INTRAMOLECULAR VIBRATIONAL ENERGY REDISTRIBUTION IN THE RELAXATION DYNAMICS OF TWO CO ON Cu(110)

REDISTRIBUCIÓN DE ENERGÍA VIBRACIONAL EN LA RELAJACIÓN DE DOS MOLÉCULAS DE CO ADSORBIDAS SOBRE Cu(100)

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The relaxation of vibrationally excited adsorbates on a metal surface is a very important dynamical process, since it constitutes a key step to understand the microscopic mechanisms underlying more complex phenomena such as the sticking of atoms and molecules on metallic substrates and surface reactions. An important aspect to be addressed in such processes is the role played by the inter-mode couplings, which can be mediated either by an interaction potential between the inter-molecular degrees of freedom or by the weak interaction between the molecules and their environment.

Unravelling the effects of inter-mode coupling on the vibrational relaxation dynamics of molecules in weak dissipative environments is a challenging problem, particularly regarding the solution of the quantum equations of motion. State-of-the-art quantum dynamical methods can not efficiently handle such systems, due to the exponential scaling of the computational cost as the number of degrees of freedom increases. The vibrational relaxation of a molecule in the vicinity of a non-rigid surface is mediated by the excitation of phonons and electron-hole pairs in the solid, the second mechanism being dominant for metallic substrates [1, 2]. Hence, molecules scattering from a surface or sticking on it may be classified as open or dissipative systems, the "bath" being the metal surface. The system-bath separation enables the use of the density matrix formalism for open quantum systems. Therefore, the dynamics of the system is described by the reduced density matrix (RDM), which is obtained by tracing out the "bath" modes.

Although considerable progress has been made in wave packets propagation techniques as applied to multidimensional dynamical problems [3, 4], simulating the time-evolution of the RDM poses much bigger challenges in terms of the associated computational cost, as compared to the numerical solution of the Schrödinger equation [5, 6]. In this work, we investigate the accuracy of an approximate representation of the vibrational relaxation dynamics, which follows from three central hypotheses: (*i*) the system-bath coupling is weak and only first-order perturbative rates are relevant, (*ii*) a contracted grid basis generated via a potential-optimised discrete variable representation (PO-DVR) can capture most of the effects of the intramolecular vibrational energy redistribution (IVR), and (*iii*) the Lindblad operators representing each dissipative channel can be represented as a tensor product of one-dimensional operators spanning the factorisable space.

These assumptions result in a marked reduction of the grid size and of the scaling of the computational cost with respect to the increase of the dimensionality of the system.

The accuracy of this treatment, as compared to the RDM propagation in the spectral basis, is illustrated for a two-dimensional system of two-coupled Morse oscillators with realistic parameters modelling two interacting CO molecules oriented perpendicular to a Cu(100)-surface. Two-dimensional models historically played a remarkable role in the development of the theory of molecule surface reactions [7, 8] and they can be regarded as a minimal representation of various phenomena such as inelastic scattering of a molecule from a substrate or the adsorption of gas phase atoms at non-rigid surfaces (i. e., the simplest model comprising the essential features of those dynamical processes). Therefore, they appear as a natural starting point to test novel theoretical approaches for which an extension to larger dimensionality problems is envisaged.

The time evolution of the reduced density matrix $\hat{\rho}(t)$ of a Markovian system is governed by the Liouville von Neumann equation

$$\dot{\rho} = -\frac{i}{\hbar}[\hat{H}_s, \hat{\rho}] + \mathcal{L}_D \hat{\rho}, \qquad (1)$$

where $\hat{H}_s$ is the system Hamiltonian and $\mathcal{L}_D$ is the Lindbladian superoperator that accounts for dissipation effects. The explicit form of this superoperator is

$$\mathcal{L}_D = \sum_{mn} \frac{1}{2}([\hat{C}_{mn}, \hat{\rho}\hat{C}_{mn}^\dagger] + [\hat{C}_{mn}\hat{\rho}, \hat{C}_{mn}^\dagger]), \qquad (2)$$

where $\hat{C}_{mn}(t)$ are the dissipative operators coupling the system and the bath, in particular representing the $(m \to n)$ dissipative channel. $|m\rangle$ and $|n\rangle$ are eigenstates of the Hamiltonian of the system. In general, the operators $\hat{C}_{mn}$ will describe the "jumps" between eigenstates of $\hat{H}_s$ induced by the interaction with the bath. They depend on the transition rates $\Gamma_{n \to m}$, which, in the weak-coupling limit, can be evaluated using the Fermi's golden rule.

