Quantum Simulations of Vibrational Dephasing of Molecules in a Cryogenic Environment: HArF in an Argon Cluster

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Abstract

The Classical Separable Potential (CSP) method, which is a mean-field approximation to multidimensional quantum dynamics, is applied to the dephasing process of a vibrationally excited HArF molecule in an argon cluster at low temperatures. Dephasing timescales of the order of 1 ps are estimated for dynamics following fundamental excitation of either the H–Ar or the Ar–F stretching mode of HArF. The CSP approach is valid over such timescales, and it is thus a viable approach to quantum simulations of dephasing at low temperatures. Vibrational relaxation is much slower: Quasi-classical molecular dynamics simulations yield a relaxation time around 100 ps for the initial v=1 Ar–F stretching excitation. Such timescales are beyond the validity range of CSP, therefore, this or similar separable methods are inapplicable for vibrational energy decay.

I. INTRODUCTION

Vibrational processes in low-temperature matrices are expected to exhibit strong quantum effects. Such processes are, therefore, a natural testing ground for quantum simulation methods. The motivation for theoretical studies of such systems is enhanced by the availability of experimental data for at least some types of vibrational processes for molecules in cryogenic matrices [1,2]. In particular, vibrational energy relaxation data are available for many diatomic molecules in rare gas solids. In the present paper, we consider briefly also the topic of vibrational energy decay, but focus primarily on the vibrational dephasing process. Experimentally, the study of such processes for small molecules in matrices is more challenging than investigating the vibrational energy decay. However, with the advent of ultrafast spectroscopy methods, such data are becoming increasingly available. In this paper, we examine the suitability of an approximate time-dependent quantum simulation method for such processes.

In studies of vibrational energy relaxation in matrices, hydrides were found to be particularly interesting [3,4]. For diatomic hydrides such as HCl, NH, OH, etc. in matrices, the vibrational energy relaxation was found to proceed via energy transfer to molecular rotation [5,6]. A triatomic hydride for which extensive experimental results are available is HCN (in Ar, Kr, and Xe) [7,8]. This system is not yet quantitatively understood theoretically, but the indications are that the rotational channel is inoperative, probably due to suppression of the molecular rotation in the matrix in this case.

In the present study, we explore the dynamics and mechanism of vibrational dephasing processes of HArF in a cryogenic argon environment. The recently discovered HArF is the only molecule yet known of argon [9], therefore, it has been already the subject of several experimental and theoretical studies [9–11]. As a consequence of these studies, realistic interaction potentials are available for this system [11]. IR spectroscopy was measured [9], but there have been no time-domain spectroscopic measurements to date. We expect experimental data pertinent to dephasing to become available in the future.

The structure of this paper is as follows. In Sec. II, the potential model and the CSP quantum simulation method are briefly described. The results of the calculations are brought and discussed in Sec. III. Concluding remarks are the topic of Sec. IV.

II. SYSTEMS AND COMPUTATIONAL METHODS

In the present study, we have modeled solvation of HArF molecule in a cluster of 17 argon atoms forming a complete first solvation shell. The symmetric double icosahedron of the rare gas solvent together with the embedded solute are depicted in Fig. 1. We see that the HArF molecule lies along the central axis of the double icosahedron. The two heavy atoms of the HArF molecules occupy the center of the cavity formed by the surrounding argon atoms with the hydrogen lying somehow asymmetrically.

The potential model consists of intra- and inter-molecular terms. The intramolecular HArF potentials has three terms, two Morse curves for the H–Ar and F–Ar stretches and a quadratic angular term for the bend. The intermolecular potentials consist from a pairwise additive Lennard–Jones argon–argon term for the solvent atoms and a two–component potential describing the solute–solvent interactions. The first term is a combination of Lennard-Jones pairwise additive H–Ar, Ar–Ar, and F–Ar potentials. The second, electrostatic term describes the partial charge–induced dipole interactions between the HArF molecule and argon atoms. This potential model, which has been validated against accurate ab initio calculations for structures close to the optimal geometry, is described in detail together with all numerical parameters in Ref. [11].

For the description of the vibrational dephasing upon vibrational excitation of the HArF molecules in the Ar_{17} cluster we have employed the Classical Separable Potential (CSP) method [12,13]. This method has been described in detail in our previous publications [12,13]. Briefly, the CSP scheme starts with a Wigner mapping of the initial quantum state of the system onto a set of classical coordinates and momenta [14] which serve as initial values for MD simulations. A set of n_T auxiliary classical trajectories is generated by solving the classical equations of motion. This set is then used to construct a separable time-dependent effective potential $V_j(q_j,t)$ for each mode j $(j = 1, 2, ..., N)$

$$V_j(q_j,t) = \sum_{\alpha=1}^{n_T} V(q_1^{(\alpha)}(t), ..., q_{j-1}^{(\alpha)}(t), q_j, q_{j+1}^{(\alpha)}(t), ..., q_N^{(\alpha)}(t))w_\alpha + \frac{1-N}{N}\overline{V}(t), \tag{1}$$

