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Density Matrix Treatment of the Nonmarkovian Dissipative Dynamics of Adsorbates on Metal Surfaces†

Andrew S. Leathers and David A. Micha*

Quantum Theory Project, University of Florida, Gainesville, Florida 32611

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A density matrix treatment is presented for the vibrational relaxation of the frustrated translational mode of a molecule adsorbed on a metal surface. The system is modeled as a vibrating adsorbate oscillator coupled to a bath of harmonic oscillators representing either phonons or electronic density fluctuations. The integrodifferential equations for time evolution of the density matrix including a (nonmarkovian) delayed dissipation are solved using a generalized Runge−Kutta scheme. The equations are also solved in the instantaneous dissipation and the Markov limits, to ascertain their validity. Numerical results are presented for Na/Cu, CO/Cu, and CO/Pt systems. The population of an initially excited state is given over time for varying temperatures and shows that memory effects are needed in a proper description valid even at short times. Calculations of populations for different coupling strengths between the adsorbate species and the substrate metal surface indicate that a weaker coupling leads to increased oscillation amplitudes and longer relaxation times. The time evolution of quantum coherence is also described.

1. Introduction

We consider the vibrational relaxation of an atom or molecule adsorbed on a metal surface and initially excited by collisions or light absorption, the subject of recent theoretical and experimental work.[1−5] This can be described by a model of an adsorbed oscillator coupled to a bath of oscillators representing the excitations of the substrate, a reservoir at a given temperature.[6] The surface excitations can be phonons or quantized electron density fluctuations (electron−hole or plasmon excitations) described by means of creation and annihilation operators.

Our theoretical treatment is based on the reduced density operator (RDOp)[7,8] for the adsorbate species and a model Hamiltonian with a bilinear coupling between adsorbate and surface.[9,10] The equation of motion for the RDOp contains a dissipative memory term, which can be written in terms of the time−correlation function of the reservoir, the metal surface in our case. This approach allows for a description of temperature effects on the relaxation of populations and quantum coherence of the system. Special cases are given by the instantaneous dissipation limit, with a time-dependent friction coefficient, and the markovian limit equivalent, in our case to the well-known Redfield equations.[11,12] Figure 1 shows a pictorial representation of delayed dissipation from the primary region (the adsorbate) to the secondary region (the substrate) over times t and t'.

Operator equations can be transformed introducing a basis set of vibrational states of the adsorbate, leading to sets of coupled integrodifferential equations for the reduced density matrix (RDM). These equations of motion for the RDM are then solved using a generalized Runge−Kutta type algorithm for integrodifferential equations[13] that we have recently implemented for dissipative molecular dynamics.[14] This is a general method applicable to models involving any Hamiltonian and memory terms and provides an alternative to methods based on path integrals,[15−17] the introduction of auxiliary density matrices,[18] or an expansion of the memory kernel in a basis set.[19] Our treatment of dissipative dynamics is further applicable to short times. It therefore bypasses the need to introduce modified initial conditions (slippage)[20,21] in the implementation of markovian treatments, and it can be applied to initial excitations of varying duration.

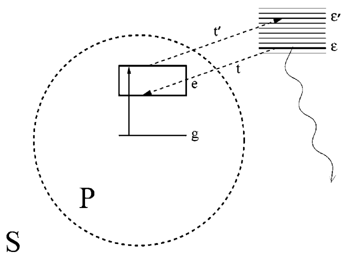

Figure 1. Pictorial representation of delayed dissipation from the primary region to the secondary region over times t and t'.

We consider as an application of our method a model of vibrational relaxation of an initially excited species adsorbed on a metal surface, coupled to phonons in the metal reservoir, and in particular, we concentrate on the systems CO/Cu(001), Na/Cu(001), and CO/Pt(111) and on the relaxation of the frustrated translation (or T-mode) of the adsorbate.[2] This model is based on extensive electronic structure calculations that gave good agreement with experimental relaxation times for the CO/Cu(001) system.[22] It is known that metal electronic excitations are also active in vibrational relaxation, but their role is less pronounced for the low-energy T-mode.[1] Our application deals only with the contribution of phonons to relaxation. The coupling constants between adsorbate vibrations and phonons appearing in our model Hamiltonian contain a contribution from intermediate short-lived electron−hole excitations of the metals, but these are not explicitly considered in the present treatment. In recently published work for these systems,[23] we have obtained good agreement with experimental measurements of the temperature dependence of collisional line shapes, using such a parametrized form for the coupling of adsorbate and surface

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motions. We use the same values in the present work. The model allows us to estimate under what conditions it would be possible to replace delayed dissipation with instantaneous dissipation or the Markov limit for the systems and conditions of interest here.

