Multiscale non-adiabatic dynamics with radiative decay, case study on the post-ionization fragmentation of rare-gas tetracomplexes

I. Janeček\textsuperscript{1,2}(a), T. Janča\textsuperscript{3}, P. Naar\textsuperscript{3}, F. Renard\textsuperscript{3,4}, R. Kalus\textsuperscript{5} and F. X. Gadea\textsuperscript{6}

\textsuperscript{1} Institute of Geonics of the AS CR, v.v.i. - Studentská 1768, 708 00 Ostrava, Czech Republic, EU
\textsuperscript{2} Institute of Clean Technologies for Mining and Utilization of Raw Materials for Energy Use Studentská 1768, 708 00 Ostrava, Czech Republic, EU
\textsuperscript{3} Department of Physics, Faculty of Sciences, University of Ostrava - 30. dubna 22, 701 03 Ostrava, Czech Republic, EU
\textsuperscript{4} Faculté des Sciences, Université du Maine - 72085 Le Mans Cedex 9, France, EU
\textsuperscript{5} Centre of Excellence IT4Innovations and Department of Applied Mathematics, VŠB - Technical University of Ostrava - 17. listopadu 15, 708 33 Ostrava, Czech Republic, EU
\textsuperscript{6} LCPQ and UMR5626 du CNRS, IRSAMC, Université de Toulouse - 118 route de Narbonne, 31062 Toulouse Cedex, France, EU

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Abstract – A novel multiscale method introducing radiative decay in realistic simulations of complex systems involving metastable states is proposed in order to address the competition between non-radiative and radiative processes. Specific implementation of the proposed method is used in a case study of the post-ionization fragmentation of heavier rare-gas tetracomplexes considered for very long times. The present multiscale approach allows to take into account the non-adiabatic dynamics typically in tens of picoseconds as well as radiative decay typically in the microsecond regime. Agreement with experimental findings that mainly monomer ion fragments are produced is found here for the first time for \( \text{Kr}_4^+ \) and to some extent also for \( \text{Xe}_4^+ \).

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Introduction. – Theory of clusters and molecular complexes faces various challenges. These systems are usually excited by photons or collisions, then evolve on a manifold of excited electronic states with many degrees of freedom involved, and usually fragment \cite{1}. In experiments, these fragments are analyzed in size and other parameters using, \textit{e.g.}, time-of-flight (TOF) techniques. For the theoretical description of the fragmentation dynamics, where non-adiabatic transitions are important, various hybrid quantum-classical methods have been developed, mainly based either on the mean-field \cite{2–4}, or on the surface-hopping approach \cite{5}. Recently we have proposed a combination of these two approaches introducing periodic decoherence into the mean-field approach, and have demonstrated that the new method gives promising results \cite{6}. The “fast” dynamics step which does not include radiative process (\textit{dark dynamics}) can thus be nowadays treated efficiently for rather complex systems. However, because the fast electronic dynamics must be treated carefully, typical time steps are about tenths of femtosecond and integrated trajectories can usually be expanded only up to tens or hundreds of picoseconds, but not much more, due to computational demands. However, experimental time scales are much longer, typically microseconds or more \cite{7–9}, and this poses a big challenge on the theory. Consequently, methods for a multiscale treatment of molecular dynamics, spanning time scales from picoseconds up to microseconds, have been proposed recently in various fields \cite{10–15}, usually leaning on an assumption that the fast, picosecond dynamics brings the system to the electronic ground state and internal conversion is achieved. However, it was demonstrated experimentally and theoretically that molecular systems may survive for a long time (microseconds or longer) after the initial excitation trapped in an excited electronic state. In that case, after the faster dark dynamics phase,
slow radiative decay is expected to play an important role, as shown experimentally for the dissociation of metastable rare-gas dimers [7–9], trimers [16,17], and larger clusters [18–20]. This interplay between non-radiative and radiative processes (representing two important decay mechanisms) is considered here for the first time in a realistic simulation.