where V is the fully coupled potential. Summation runs over all MD trajectories and w_α is the Wigner weight of trajectory α calculated using the initial wavepacket. The coordinate-independent constant $\overline{V}$

$$\overline{V}(t) = \sum_{\alpha=1}^{n_T} V(q_1^{(\alpha)}(t), ..., q_{j-1}^{(\alpha)}(t), q_j^{(\alpha)}(t), q_{j+1}^{(\alpha)}(t), ..., q_N^{(\alpha)}(t))w_\alpha \tag{2}$$

does not influence the dynamics, and only ensures that the single-mode potentials sum up approximately to the total potential energy of the system. As a final step, the time-dependent Schrödinger equation in the separable approximation is solved for each mode j

$$i\hbar\frac{\partial\psi_j(q_j,t)}{\partial t} = (\hat{T}_j + V_j(q_j,t))\psi_j(q_j,t), j = 1, ..., N. \tag{3}$$

Here, $\hat{T}_j$ is the kinetic energy operator of mode j and $\hbar$ represents the Plank's constant. The total wavepacket for the system under study is then given as a product of the single-mode wavefunctions

$$\Psi(q_1, ..., q_N, t) = \prod_{j=1}^{N} \psi_j(q_j,t). \tag{4}$$

The principal difference from the Time-Dependent Self-Consistent Field (TDSCF) method [15] is that the effective single mode potentials are evaluated using auxiliary Wigner trajectories [14], which makes the CSP approach computationally feasible also for large systems containing tens to hundreds of degrees of freedom. The single mode quantum simulations within the CSP calculations have been performed using the split-operator propagator [16], employing the Fast Fourier Transform for the evaluation of the action of the kinetic part of the evolution operator [17]. A time step of 0.24 fs has been employed with a total propagation time of each run of 2.4 ps. Nuclear degrees of freedom have been described using normal mode coordinates, adopting discretization on equidistant grids. 256 grid point have been used for the first four modes, describing motions of the HArF molecules, while 32 grid points have been adopted for the cage modes.

Vibrational relaxation following vibrational excitation of the embedded molecule has been studied using quasi–classical Wigner trajectories. More specifically, as in the case of auxiliary trajectories for the CSP propagation, we have applied the Wigner transformation to all modes except the excited mode (either the H–Ar or Ar–F stretch) of the HArF molecule. For this mode, we have generated initial positions and momenta using a quantum/classical energy matching criterion [18] in order to avoid Wigner trajectories with negative weights. These trajectories reflect the initial quantum vibrational delocalization but treat the relaxation dynamics classically. Simulations of 100 trajectories using the Gear propagator [19] with a time step of 0.24 fs have been carried out for 250 ps.

III. RESULTS AND DISCUSSION

The collinear HArF molecule possesses two stretching modes (one principally H–Ar at 1912 cm^{-1} and the other principally Ar–F at 473 cm^{-1}) and a pair of degenerate bending modes with a frequency of 704 cm^{-1} [10]. We have modeled quantum dephasing following the fundamental vibrational excitation of either the H–Ar or the Ar–F stretching mode of HArF embedded in the Ar_{17} cluster. More precisely, we have taken as the initial state a product of harmonic functions of an isolated HArF molecule (with v=1 excitation of one of the stretching modes, the other two modes being in their ground state) and ground state harmonic functions of the cage. In the absence of the argon cage exact excited vibrational states would be stationary with an infinite dephasing time. Within the present approximations, even for the case of the isolated HArF molecule a very slow dynamics would be observed due to the harmonic approximation invoked in the construction of the initial vibrational wavefunction. However, a much more rapid dephasing is caused by the presence of the argon cage, which can be viewed as an anharmonic bath of vibrational modes. This solvent induced dephasing is a real physical effect, which will reflect itself, e.g., in a broadening of the corresponding experimental IR absorption lines [20,21].

A convenient quantity to discuss vibrational dephasing for the present system (where relaxation is much slower than dephasing) is the autocorrelation function C_A:

$$C_A = < \Psi(0)|\Psi(t) > . \tag{5}$$

Here, $\Psi(0)$ is the initial total CSP wavefunction of the $HArFAr_{17}$ system (with a v=1 excitation of either the H–Ar or Ar–F stretching mode) and $\Psi(t)$ is this vibrational wavefunction evolving at time t. The autocorrelation functions, corresponding to an initial fundamental excitation of the H–Ar (resp. Ar–F) stretch of the HArF molecule, are depicted in Fig. 2a (resp. Fig. 2b). Both autocorrelation functions decay almost to zero within 2.5 ps. The exponential decay is modulated by two recurrences. For both autocorrelation functions the revivals, spaced by ≈800 fs, reflect characteristic vibrations of the argon cage. The dephasing of the excited H–Ar stretch, which corresponds to a rapid hydrogen motion, is slightly faster than that of the excited Ar–F stretch with more slowly moving heavy atoms. We can, however, conclude that in both cases the dephasing time is roughly 1 ps. Since the dipole–dipole correlation function [20] decays at the same timescale as the above autocorrelation function we can estimate the corresponding homogenous linewidth to be around 5 cm^{-1}, in good agreement with the experimental lineshape of the H-Ar fundamental excitation [9].