In what follows, we first present a brief description of the density operator approach and a model Hamiltonian, which can be used for either phonon or electron−hole excitations of the metal surface. The numerical procedure is presented for integration of the coupled matrix integrodifferential equations in the general case, with delayed dissipation. The special cases of instantaneous dissipation and the Markov limit are also given. Results on state populations and quantum coherence vs time have been obtained for the systems Na/Cu(001), CO/Cu(001), and CO/Pt(111) at several temperatures. Results are also presented in the limit of instantaneous dissipation and in the Markov limit. Calculations have furthermore been done for varying coupling strengths. Finally, the time evolution of quantum coherence has been considered and is reported for the CO/Cu system.

2. Vibrational Relaxation of Adsorbates

2.1. Density Matrix Treatment. When studying dissipative dynamics using the density matrix framework, we start with the Liouville von-Neumann equation[8,10] for the density operator $\hat{\Gamma}(t)$ for the whole system, composed of a species A interacting with the surface or reservoir R, and proceed to define a RDOp $\hat{\rho}(t) = tr_R[\hat{\Gamma}(t)]$, which satisfies the following equation in compact form,

$$\frac{d\hat{\rho}(t)}{dt} = \mathcal{L}\hat{\rho}(t) \tag{1}$$

where $\mathcal{L} = \mathcal{L}_H + \mathcal{L}_D$ is the Liouvillian superoperator. Here, $\mathcal{L}_H$ is defined by

$$\mathcal{L}_H\hat{\rho} = -\frac{i}{\hbar}[H,\hat{\rho}] \tag{2}$$

The operator $\mathcal{L}_D$ contains dissipative terms and may take one of several forms. It can generally be expressed in terms of a memory kernel superoperator, $\mathcal{K}(t,t')$, and the equation now reads

$$\frac{d\hat{\rho}(t)}{dt} = \mathcal{L}_H\hat{\rho}(t) + \int_0^t \mathcal{K}(t,t')\,\hat{\rho}(t')\,dt' \tag{3}$$

This equation must be solved for the initial condition $\hat{\rho}(0) = \hat{\rho}_0$ corresponding to the preparation of the system before relaxation.

We are thus interested in numerical methods for equations of the general form

$$\frac{d\rho(t)}{dt} = g[t,\rho(t)] + \int_0^t K[t,t',\rho(t')]\,dt' \tag{4}$$

which is a Volterra integrodifferential equation.

2.2. Model System. We treat the frustrated T-mode of the adsorbate (the primary region or A subsystem) as a harmonic oscillator bilinearly coupled to the surface (the secondary region or R subsystem), treated as a reservoir of harmonic oscillators. The Hamiltonian for the total system is then

$$\hat{H} = \hat{H}_A + \hat{H}_R + \hat{H}_{AR} \tag{5}$$

$$\hat{H}_A = \hbar\,\omega_0\,\hat{a}^\dagger\,\hat{a} \tag{6}$$

$$\hat{H}_R = \sum_j \hbar\,\omega_j\,\hat{b}_j^\dagger\,\hat{b}_j \tag{7}$$

$$\hat{H}_{AR} = \hbar\sum_j \kappa_j\,(\hat{a}^\dagger\,\hat{b}_j^\dagger + \hat{a}^\dagger\,\hat{b}_j + \hat{a}\,\hat{b}_j^\dagger + \hat{a}\,\hat{b}_j) \tag{8}$$

where $\hat{a}$ and $\hat{a}^\dagger$ are the creation and annihilation operators for the frustrated T-vibrational mode of the adsorbate A with frequency ω_0, $\hat{b}_j$ and $\hat{b}_j^\dagger$ are the creation and annihilation operators for the reservoir R excitations of frequencies ω_j, and the κ_j values are coefficients that determine the coupling strength. The $\hat{a}$ and $\hat{a}^\dagger$ operators are related to the vibrational displacement $\hat{q}$ and momentum $\hat{p}$ of the adsorbate vibration. The operators $\hat{b}_j$ and $\hat{b}_j^\dagger$ are left undefined for now and may correspond to normal mode displacements $\hat{Q}_j$ and momenta $\hat{P}_j$ for boson excitations, which can be phonons with spectral density per unit frequency $g_{ph}(\omega) = \sum_j \delta(\omega - \omega_j)$ or quanta of electronic density fluctuations with spectral density $g_{el}(\omega)$.[24] If we now define the operators

$$\hat{q} = \frac{1}{\sqrt{2}}\,(\hat{a}^\dagger + \hat{a}) \tag{9}$$

$$\hat{B} = \hbar\,\sqrt{2}\sum_j \kappa_j\,(\hat{b}_j^\dagger + \hat{b}_j) = 2\hbar\sum_j \kappa_j\,\hat{Q}_j \tag{10}$$

we have

$$\hat{H}_{AR} = \hat{q}\,\hat{B} \tag{11}$$

where $\hat{q}$ is dimensionless, while $\hat{B}$ has the dimensions of energy. We now have a coupling, $\hat{H}_{AR}$, which is factored into two operators, one that acts only on the adsorbate and one that acts over only the surface.