Method outline. – In this work, we propose a hybrid multiscale dynamics scheme comprising generally the following sequence of steps:

1) preparing the statistical ensemble of initial states (typically excited states) of the system under study;

2) employing an appropriate non-adiabatic dynamics model for the initial, fast non-radiative (“dark”) phase spanning times up to the appropriately chosen $t_{DD}$, during which saturated population of metastable products is formed; the output of this step is a representative statistical ensemble of system states resulting from non-radiative phase;

3) calculation of rate constants for relevant slow processes (typically relaxation through radiative transitions or long-time non-radiative de-excitation processes) for the ensemble prepared in the preceding step and for each channel to be considered for $t \geq t_{DD}$;

4) analysis the stability of products, which can be formed through the each channel considered in the previous step; and subsequent determination of type of each final stable product by the energetic considerations or through an additional dark dynamics simulation;

5) evaluation of the final products statistics through the kinetic rate theory.

In step 2) (and 4)), the hemiquantal dynamics considering a large enough number of adiabatic electron states will be usually used. Typically, many trajectories must be calculated and, as the output, a representative set of nuclear configurations and momenta as well as electronic amplitudes must be obtained to be used for simulation times $t \geq t_{DD}$. The term “representative statistic sample” accentuated in description of step 2) means that the results of steps 2)–4) should be in general case averaged for each trajectory over a range of $t_{DD}$ corresponding to the longest vibrational period of the metastable products. The computation of the rate constants in step 3) needs an appropriate model to evaluate dipole moments for radiative transitions, or, if non-radiative processes are included, an approximation for transition probabilities, e.g., Tully’s algorithm [5].

In the present study, we demonstrate the good performance of a particular implementation of the proposed method in the specific case of the fragmentation of krypton and xenon tetraters after electron-impact ionization.

Case study — rare-gas clusters. – In ionized rare-gas clusters, the positive charge localizes on a strongly bound sub-unit, mainly trimer or dimer, with the remaining atoms bound to this ion core weakly via polarization and dispersion forces, and the cluster, although formed of identical atoms, becomes heterogeneous like in solvated species [21–24]. These clusters are thus representatives of complex systems with heterogeneous bondings. The equilibrium geometries of neutral and ionic rare-gas clusters are different and the ionization leads, in addition to the electronic excitation, to a strong vibrational excitation. The spin-orbit coupling is also important, particularly for krypton and xenon. There is a qualitative discrepancy between the fragmentation patterns observed for krypton and xenon experimentally and those predicted by theory [6,25,26].

As shown by recent experiments, after ionization, small argon clusters fragment both in ionic monomers and dimers, while almost exclusively monomer fragments are detected for krypton and xenon clusters [26,27]. Theory, on the other hand, strongly overestimated the production of ionic dimer fragments. For the trimers, for example, theoretical studies reported both monomer and dimer fragments for all rare gases, in contradiction with the experimental findings, which led us recently to a proposal of a new dynamical method into which quantum decoherence was introduced [6]. Even though this enhanced approach yields quantitatively accurate predictions for trimers, it fails already for tetraters. This is mainly due to metastable, electronically excited fragments emerging from the decay of ionized tetraters. Since electronically metastable fragments have been detected in large extent in experiments and other simulations of both post-ionization fragmentation and photodissociation, we decided to introduce radiative electronic transitions in the simulations.

In the specific case of rare-gas tetraters, the methodology proposed in this work is employed as follows.

1) Configurations and velocities of neutral clusters are sampled at a given internal energy using microcanonical Monte Carlo and molecular dynamics techniques, the ionization by fast electrons (70 eV in experiment) is modeled for each nuclear configuration as an instant vertical transition to a particular adiabatic electronic state of the ionized cluster, the interaction in the ionized cluster is described by a widely used implementation of diatomics-in-molecule model [28].