For an adsorbate approaching a metallic surface, the mechanism of energy transfer between the vibrational degrees of freedom of the molecule and the electronic degrees of freedom of the surface is mediated by the creation of electron-hole pairs in the metal associated to the transfer of population between two vibrational states of the molecule. In this particular case, the system-bath coupling is the kinetic energy operator of the adsorbate nuclei. The approximate form of the transition rates thus reads

$$\Gamma_{n \to m} \approx \sum_q \Gamma^{(q)} \left| \langle n | \nabla_q | m \rangle \right|^2, \qquad (3)$$

where

$$\Gamma^{(q)} \simeq \frac{2\pi\hbar^3}{M_q} \sum_{if} \langle i | \nabla_q | f \rangle \delta(E_i - \varepsilon_F)\delta(E_f - \varepsilon_F). \qquad (4)$$

$E_i, |i\rangle$ and $E_f, |f\rangle$ are all possible initial and final state energies and wavefunctions of the bath modes, while M_q is the mass corresponding to the motion along the q-th degree of freedom and ε_F denotes the Fermi energy .

It is important to stress that constructing the Lindblad operators in the representation of the system eigenstates demands the knowledge of the multidimensional nuclear wave-functions, $|n\rangle$. In practice, this requirement limits the amount of degrees of freedom that can be treated, especially if a great number of dissipative channels have to be considered. Depending on the number of dissipation channels to be considered, diagonalizing the Hamiltonian may require a tremendous effort from the computational standpoint. This constitutes the main drawback of this particular choice of Lindblad operators when considering multiple channels and several degrees of freedom.

In order to make of numerically converged calculations of larger systems feasible, we propose to express Lindblad operators in a tensor product basis set. Within this approach, the transition rates become decoupled. The advantages of this *ansatz* to tackle the quantum reaction dynamics of multidimensional

systems are striking: the numerical effort associated with the computation of the transition rates scales linearly with the system size. As stated above, this formalism was applied to the study of the vibrations of two CO molecules interacting with each other and approaching a Cu(100) surface. The molecules are assumed to be oriented perpendicularly to the metallic surface, while CO bond length is regarded as fixed (see Fig. 1).

The Hamiltonian of the system is given by

$$\hat{H} = \hat{T}_{q_1} + \hat{T}_{q_2} + \hat{V}_1(q_1) + \hat{V}_2(q_2) + V^{cpl}(q_1, q_2), \qquad (5)$$

where q_i are the separations from each of the CO-centre of masses to the surface, $\hat{T}_{q_i}$ are the one-dimensional kinetic energy operators while $\hat{V}_i$ and V^{cpl} designate, respectively, the potential energy operators corresponding to the motion along the coordinates q_i and the coupling between these two vibrational modes. The parameters of the interaction potentials are chosen to resemble the realistic interactions between the CO molecules and the copper substrate [10].
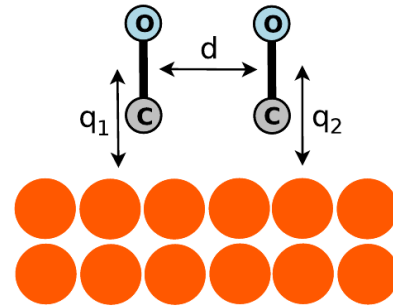

Figure 1: Scheme of the system: two CO molecules approaching a Cu(100) surface. q_1 and q_2 are the distances from each CO centre of mass to the surface, respectively. d corresponds to the distance between the centre of mass of each molecule.

The solution of Eq. (1) requires the specification of an initial state, generally mimicking certain experimental conditions. Here, the initial density matrix corresponds to a pure vibrational state along each degree of freedom, which is denoted as $|2\rangle_{q_1} \otimes |0\rangle_{q_2}$ in product representation, or as $|(n_{q_1}, n_{q_2}) = (2,0)$ in pseudo-spectral form.

A fourth-order Adams-Moulton predictor-corrector method, initiated by the fourth-order Runge-Kutta integrator, was used to evolve in time the matrix elements of the reduced density matrix according to the dissipative Liouville-von Neumann equation. Convergence tests were carried out for the different parameters influencing the numerical propagation, e.g., the time step and the number of basis functions in the grid representation introduced in the following section, and a step size of 5 a.u. was chosen. The total propagation time was set to 24 ps.