The energy eigenvalue problem for this Hamiltonian can be formally solved using a transformation to normal modes of the whole system, and the total density operator $\hat{\Gamma}$ can be formally obtained in terms of normal mode amplitudes. Here, however, we are interested in the solution of the equation of motion for the RDOp and on the treatment of delayed dissipation due to coupling of the p and s regions. A formally exact expression can be obtained for the dissipative kernel of bilinearly coupled oscillators. However, in what follows, we construct a simpler expression, based on the well-known approximation to the memory kernel to second order in the coupling.[8,10] This relates the dissipation to correlation functions of the reservoir (the surface in our case) and provides insight on conditions under which the dissipation might become instantaneous, or simply represented by a time-independent friction coefficient. In addition, we assume that the total density operator can be written at all times as $\hat{\Gamma}(t) = \hat{\rho}(t)\,\hat{\Gamma}_{eq}(\beta)$, where the second factor is given by the density operator of the reservoir at thermal equilibrium at temperature $T = 1/(k_B\beta)$.

The equation of motion for $\hat{\rho}$ is written in terms of the basis set $\{\phi_r\}$ of eigenstates of $\hat{H}_A$, with eigenenergies $E_r = \hbar\,\omega_0(r + 1/2)$. The operator equation is transformed into a matrix-valued generalized master equation for elements of the RDM[10]

$$\frac{\mathrm{d}}{\mathrm{d}t}\rho_{rs} = -i\,\omega_{rs}\,\rho_{rs} + \frac{i}{\hbar}\sum_{c}\langle\langle\,\hat{B}\,\rangle\rangle\,(q_{cs}\,\rho_{rc} - q_{rc}\,\rho_{cs}) - \sum_{cd}\int_0^t \mathrm{d}t'\,\{M_{cd,ds}\,[-(t-t')]\,e^{i\omega_{dr}(t-t')}\,\rho_{rc}(t') + M_{rc,cd}\,(t-t')\,e^{i\omega_{sc}(t-t')}\,\rho_{ds}(t') - M_{ds,rc}\,[-(t-t')]\,e^{i\omega_{sc}(t-t')}\,\rho_{cd}(t') - M_{ds,rc}\,(t-t')\,e^{i\omega_{dr}(t-t')}\,\rho_{cd}(t')\} \quad (12)$$

where $\omega_{rs} = (E_r - E_s)/\hbar$, $\hat{H}_A\phi_r = E_r\phi_r$, $\langle\langle\,\hat{B}\,\rangle\rangle = tr_R[\hat{B}\,\hat{\Gamma}_{eq}(\beta)]$, $q_{rs} = \langle\phi_r|\,\hat{q}\,|\phi_s\rangle$, and

$$M_{rs,cd}(t) = \frac{1}{\hbar^2}\,C(t)\,q_{rs}\,q_{cd} \quad (13)$$

where $C(t) = \langle\langle\,\hat{B}(t)\,\hat{B}(0)\,\rangle\rangle$ is the correlation function of the vibrational displacements of the reservoir.

Note that

$$q_{rs} = q_{sr} = \frac{1}{\sqrt{2}}\,(\delta_{r,s+1}\sqrt{s+1} + \delta_{r,s-1}\sqrt{s}),\ q_{rr} = 0 \quad (14)$$

and that for our choice of $\hat{B}$, $\langle\langle\,\hat{B}\,\rangle\rangle = 0$.

If we consider only the ground and first excited state for the adsorbate, valid for temperatures $k_BT < \hbar\,\omega_0$ and initial low excitation, then we arrive at the following expressions written for atomic units where $\hbar = 1$,

$$\frac{\mathrm{d}}{\mathrm{d}t}\rho_{00} = -\frac{1}{2}\int_0^t (4\cos[\omega_0\,(t-t')]\,Re\,[C(t-t')]\,\rho_{00}(t') - \{C\,[-(t-t')]\,e^{-i\omega_0(t-t')} + C(t-t')\,e^{i\omega_0(t-t')}\})\,\mathrm{d}t' \quad (15)$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\rho_{11} = -\frac{1}{2}\int_0^t (4\cos[\omega_0\,(t-t')]\,Re\,[C\,(t-t')]\,\rho_{11}(t') - \{C\,[-(t-t')]\,e^{i\omega_0(t-t')} + C(t-t')\,e^{-i\omega_0(t-t')}\})\,\mathrm{d}t' \quad (16)$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\rho_{01} = i\,\omega_0\,\rho_{01} - i\int_0^t 2Re\,[C(t-t')]\,Im\,[\rho_{01}(t')]\,\mathrm{d}t' \quad (17)$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\rho_{10} = -i\,\omega_0\,\rho_{10} - i\int_0^t 2Re\,[C(t-t')]\,Im\,[\rho_{10}(t')]\,\mathrm{d}t' \quad (18)$$