2) Non-radiative, dark dynamics, are simulated by a hemiquantal dynamical method MFQ-AMP/S [6], up to $t_{DD} = 600$ ps. 3) Rate constants for each radiative transition are evaluated from the transition dipole moments calculated within an extended model.
Multiscale non-adiabatic dynamics with radiative decay

Table 1: Relative abundances (%) of ionic fragments obtained from 600 ps molecular dynamics calculations (dark dynamics columns) and from subsequent radiative transition modelings performed for $t = 1 \mu s$, $t = 10 \mu s$, and $t \rightarrow +\infty$ (radiative decay columns). The abundances of $Rg^+$ and $Rg^+_2$ in the radiative decay columns do not necessarily sum up to 100% due to long-lived trimers and tetramers. The starting levels in the first column represent electronic states immediately after vertical ionization.

| Starting level | Dark dynamics 600 ps | Radiative decay 1 µs | Radiative decay 10 µs | Radiative decay $\infty\mu s$ |
|----------------|----------------------|----------------------|----------------------|----------------------|
|                | $Rg^+$  | $Rg^+_2$  | $Rg^+_3$  | $Rg^+_4$  | $Rg^+$  | $Rg^+_2$  | $Rg^+_3$  | $Rg^+_4$  | $Rg^+$  | $Rg^+_2$  | $Rg^+_3$  | $Rg^+_4$  |
| KRYPTON        |         |           |           |           |         |           |           |           |         |           |           |           |
| 9              | 7       | 2        | 30       | 61       | 29      | 23       | 52       | 47       | 53      | 47        |           |           |
| 10             | 3       | 6        | 91       | 0        | 35      | 12       | 77       | 22       | 78      | 22        |           |           |
| 11             | 2       | 58       | 40       | 0        | 44      | 33       | 86       | 13       | 88      | 12        |           |           |
| 12             | 7       | 78       | 15       | 0        | 38      | 52       | 71       | 27       | 82      | 18        |           |           |
| XENON          |         |           |           |           |         |           |           |           |         |           |           |           |
| 9              | 0       | 0        | 0        | 100      | 1       | 86       | 1        | 99       | 1       | 99        |           |           |
| 10             | 0       | 0        | 12       | 88       | 9       | 53       | 11       | 89       | 11      | 89        |           |           |
| 11             | 0       | 0        | 25       | 75       | 22      | 39       | 28       | 72       | 28      | 72        |           |           |
| 12             | 1       | 2        | 97       | 0        | 75      | 7        | 92       | 8        | 92      | 8         |           |           |

point-charge approximation [29]. 4) An additional 200 ps dark dynamics simulations or a computationally cheaper energetic analysis are performed to investigate fragments stability. 5) Fragments abundances are re-adjusted for selected radiative decay times. (For details, see also review in the supplementary material [30].)

Initial vibration excitation of the neutral precursor is close below the dissociation energy [6,28]. No direct experimental information about the electronic states of the ionized clusters is known, hence we investigate all adiabatic electronic states relevant for electron-impact experiments [7–9,31,32] one by one. For an ionic cluster containing $N$ atoms, $3N$ doubly degenerate electronic states are available within the interaction model we use (diatomics-in-molecule models [33] with the spin-orbit coupling included [34]). These $3N$ states are divided into two groups. The lower group (the ground state and lowest $2N−1$ excited states) correlate asymptotically to ground-state ($2P_{3/2}$) atomic ions while the upper group ($N$ highest excited states) dissociate to excited atomic ions ($2P_{1/2}$). As shown previously [6,17], non-adiabatic transitions between the two groups are not very probable for krypton and even less for xenon. From the twelve states for krypton and xenon ionic tetramers (denoted L01–L12), the lower group comprises eight of them (L01–L08) and the upper group the remaining four (L09–L12). We ran 500 trajectories for each electronically excited state of krypton and xenon tetramers from the upper family of states. As emphasized by Fedor et al. [7–9] mainly these highly excited states are populated upon ionization because of favorable Franck-Condon factors. The four highest excited states of the ionic tetramers present regular tetragonal equilibrium structures with inter-atomic distances comparable to the distance in neutral tetramers, which should lead to favorable Franck-Condon factors. For example, for krypton this distance is 4.04 Å for the neutral cluster while for the four highest excited states of the ionic cluster they range between 3.9–4.4 Å. It should be emphasized that for the lower excited states similar structures can also be found as local minima on the respective PESs, but with much shorter distances and, therefore, with much smaller Franck-Condon factors.