The separable CSP approach allows to evaluate not only the total but also single mode autocorrelation functions, which might help to shed light on the detailed mechanism of the dephasing process. We have monitored all the single mode autocorrelation functions finding, however, that the decay of the total autocorrelation function cannot be attributed to single mode or to a small number of modes. Rather, all the modes contribute weakly, albeit not equally, to the total decay. Among the most strongly contributing modes is, in both cases, the degenerate pair of bending modes of the HArF molecule.

It is important to keep in mind that the quantum dynamical CSP method, employed for the evaluation of the autocorrelation functions, is inevitably only approximate. Therefore, it is crucial to establish the accuracy of the calculation, which, as for any separable mean–field method, will decrease in time. The first thing to check for the CSP calculation is the convergence with the number of auxiliary Wigner trajectories used for the evaluation of the single mode mean–field potentials. Fig. 2 shows the autocorrelation functions obtained from CSP calculations employing 100–500 trajectories. We see that for the case of the initial H–Ar fundamental excitation convergence is reached at about 400 trajectories. For the Ar–F excitation, 500 trajectories (which correspond to a calculation close to our limit of computational feasibility) provide almost converged results.

The major deficiency of mean–field methods is their tendency to underestimate mode–mode couplings, which effectively makes them usable only for short time propagations. Recently, we have developed an error measure based on the auxiliary Wigner trajectories (which run on the fully coupled potential), which gives a good estimate of the deviation of the time dependent mean–field potentials from the exact one [22]. Fig. 3 shows the time evolution of the relative error of the CSP potentials for both H–Ar and Ar–F initial excitations. First, we see that one needs about 100 trajectories to obtain a faithful error estimate. This is also consistent with the convergence of the effective single-mode CSP potentials with the number of trajectories. We have verified, that 100–500 trajectories provide converged CSP potentials at the picosecond time scale. Second, it follows from Fig. 3 that in both cases the CSP method should provide very accurate results (errors smaller than 5 %) for the first picosecond of the dynamics, which is also the dephasing time discussed above. After the first picosecond the error starts to increase, being about 20 % at 1.5 ps, reaching almost 50 % at 2.5 ps, and steeply rising afterwards.

Unlike dephasing, which takes place on the picosecond timescale, intermolecular energy transfer is a much slower process. The error estimate shows that there is little hope for the CSP method to perform satisfactorily beyond several picoseconds. In principle, one can try to go beyond the mean-field approximation, e.g., in the direction of the Configuration Interaction CSP approach [23]. However, for the 100 ps (or longer) timescale anticipated for the energy transfer, even this method will not perform quantitatively, not to mention the enormous computational cost. For this reason, we have employed for the study of the vibrational de-excitation of the HArF molecule in the argon cage the quasi-classical method of Wigner trajectories. The quasi-classical approach can be partly physically justified by the fact that, unlike dephasing which is purely of a quantum nature, non-resonant energy transfer tends to be a more robust, classical-like process. Since a fully coupled quantum treatment is not computationally feasible for the present system, we employ classical trajectories also because it has been shown recently that vibrational relaxation in model quantum systems is better approximated by a fully classical theory than by a mixed quantum-classical approach [24].

Due to the fact that all the vibrational modes of the system are coupled to each other (although there is only weak coupling between intra- and inter-molecular modes) it is not totally obvious which quantity should be monitored as a signature of vibrational relaxation. We have found it most straightforward to follow the time evolution of the kinetic energy of the excited mode, which is, in normal modes, a strictly separable, single mode quantity. For vibrations deviating only slightly from harmonicity, such as the fundamental excitations of the H–Ar or Ar–F stretches, the average value of the kinetic energy should of course amount to one half of the mode energy.

Fig. 4 depicts the time evolution of the averaged (over the trajectories) kinetic energy in the initially excited Ar–F intramolecular stretching mode. It can be seen that the v=1 excited Ar–F stretch relaxes (in the quasi-classical sense of box quantization) to its ground state on the timescale of 100 ps. This is relatively fast, compared to nano- to microsecond vibrational relaxation times of typical small molecules in solid argon. Clearly, due to the high polarity of the HArF molecules the coupling to the argon cage is non-negligible, as demonstrated also by relatively large matrix shifts of the intermolecular vibrations [11]. The relaxation of the fundamental H–Ar vibration is slower and does not occur on the (sub)nanosecond timescale covered by the present MD simulations. This is primarily due to the unfavorable mass ratio between hydrogen and argons of the solvent cage, as well as to the large energy mismatch between the stiff H–Ar stretch and soft argon modes, which both prevent efficient energy transfer.