where we used $\rho_{00} + \rho_{11} = 1$. The time correlation function can be written in terms of the spectral function $J(\omega)$ given by $\omega^2\,J(\omega) = 2g(\omega)\,|\kappa(\omega)|^2$, and it takes the form

$$C(t) = \int_0^\infty \left[\cos(\omega t)\coth\left(\frac{\hbar\,\omega}{2k_BT}\right) - i\sin(\omega t)\right]\omega^2\,J(\omega)\,\mathrm{d}\omega \quad (19)$$

Because of the form of q_{sr}, there are no couplings between the diagonal elements of the density matrix corresponding to populations and the off-diagonal ones corresponding to quantum coherence. If we consider more than two states, couplings do appear.

Properties of the adsorbate varying over time can now be obtained from the density matrix. In particular, the amount of energy left in the adsorbate motion after its initial excitation is obtained as $\Delta E_A = E_A(t) - E_A(0)$, with $E_A(t) = tr_A[\hat{\rho}(t)\,\hat{H}_A]$, which reduces in our model to $E_A(t) = \hbar\,\omega_0\sum_{r=0}^{1}\rho_{rr}(t)\,(r + 1/2)$ so that $\Delta E_A(t) = -\hbar\,\omega_0\,\rho_{00}(t)/2$.

2.3. Instantaneous Dissipation and the Markov Limit. The above equations include memory terms from the initial time $t = 0$ to t, and we refer to this as the delayed dissipation case. We consider two additional ways of dealing with dissipation, applicable to cases where the correlation of reservoir amplitudes decays rapidly with time, as compared to the period of vibration of the adsorbate. This is likely to be the case when the reservoir excitations are due to electronic fluctuations, with fast relaxation times as compared to the adsorbate period. The first limit is what we refer to as the instantaneous dissipation limit. If the dissipation takes place in a short time during which the density matrix remains nearly constant, then we can set $\hat{\rho}(t') = \hat{\rho}(t)$ in the equations, leading to expressions of the form

$$\frac{\mathrm{d}}{\mathrm{d}t}\rho_{00}^{(\mathrm{ID})}(t) = \rho_{00}^{(\mathrm{ID})}(t)\,I(t) + J(t) \quad (20)$$

Here the superscript ID refers to the instantaneous dissipation limit, and the $I(t)$ and $J(t)$ integrals are

$$I(t) = -\int_0^t 2\cos[\omega_0(t-t')]\,Re\,[C(t-t')]\,\mathrm{d}t' \quad (21)$$

$$J(t) = \frac{1}{2}\int_0^t \{C\,[-(t-t')]\,e^{-i\omega_0(t-t')} + C(t-t')\,e^{i\omega_0(t-t')}\}\,\mathrm{d}t' \quad (22)$$

This approximation is valid when the kernel multiplying ρ in the integral is large around $t = t'$ and close to zero everywhere else.

If we further find that the upper limit of the integral can be extended to infinity, we have the Markov limit, which looks like

$$\frac{\mathrm{d}}{\mathrm{d}t}\rho_{00}^{(\mathrm{M})}(t) = \rho_{00}^{(\mathrm{M})}(t)\,I(\infty) + J(\infty) \quad (23)$$

There is no time dependence in I or J so the equation can be solved exactly, as

$$\rho_{00}^{(\mathrm{M})}(t) = \left[\rho_{00}^{(\mathrm{M})}(0) + \frac{J(\infty)}{I(\infty)}\right]e^{I(\infty)t} - \frac{J(\infty)}{I(\infty)} \quad (24)$$

and is a special case of the multilevel Redfield equations.[12] This then gives the asymptotic limit for the population of the $0 - th$ state as $\hat{\rho}_{00}(\infty) = -J(\infty)/I(\infty)$, a function of the temperature. This agrees with the asymptotic form for the general case with delayed dissipation, as can be seen integrating by parts the first term to the right in eq 15 and taking the limit $t \rightarrow \infty$.