The Hamiltonian (5) can be rewritten as:

$$\hat{H} = \left(\hat{T}_{q_1} + \hat{V}_{q_1}^{eff}\right) + \left(\hat{T}_{q_2} + \hat{V}_{q_2}^{eff}\right) + \Delta\hat{V} \qquad (6)$$

The definition of the effective Hamiltonians in (6) is not unique. However, a clever partitioning of the total Hamiltonian may help to shift large parts of the coupling into the operators $\hat{V}_{q_i}^{eff}$.

Thus, the diffusion term in Eq. (1) gets reduced, ultimately becoming negligible and yielding a purely dissipative dynamics (in the interaction representation). Using a PO-DVR procedure [9], we define the effective contributions so that the coupling $\Delta \hat{V}$ is minimal.

Fig. 2 and Fig. 3 depict the evolution of the wave packets along the q_1 and the q_2 axis, corresponding to distinct coupling strength parameters and to both computational approaches employed in this work, namely, the full spectral representation and the tensor product representation of the Lindblad operators. The representative snapshots were chosen to highlight important changes in the nodal structures along the dissipative reaction path.
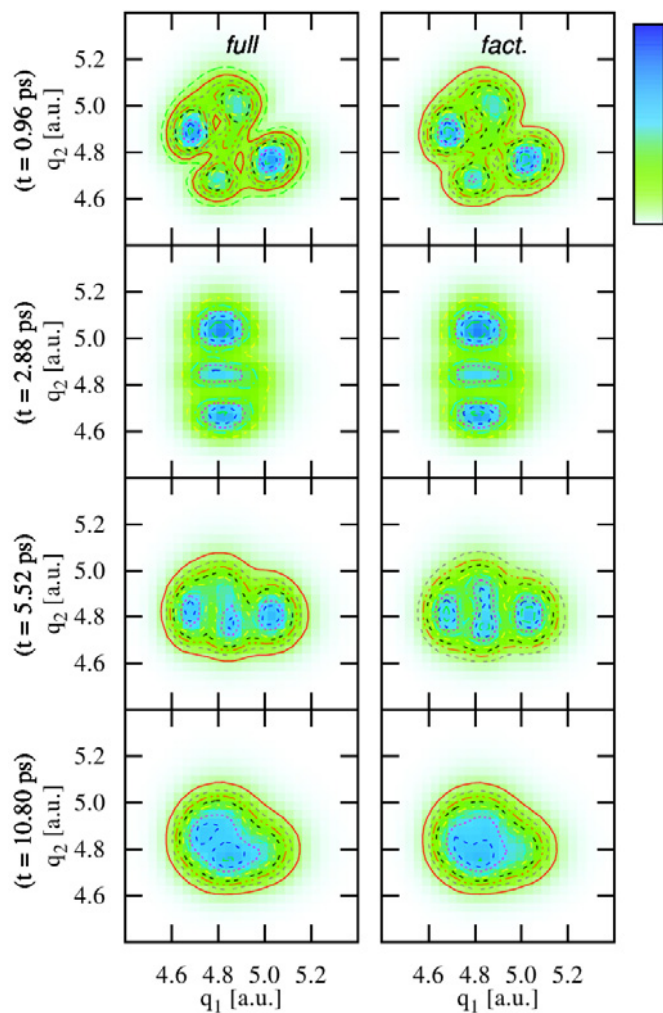

Figure 2: Snapshots of the evolution of the probability distribution for certain points in time, and for weak inter-molecular coupling, ($a = 0.1$) calculated using bi-dimensional Lindblad operators (left panels) and the factorisation *ansatz* (right panels).

The scenario depicted in Fig. 2 corresponds to $a = 0.1$, the small coupling strength (a is the ratio between the well depth of the coupling V^{cpl} and that of the potentials $\hat{V}_i$), in which the two modes are influencing each other and the IVR causes an ultrafast energy flow between them. The energy exchange leads to the inversion of population along each degree of freedom, compared to the initial state, i.e., going from state (2,0) to state (0,2) (see the intermediate panels in Fig. 2). This particular