IV. CONCLUSIONS

The CSP method was applied to calculate dephasing times for HArF in an argon cluster environment at T=0 K. The dephasing times for both the H–Ar and Ar–F fundamental stretching excitations are of the order of a picosecond. The results indicate that CSP is appropriate for simulations of dephasing processes in such systems. In principle, the method can be also extended to finite bath temperatures, either employing a density matrix description or ensembles of initial wavefunctions. For vibrational relaxation processes, the situation is very different. The relevant timescales are very long, well beyond the validity of CSP. Description of the vibrational energy decay obviously requires non-separable or perturbative methods.

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FIGURE CAPTIONS

Figure 1:

Geometry of the HArF molecule embedded in 17 argon atoms forming the first solvation shell. Note the position of the embedded molecule along the principal axis of the double icosahedron with an asymetric position of the hydrogen atom.

Figure 2:

Autocorrelation function, the decay of which monitors the wavepacket dephasing after initial fundamental excitation of the a) H–Ar, or b) Ar–F stretching mode. Comparison of CSP propagations employing 100–500 auxiliary Wigner trajectories.

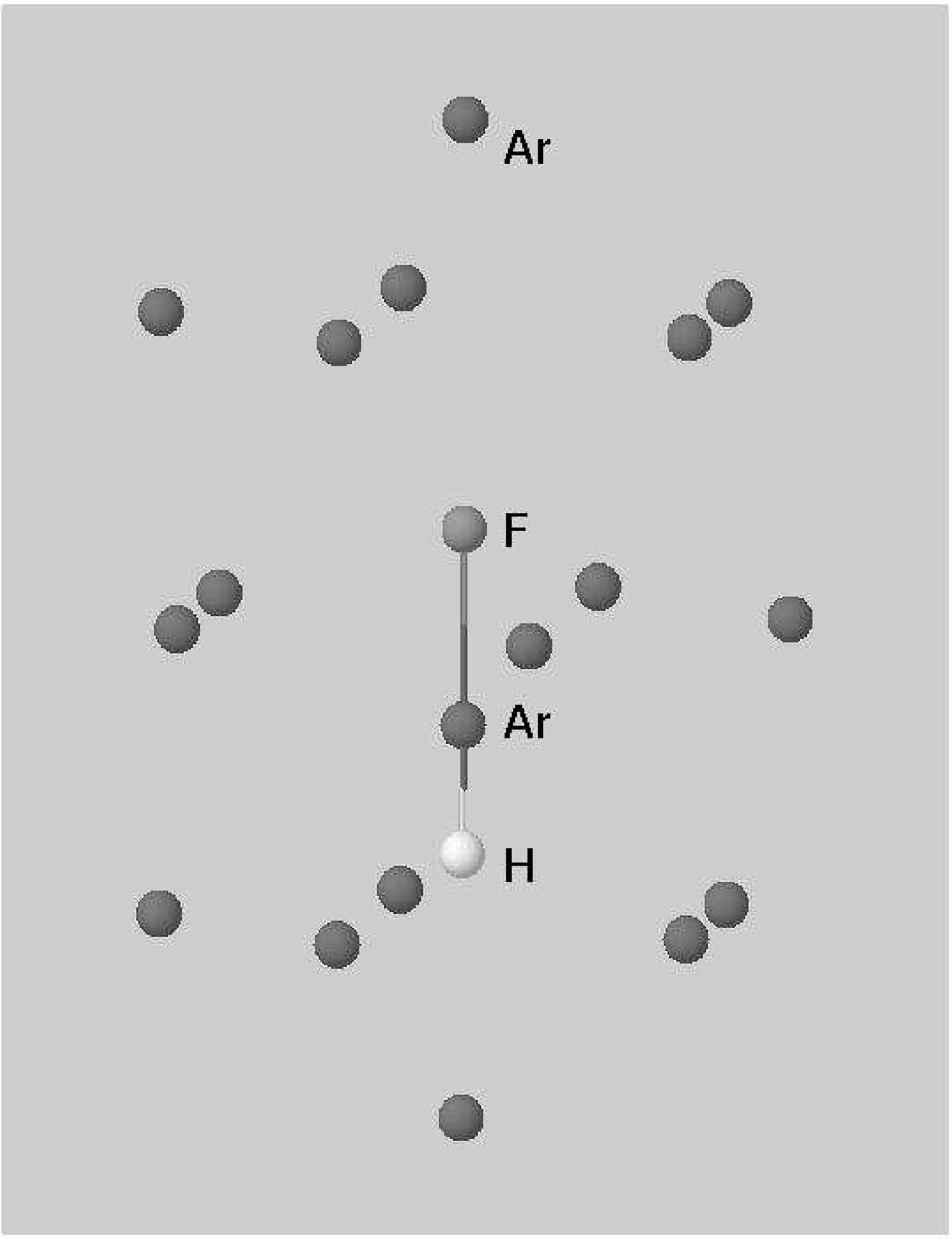
Figure 3:

The relative error of the CSP propagation after initial fundamental excitation of the a) H–Ar, or b) Ar–F stretching mode. Calculations employing 100 and 200 trajectories give almost the same result.