2.4. Numerical Method. To begin, we write eq 4 in a more compact form,

$$\frac{\mathrm{d}\rho(t)}{\mathrm{d}t} = f\,[t,\rho(t),z(t)] \quad (25)$$

with

$$z(t) = \int_0^t K\,[t,t',\rho(t')]\,\mathrm{d}t' \quad (26)$$

A generalized Runge−Kutta scheme then introduces time increments $\Delta t = h$ and a sequence of $j = 1$ to m stages of iteration, with values $P_{n,j} = \rho(t_0 + nh)^{(j)}$ and $Z_{n,i} = z(t_0 + nh)^{(i)}$, and uses the following relations[13]

$$P_{n,j} = \rho_n + h\sum_{i=1}^{m} a_{ji}\,f\,[t_n + c_i\,h,\,P_{n,i},\,Z_{n,i}] \quad (27)$$

$$Z_{n,i} = F_n\,(t_n + c_i\,h) + h\sum_{l=1}^{m} a_{il}\,K\,[t_n + c_i\,h,\,t_n + c_l\,h,\,P_{n,l}] \quad (28)$$

$$F_n(t) = h \sum_{l=0}^{n-1} \sum_{j=i}^{m} b_j K\,[t, t_l + c_j h, P_{l,j}] \qquad (29)$$

$$\rho_{n+1} = \rho_n + h \sum_{j=1}^{m} b_j f\,[t_n + c_j h, P_{n,j}, Z_{n,j}] \qquad (30)$$

where m is the number of stages of the method and the a_{ij}, b_i, and c_i are real coefficients. The values chosen here are for $m = 4$,[13]

$$[a_{ij}] = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 1/2 & 0 & 0 & 0 \\ 0 & 1/2 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}, [b_i] = \begin{pmatrix} 1/6 \\ 1/3 \\ 1/3 \\ 1/6 \end{pmatrix}, [c_i] = \begin{pmatrix} 0 \\ 1/2 \\ 1/2 \\ 0 \end{pmatrix} \qquad (31)$$

The matrix version is straighforward and does not involve any inversions, so it is readily applicable to many quantum states. This method has been previously tested by us and found to be reliable.[14] It includes as special cases the propagation algorithm for instantaneous and markovian dissipation. As expected, the general case of delayed dissipation is more time-consuming, insofar that it scales as N_T^2, where N_T is the number of time steps, instead of the N_T scaling for instantaneous cases. However, it involves only the physical matrix elements of the density operator, unlike some of the alternative propagation methods.

3. Results for Populations and Quantum Coherence

So far, we have presented a treatment valid for a reservoir with unspecified harmonic vibrations. In what follows, we concentrate on adsorbate relaxation due to coupling to phonons in the substrate.[22] The couplings κ_j contain contributions both from direct coupling of vibrations and from their indirect coupling through short-lived electron−hole excitations in the metal and have been obtained from experiment.[23] The phonon frequencies ω_j may be considered to form a continuum with spectral density $g(\omega)$.

The time−correlation function for the reservoir requires knowledge of the spectral density $g(\omega)$ and of the strength $\kappa(\omega)$ of the coupling between adsorbate and surface. For the first one, we use a simple Debye model so that

$$g(\omega) = 18\pi\, N\, \omega^2/\omega_D^{\,3} \qquad (32)$$

with $g(\omega) = 0$ for $\omega > \omega_D$ and where N is the number of lattice atoms and ω_D is the Debye phonon cutoff frequency. We use a parametrization for $\kappa(\omega)$ in the neighborhood of ω_0 from ref 23 of the form

$$|\kappa(\omega)|^2 = [p + q(\omega - \omega_0)]/N \qquad (33)$$

where p and q are parameters, which depend on the system; the values of these and other parameters used in the calculations are given in Table 1.

Therefore, the correlation function has been obtained from the spectral function

$$J(\omega) = 36N\pi\, |\kappa(\omega)|^2/\omega_D^{\,3} \qquad (34)$$

where $J(\omega) = 0$ for $\omega > \omega_D$.

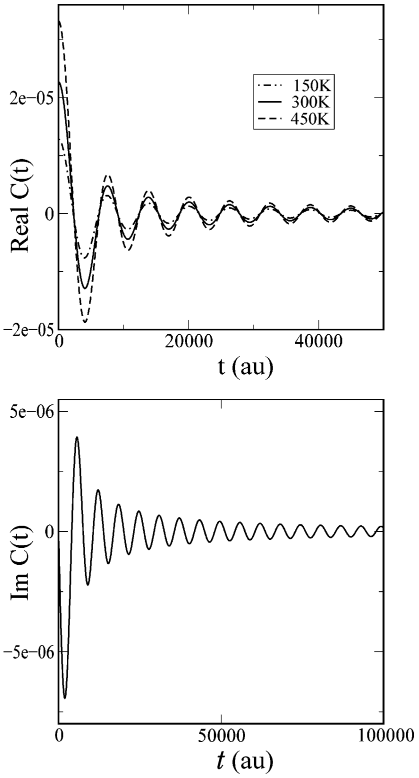

Figure 2. Real part of $C(t)$ for CO/Cu(001) at 150, 300, and 450 K (upper) and the imaginary part of $C(t)$ for CO/Cu(001) at 150 K (lower).