feature is present at several points in time and it occurs more frequently as the coupling parameter increases. Upon further enlarging the coupling strength, the two-dimensional wave packet can not be described approximately as a Hartree product of single-particle wave-functions corresponding to each dynamical variable. As a consequence, the wave-packet turns out to exhibit the intricate shape observed in Fig. 3. Additionally, it can be confirmed that for intermediate couplings the full-dimensional and the factorization approaches converge approximately to the same values.
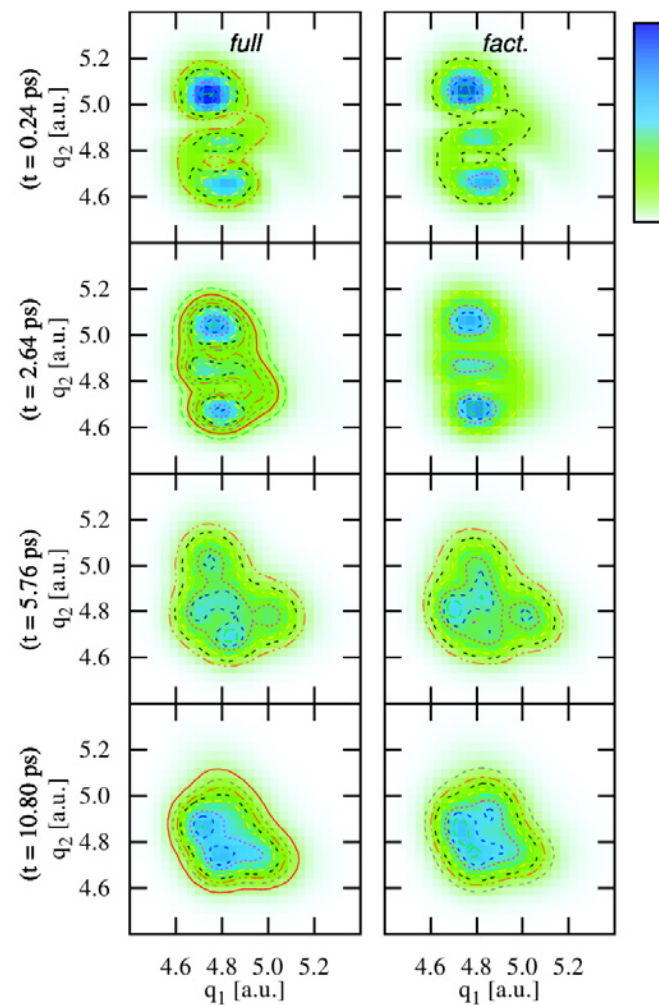

Figure 3: Snapshots of the evolution of the probability distribution for certain points in time, and for strong inter-molecular coupling, ($a = 0.8$) calculated using bi-dimensional Lindblad operators (left panels) and the factorisation *ansatz* (right panels).

In summary, we have analyzed the accuracy of approximating the dissipative operators appearing in the Liouville-von Neumann equation by a tensor product of effective one-dimensional operators. We applied this approach to a system consisting in two CO molecules adsorbed on a Cu(100) surface. The proposed method yields results in close agreement with the propagation scheme based on fully coupled multidimensional Lindblad operators, thereby confirming the validity of the factorisation *ansatz*. The advantage of the form of the dissipative operators presented in this work over the standard spectral approach, lies in the possibility to investigate the

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quantum dissipative dynamics in larger systems, that would be otherwise inaccessible.

[1] B. Gergen, H. Nienhaus, W. H. Weinberg and E. W. McFarland, Science **294**, 2521 (2001)

[2] N. Shenvi, S. Roy and J. C. Tully, J. Chem. Phys. **130**, 174107 (2009)

[3] M. H. Beck, A. Jackle, G. Worth and H. D. Meyer, Phys. Rep. **324**, 1 (2000)

[4] D. V. Shalashilin and M. S. Child, J. Chem. Phys. **115**, 5367 (2001)

[5] H. Guo and R. Chen, J. Chem. Phys. **110**, 6626 (1999)

[6] M. Bennant, R. Koslofft and H. Tal-Eze, Phys. A: Math. Gen. **25**, 1283 (1992)

[7] P. Saalfrank, G. Boendgen, K. Finger and L. Pesce, Chem. Phys. **251**, 51 (2000)

[8] S. Li and H. Guo, J. Chem. Phys. **117**, 4499 (2002)

[9] J. Echave and D. C. Clary, Chem. Phys. Lett. **190**, 225 (1992)

[10] J. C. Tremblay, G. Füchsel and P. Saalfrank, Phys. Rev. B **86**, 045438 (2012)