Figure 4:

Time evolution of the excited mode kinetic energy reflecting the intermolecular vibrational energy transfer after initial fundamental excitation of the Ar–F stretching mode.

Figure 1, Jungwirth and Gerber



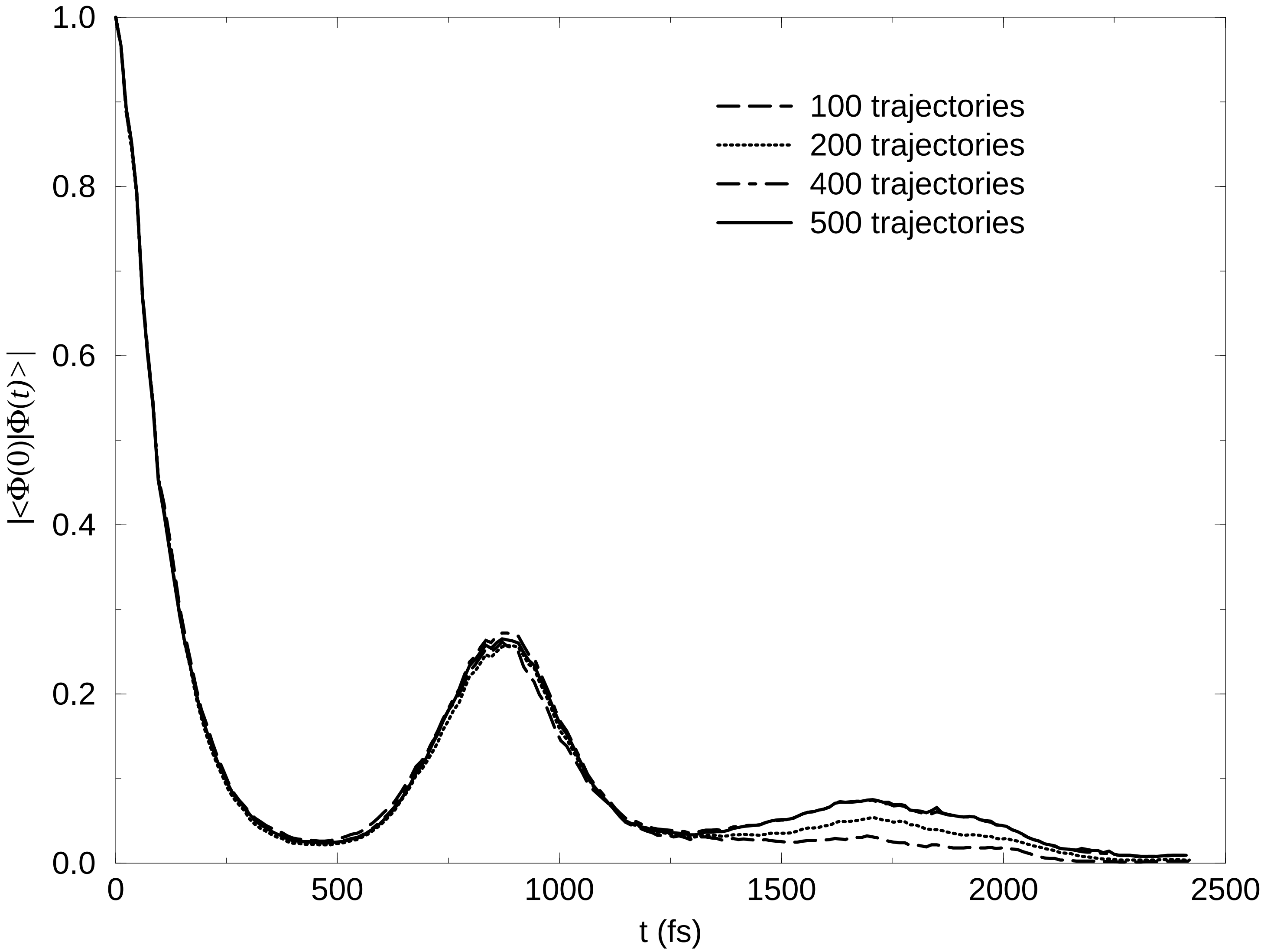
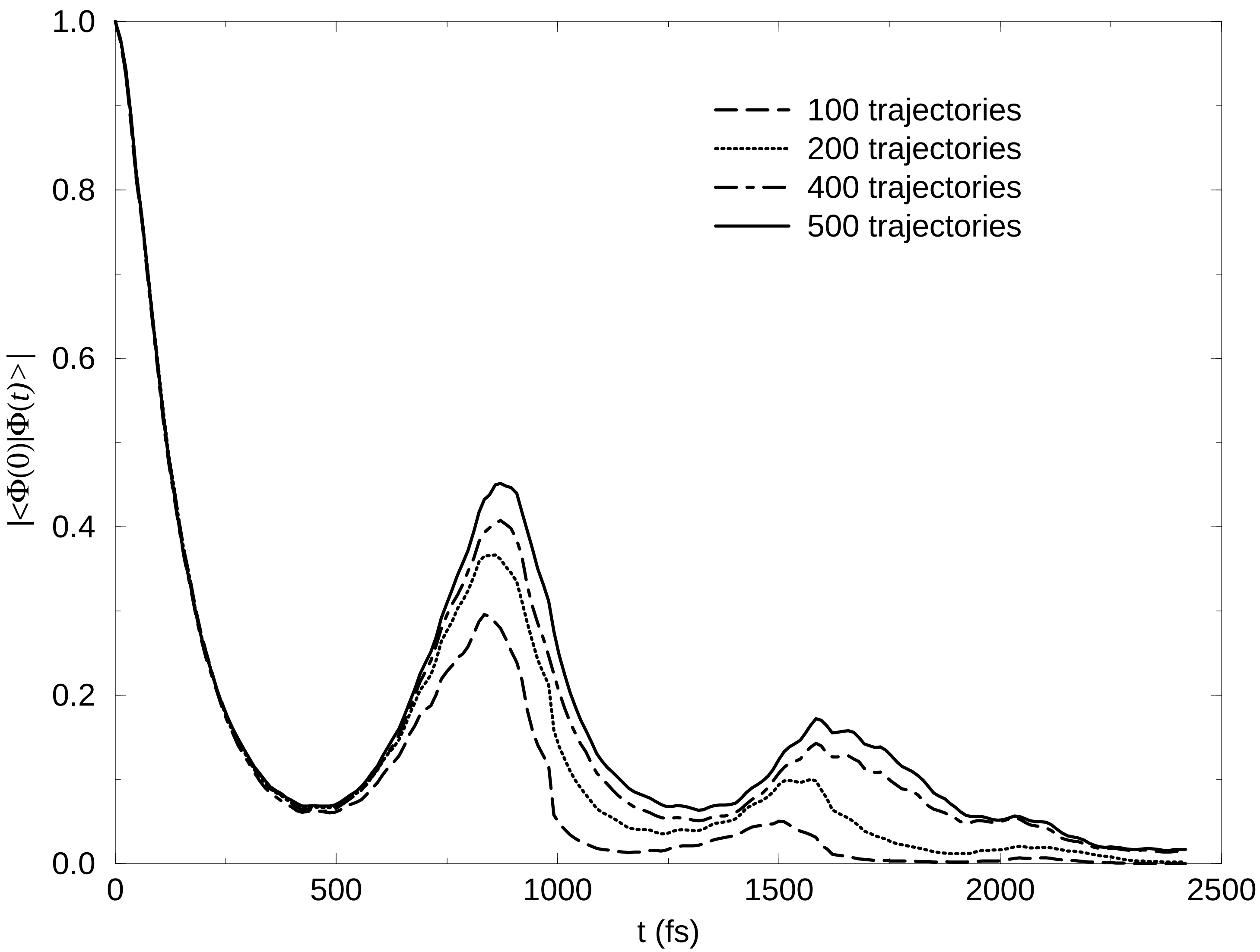