TABLE 1: Frequencies and Coupling Parameters for Different Systems

	Na/Cu	CO/Cu	CO/Pt
ω_0	2.205×10^{-4} au^{-1}	1.448×10^{-4} au^{-1}	2.183×10^{-4} au^{-1}
ω_D	1.013×10^{-3} au^{-1}	1.013×10^{-3} au^{-1}	7.283×10^{-4} au^{-1}
p	2.31×10^{-7} au^{-2}	6.44×10^{-8} au^{-2}	1.10×10^{-8} au^{-2}
q	-5.80×10^{-5} au^{-1}	1.58×10^{-5} au^{-1}	3.98×10^{-6} au^{-1}

For computational purposes, we construct $C(t)$ in three parts. The imaginary portion can be integrated exactly, so no approximation is required. For the real part, at $t = 0$, the cosine term disappears and we can integrate the real part exactly. However, for $t > 0$, this is not the case, and we use the approximation

$$\coth\left(\frac{\hbar\,\omega}{2k_B T}\right) \approx \frac{2k_B T}{\hbar\,\omega} + \frac{\hbar\,\omega}{6k_B T} \qquad (35)$$

provided T is large enough and $t > \Delta t$, a small value; for our applications, it gives good agreement down to 100 K. For very small values of t, the real part is obtained from an expansion around $t = 0$, and we use $C(0)$ as the maximum value of $C(t)$. This has provided accurate results over all times. Results for the real and imaginary parts of the correlation function of CO/Cu are shown in Figure 2 for temperatures of 150, 300, and 450 K. Because the imaginary part of $C(t)$ is independent of temperature, only results for 150 K are shown. The time is given in atomic units, with 1.0 au(T) = 0.0242 fs, and the correlation function is in units of $\hbar^2$. The imaginary part is relatively small, and the real part oscillates out to about 50000 au(T), with a period around 6500 au(T) or about 160 fs, close to the Debye frequency ω_D for Cu. It is seen that as the temperature goes up, the decay of the oscillations is more pronounced.

We have obtained the elements of the RDM for each of the systems Na/Cu, CO/Cu, and CO/Pt at 150 and 300 K, starting with initial values $\rho_{11} = 1$, $\rho_{00} = 0$, and $\rho_{01} = 0$. The results for the population $\rho_{00}(t)$ are shown in Figures 3−5, from which the relaxation of the initial $r = 1$ state population can be followed, since $\rho_{11} = 1 - \rho_{00}$. In each case, higher temperatures lead to decreased oscillation peaks and a faster relaxation to

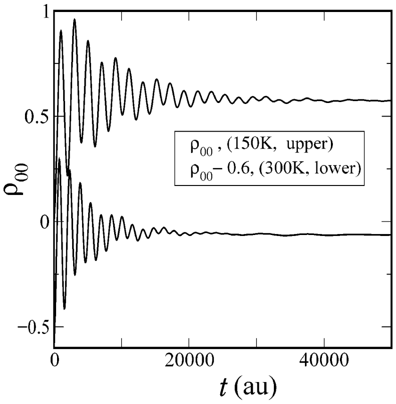

Figure 3. Population of the ground state (ρ_{00}) for CO/Cu(001) at 150 and 300 K.

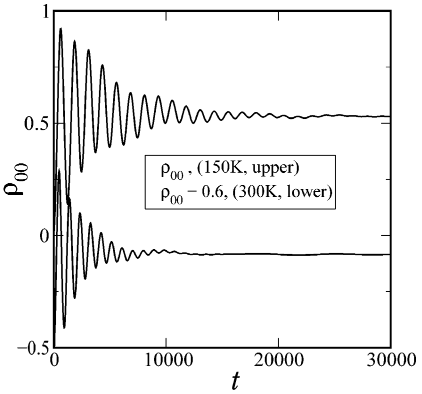

Figure 4. Population of the ground state (ρ_{00}) for Na/Cu(001) at 150 and 300 K.

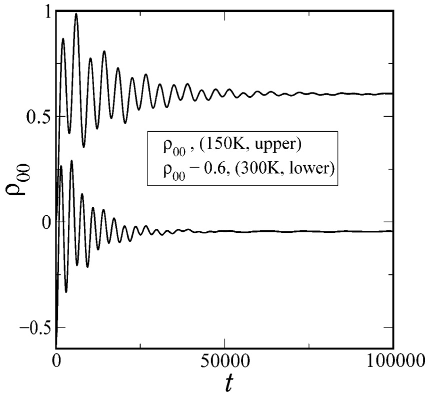

Figure 5. Population of the ground state (ρ_{00}) for CO/Pt(111) at 150 and 300 K.

