$ in the neighborhood of ω_0 from [10]. This gives [4] $\omega^2 J(\omega) = 36\pi\omega^2 [p + q(\omega - \omega_0)/\omega_0^2]$ where p and q are parameters, $p = 6.44 \times 10^{-8} \text{ au}^{-2}$, $q = 1.58 \times 10^{-5} \text{ au}^{-1}$, $\omega_0 = 1.448 \times 10^{-4} \text{ au}^{-1}$, and ω_D is the Debye cutoff frequency, $1.013 \times 10^{-3} \text{ au}^{-1}$. For Ag/Si(111):H, we have obtained a spectral density from density functional theory calculations including lattice vibrations [3]. The TCFs that follow from these spectral densities are shown in Figure 3.

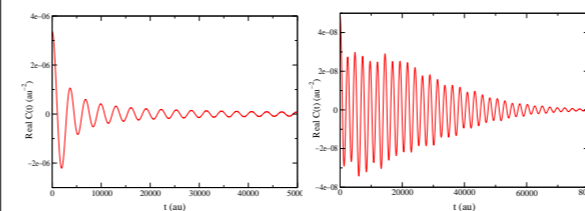


Figure 3: The real part of the slow TCF, $C(t)$, for CO/Cu(001) (left) and fast TCF for Ag₃/Si(111):H (right)

3.3 Numerical Procedure

To begin, we write the integro-differential equation in a more compact form,

$$\frac{d\rho}{dt} = f[t, \rho(t), z(t)], \quad z(t) = \int_0^t K(t, t') \rho(t') dt'$$

A Runge-Kutta integration scheme then uses the following relations

$$Y_{n,j} = \rho_n + h \sum_{i=1}^m a_{j,i} f[t_n + c_i h, Y_{n,i} \tilde{F}_n(t_n + c_i h) + h Z_{n,i}] \quad (8)$$

$$Z_{n,i} = \sum_{l=1}^m \bar{a}_{i,l} K(t_n + d_i, t_n + c_l h, Y_{n,l})$$

$$\tilde{F}_n(t) = h \sum_{l=0}^{n-1} \sum_{j=1}^m b_j K(t, t_l + c_j h, Y_{l,j})$$

$$\rho_{n+1} = \rho_n + h \sum_{j=1}^m b_j f[t_n + c_j h, Y_{n,j}, \tilde{F}_n(t_n + c_j h) + h Z_{n,j}]$$

Where m is the number of stages of the method, and the coefficients depend on the choice of the Runge-Kutta (RK) method. The values chosen here are for the standard fourth order RK method (RK4), $\mathbf{b} = (\frac{1}{6}, \frac{1}{3}, \frac{1}{3}, \frac{1}{6})$, $\mathbf{c} = (0, \frac{1}{2}, 1)$, and \mathbf{a} is in lower diagonal form, with the only nonzero elements being $a_{21} = a_{32} = \frac{1}{2}$, $a_{43} = 1$. The procedure gives a simple recursion because the \mathbf{a} matrices are in lower diagonal form, convenient for numerical work.[7]

4 Results for CO/Cu(001)

In Figure 4 we see the ground electronic and vibrational population (g_0), along with the real part of the coherence between g_0 and g_2 , called g_{02} . Because the TCF decays so slowly, the ps-coupling never disappears, and the system settles into a constant pattern of oscillations. If we were to add a pulse to the beginning of the simulation, the effects could be lost in the initial time evolution. Instead, we add a pulse after 100,000 au(T), when the system has settled into a pattern. We subtract the RDM result from the RDM there is no pulse to get the net effect of the pulse. Results are shown in Figure 5. The pulse is gaussian, with a fluence of 3.0 mJ/cm^2 and a width of 100 fs (or $4.214 \times 10^3 \text{ au(T)}$). The pulse excites from the ground electronic state to the electronically excited state, and

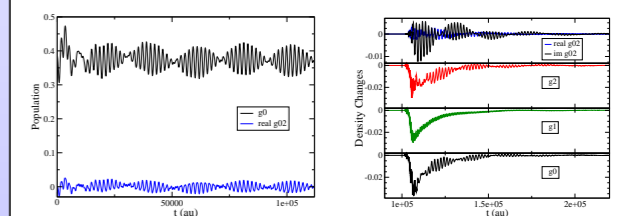


Figure 4: Populations for CO/Cu(001) with no pulse added, at 300K (left). Change in the populations from the no-pulse to the pulse-added case at 300K (right)

5 Results for Ag/Si(111):H

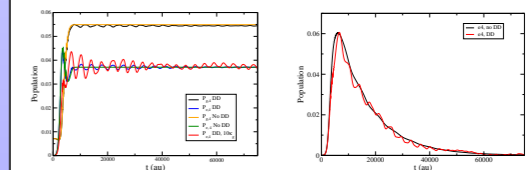


Figure 5: Change in the populations of the $v = 4$ vibrational state in the ground and excited electronic states, with and without delayed dissipation (DD), and no electronic relaxation (left). Results with electronic relaxation (right)

6 Conclusions

- A density operator treatment allows for fluctuation and dissipation phenomena in a medium displaying both instantaneous and delayed dissipation.
- The rate and strength of the delayed dissipation depends on the TCF of the medium and can be fast or slow.
- A slow delayed dissipation is found for CO/Cu(001), where the TCF envelope decays as t^{-1} . In this case we must subtract the unperturbed system RDM from the RDM including a pulse, to obtain the pulse effect.
- A fast delayed dissipation is seen for Ag/Si(111):H, where the TCF decays exponentially; the effects of a light pulse can be directly calculated.

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