Figure 2a, Jungwirth and Gerber



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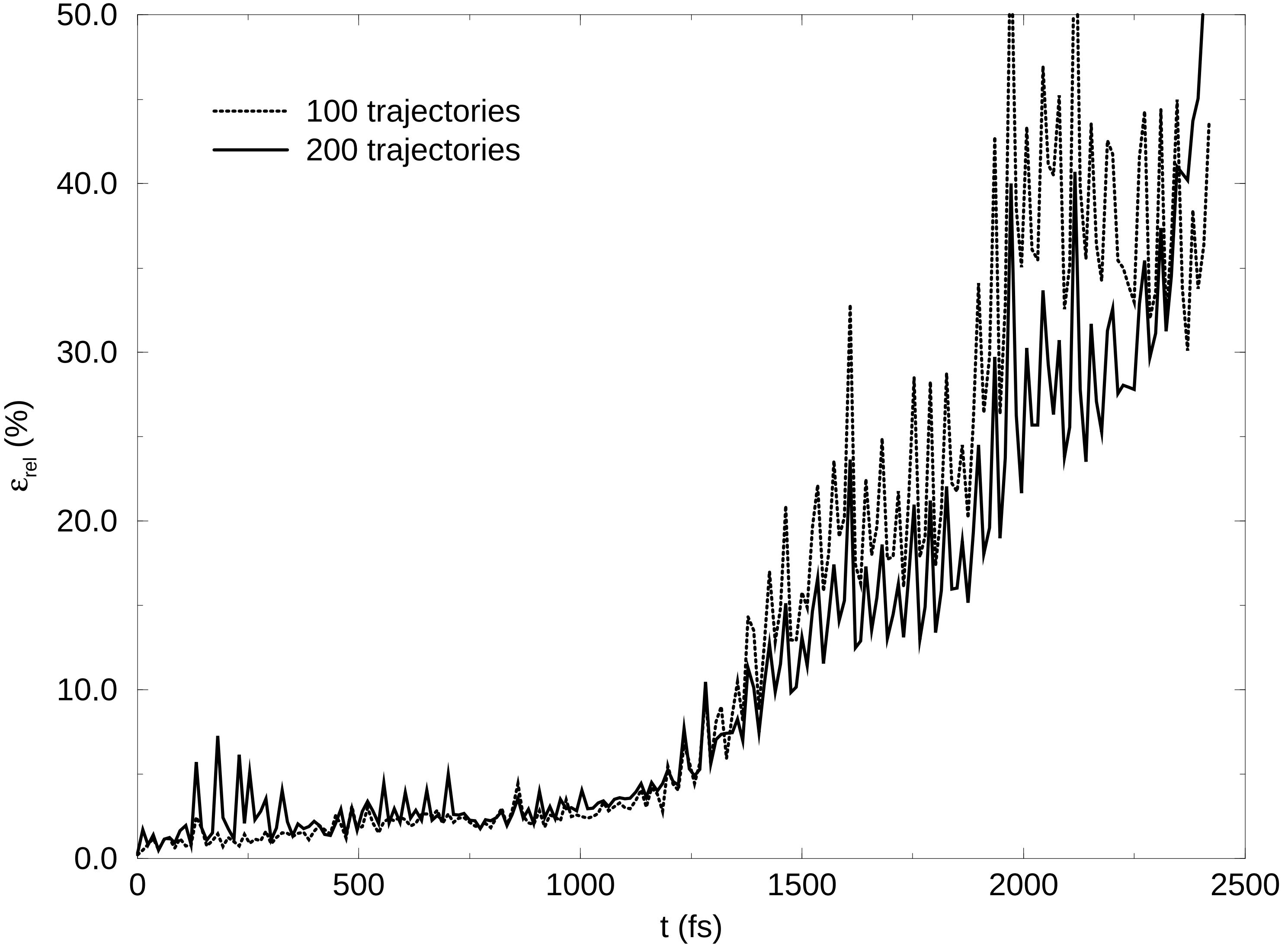

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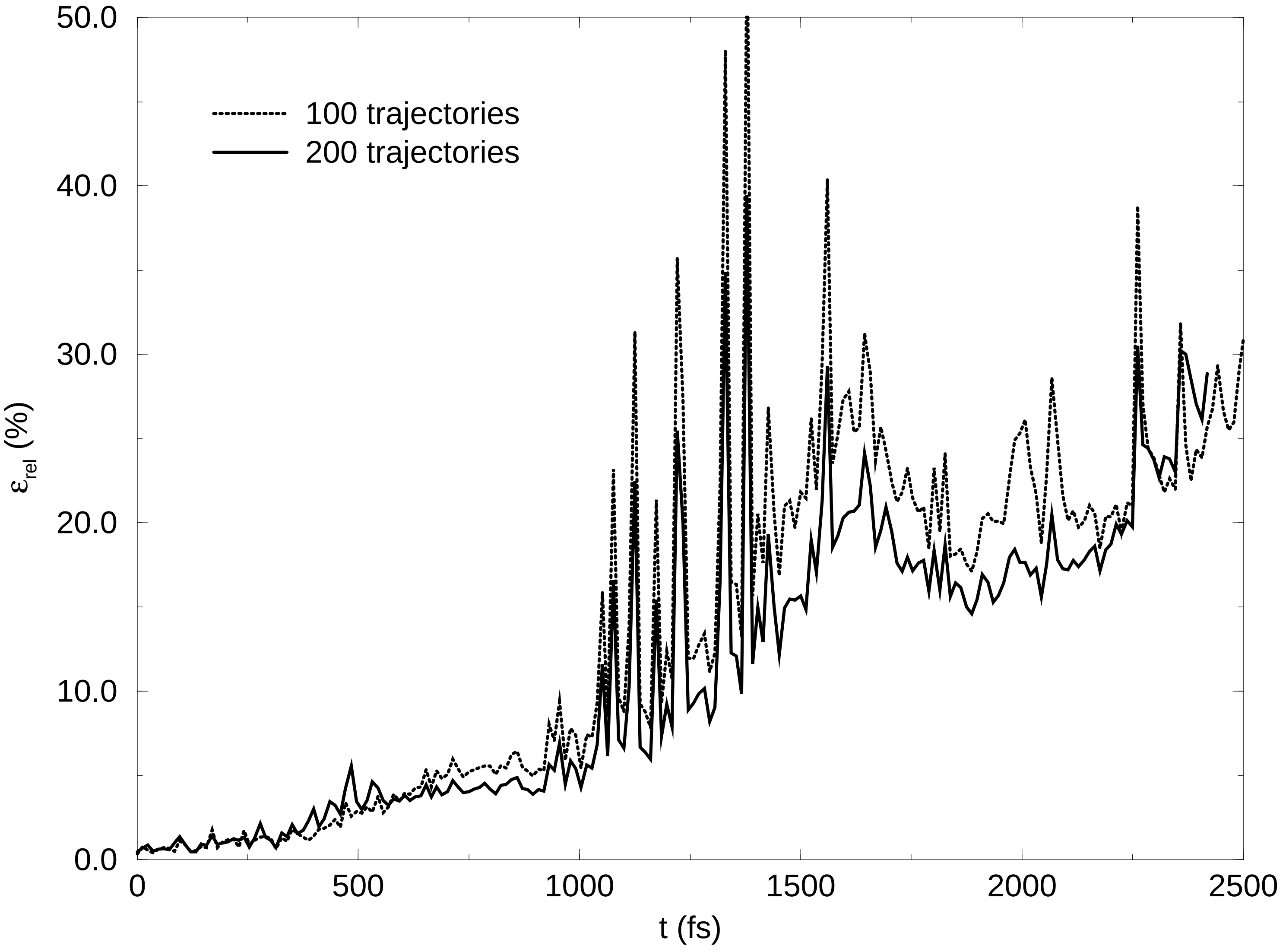