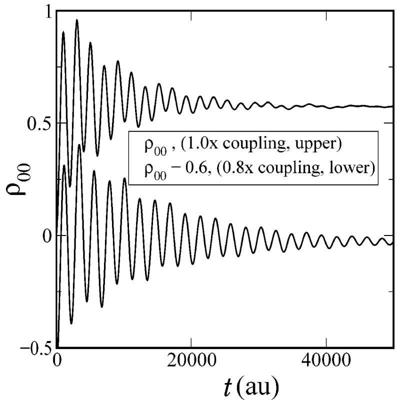

Figure 6. Population of the ground state (ρ_{00}) for CO/Cu(001) at 150 K for normal coupling strength and at 0.8 times the coupling strength.

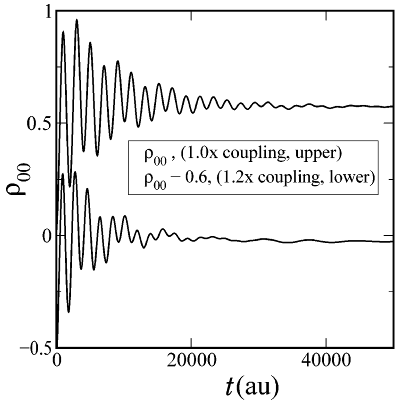

Figure 7. Population of the ground state (ρ_{00}) for CO/Cu(001) at 150 K for normal coupling strength and at 1.2 times the coupling strength.

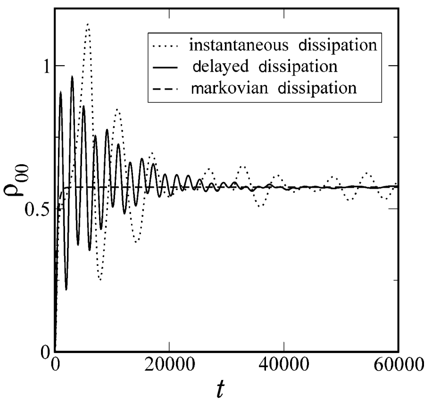

Figure 8. Population of the ground state (ρ_{00}) for CO/Cu(001) at 150 K using delayed dissipation, the instantaneous dissipation limit, and the Markov limit.

equilibrium. For CO/Cu, the population of the ground state $r = 0$ oscillates with a period around 2000 au(T) at both temperatures. Comparing this with the decay time of the correlation function, one concludes that the correlation of reservoir vibrations does not decay rapidly enough to justify an approximation of instantaneous dissipation. Similar conclusions are reached for Na/Cu and CO/Pt. From Figure 3, the CO/Cu populations are found to relax within about 4×10^4 au(T), or about 1.0 ps, at 150 K, with this time increasing at lower temperatures. This is in qualitative agreement with experimental results.[5]

We have explored the dependence of population relaxations on the adsorbate−surface coupling strength. In Figures 6 and 7, we plot ρ_{00} at 150 and 300 K for CO/Cu(001) at the values of $|\kappa|^2$ from the tabulated p and q values and also at p and q values multiplied by 0.8 and by 1.2. The observed trend is that weaker couplings lead to longer relaxation times, as expected due to decreased interaction with the reservoir.

The results for the instantaneous dissipation limit and the Markov limit are shown in Figure 8 for CO/Cu(001) at 150 K. In the Markov limit, the population goes smoothly and almost immediately to the equilibrium value. The instantaneous dissipation limit shows an unphysical behavior. In the case of 150 K, the population here goes above one, violating the positivity of the density matrix, and it also shows repeating oscillations at long times, after the population from the delayed dissipation calculation has already reached equilibrium. It can be concluded from this that the markovian limit is of some use if one needs only long time results but that instantaneous dissipation would not give a realistic picture of time evolution of populations.

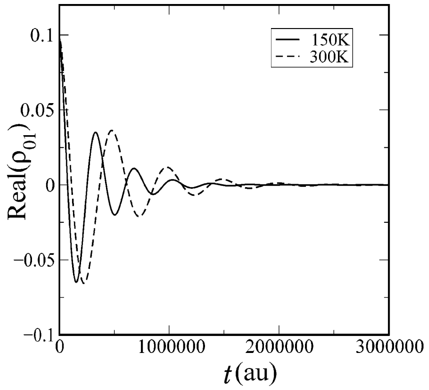

Figure 9. Real part of the quantum coherence ρ_{01} for CO/Cu(001) at 150 (solid line) and 300 K (dashed line).