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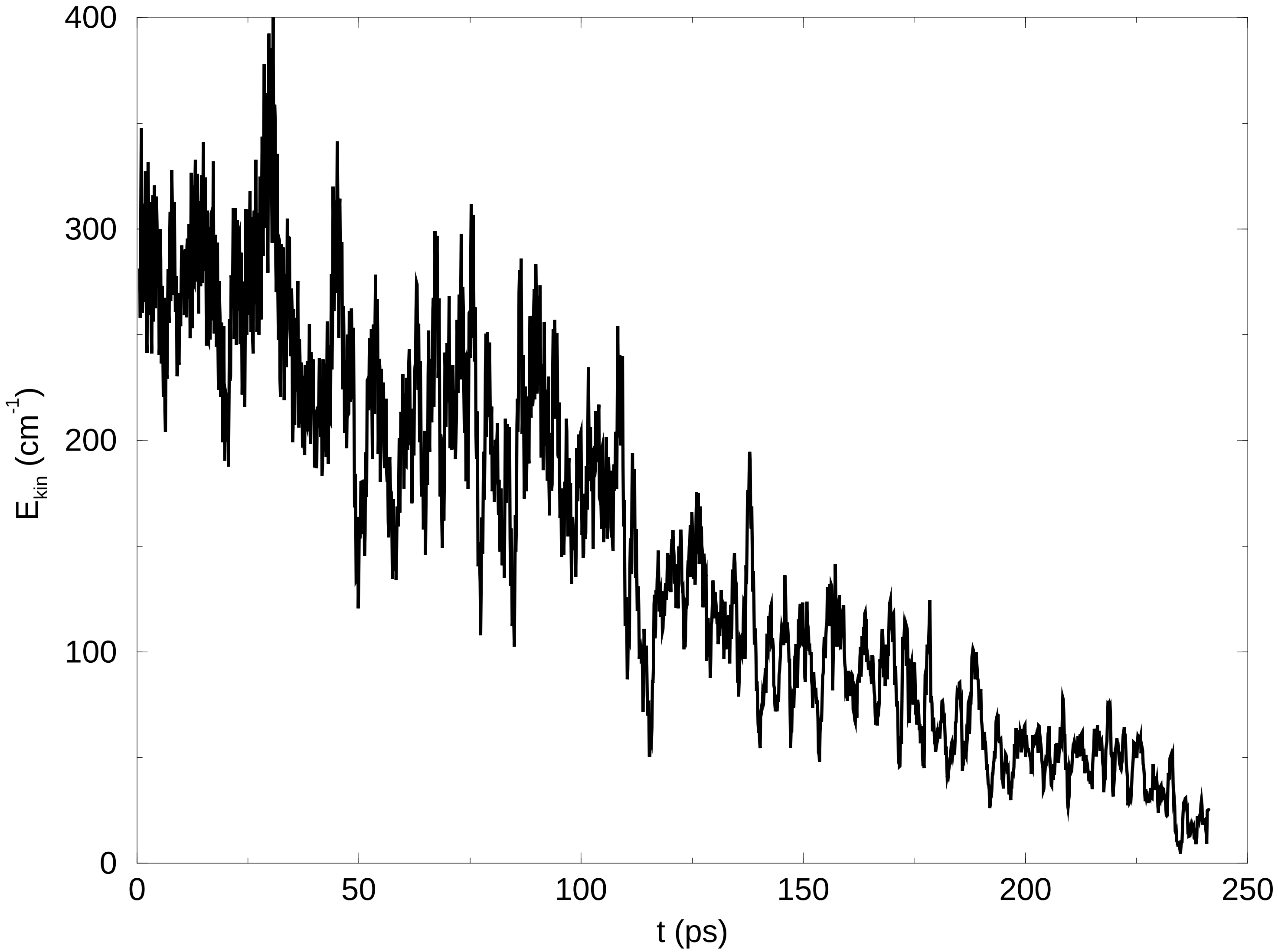

Figure 4, Jungwirth and Gerber