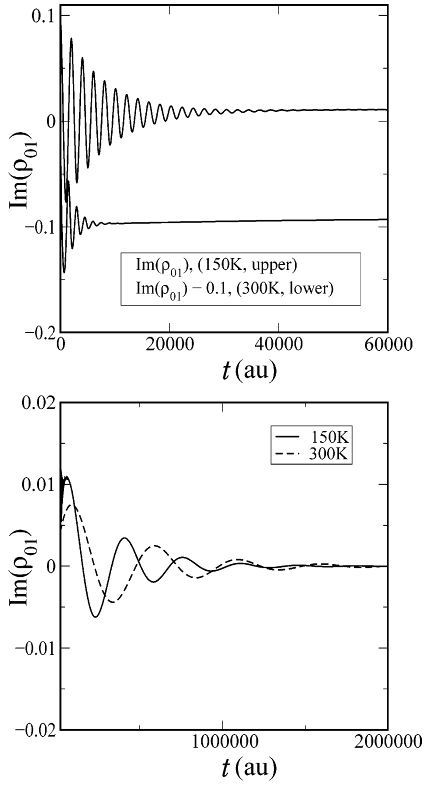

Figure 10. Imaginary part of the quantum coherence ρ_{01} at short times for CO/Cu(001) at 150 and 300 K (upper) and long times (lower).

In all of the above cases, we set the initial quantum coherence ($\rho_{01} = \rho_{10}^*$) equal to zero, in which case it remains zero in our model. Figures 9 and 10 show our results for real and imaginary parts of ρ_{01} using an initial value of $\rho_{01}(0) = 0.1 + 0.1i$. The imaginary part of ρ_{01} shows a pattern of oscillations similar to that in the populations at short times, followed by a slow oscillation with a frequency of order ω_0 relaxing to zero over very long times. The real part shows only these slow oscillations. Hence, here again, the treatment of dissipation must incorporate memory effects. The density matrix element ρ_{01} does not couple to the populations in our model, as can be seen from eqs 17 and 18, so that our previous observations about population changes with time and temperature remain valid.

4. Conclusion

We have described a general theoretical method applicable to a quantum system evolving with delayed dissipation due to its coupling to a medium. The treatment is readily applicable to models where the medium undergoes bosonic excitations (phonons or electron−hole pairs). A numerical procedure has been described that can be used for a primary region with many quantum states, coupled to a medium with a general distribution of excitation energies.

As an application, we have calculated the populations over time of the frustrated T-mode of an adsorbate on a metal surface using the model of a harmonic oscillator coupled to a bath of harmonic oscillators and have examined the effects of coupling strength and the importance of memory terms. We have presented results for a two-state model of the adsorbate for initial conditions $\rho_{11} = 1$ and $\rho_{00} = 0$ corresponding to an initially excited adsorbate, without and with an initial quantum coherence.

When the couplings are stronger, we see fewer oscillations and a shorter relaxation time. This behavior is expected; the dissipation of energy into the reservoir happens more rapidly with a stronger interaction, and the system comes to equilibrium sooner.

Each of the different treatments of dissipation lead to the same equilibrium value, but the dynamics at short times are very different. The delayed dissipation limit shows some strong oscillations at short times before settling into equilibrium, and their relaxation times agree in magnitude with experimental values. In the markovian case, we see only a smooth exponential rise nearly immediately to the equilibrium value. The instantaneous dissipation limit leads to oscillations around the equilibrium value even at long times and does not appear to be valid in this case, insofar that there are no experimental indications of long-time oscillations. From the calculated trends for varying coupling strength, it is found that stronger coupling leads to faster decay of oscillations and that the markovian dissipation more closely resembles delayed dissipation in this case. This suggests that the Markov limit will be more accurate at stronger couplings. At weak couplings, only the delayed dissipation treatment will give accurate results. We see a similar trend when looking at temperature effects. With higher temperatures, we have fewer oscillations and a faster settling to equilibrium. This suggests that the Markov limit will be more accurate at high temperatures but that the delayed dissipation treatment is required to study low-temperature dynamics at short times.

Our calculations relate to a physical situation where excitation of the adsorbate is brief, and we have started the numerical propagation in time with the adsorbate initially in its first excited vibrational state. However, our numerical procedure is general and could also be applied to other situations such as excitation by a long lasting light pulse or for conditions corresponding to slippage of initial values of the density matrix due to an average over an initial distribution of adsorbates. These situations may lead to different patterns of oscillations at short times.

Experiments have been done with laser light pulses to probe relaxation in the present systems[25,26] and have measured relaxation times of the order of picoseconds. It would be of great interest to explore what happens in the femtosecond time scale, to provide insight on both nonmarkovian phenomena and the relative contributions of phonons and electronic excitations to the relaxation times and quantum decoherence.

The equations and computational procedures presented in this paper can also be applied to problems involving electronic excitations at short times, as measured in femtosecond spectroscopy with visible or UV light. In our previous work on femtosecond photodesorption,[27,28] we worked within an instantaneous dissipation limit due to the fast decay of electronic excitations, which could now be reconsidered using the present treatment. Statistical density matrices, with elements giving populations and quantum decoherence, provide a suitable language to describe and calculate the dynamics of electronically excited systems,[29−31] and together with temperature-dependent dissipation terms, they can also be used for electronically excited extended systems such as adsorbates on surfaces.

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