For the radiative transition from state $I$ to a lower state $J$ we have used the first order transition rates,

$$
\Gamma_{IJ} = \frac{1}{3\pi\varepsilon_0 \hbar^4 c^3} (E_I − E_J)^3 |\mu_{IJ}|^2
$$

(1)

with the transition dipole moments, $\mu_{IJ}$, calculated within the point-charge approximation [21] amended by polarization effects [35] as described in ref. [29]. Since the $I → J$ transitions can be considered parallel first order processes, the occupation numbers of states, $n_I$ and $n_J$, obey first order kinetic equations leading finally for $n_I(0) = n_{Io}$ and $n_J(0) = 0$ to

$$
n_J(t) = n_{Io}(1 − e^{−Γt})\Gamma_{IJ}/Γ, \quad n_I(t) = n_{Io}e^{−Γt},
$$

(2)

where $Γ = \sum_{K=1}^{I-1} \Gamma_{IK}$. After decay, each trajectory is weighted by these occupation numbers for final statistical averaging. Note: We have found from tests, that the final results are only marginally sensitive to the choice of $t_{DD}$ and have thus decided to avoid in the studied case the averaging over the range of vibration periods.

Results and discussions. – Here we focus mainly on the fragmentation ratios and on the electronic states reached as a function of time. More detailed results will be published elsewhere. The main results are reported in table 1 and illustrated for krypton in figs. 1 and 3. It is clear from the table and fig. 1 that large fragments prevail after the dark dynamics, particularly for xenon. These results remarkably differ from the experimental finding that only monomer ionic fragments originate from post-ionization fragmentation of krypton [27] and xenon [26].
Fig. 1: (Color online) Short-time evolution of relative abundances (%) of ionic fragments: monomers (solid line), dimers (dashed line), trimers (dash-dotted line) and tetramers (dotted line) produced from adiabatically ionized krypton tetramer during the dark fragmentation dynamics step. Labels L09–L12 denote the starting levels, i.e. adiabatic electronic levels immediately after ionization. For comparison, relative abundance of ionic monomer fragments recorded experimentally (96.1%) [27] is added as a horizontal dotted line (experiment Kr$^+$).

Noteworthy, the long-time radiative decay leads to a completely different picture. Even after 1 $\mu$s of radiative decay, most of the tetramers and trimers resulting from the initial dark dynamics undergo a rapid fragmentation, and convergence of the radiative data is almost reached at 10 $\mu$s. Depending on the experimental conditions some specific time window is investigated in each particular experiment, usually a few $\mu$s, and we see in table 1 that the relative abundance of the fragments may be sensitive to this time window. Let us emphasize that the numbers of table 1 are basically converged with respect to $t_{DD}$, while in a previous study using a similar semi-classical approach [10] calculations were stopped at 10 ps and, moreover, full internal conversion was assumed. In addition, quantum decoherence was only partly included in that study and the spin-orbit coupling was ignored.

For the analysis of fragments resulting from the post-radiative decay, two approaches have been considered: a) an additional 200 ps dark dynamics simulation carried out with the initial electronic state corresponding to that reached after the photon emission (these states have been weighted by the occupation numbers given by eq. (2), and b) energetic analysis of the system after the radiative transition assuming that the system will fragment via the highest energetically open channel (no dynamical calculation).

Interestingly, the two approaches lead to almost identical or only negligibly different (< 5%) fragments abundances and, therefore, only computationally cheaper data obtained from the energetic analysis (approach b)) are reported in table 1 as well as in fig. 3. The good performance of the approximate approach (b)) can easily be understood if we take into account that the radiative decay preferably drives the system to a strongly repulsive state (L08) which rapidly fragments towards the highest accessible channel. This has not a general validity, however, as a large part of the internal energy is taken off by the emitted photon and the internal conversion may now be more probable than before the radiative transition.

The time dependence of the relative abundances of the ionic fragments calculated for the dark dynamics phase are illustrated for krypton in fig. 1 together with experimental abundance of Kr$^+$. After a few hundred picoseconds, there is not much change in the curves and a large amount of metastable ionic trimers and tetramers remain trapped in one of the highest four electronically excited states, mainly L09 as shown for $t_{DD}$ in fig. 2. Internal conversion is not effective here because of very

Fig. 2: (Color online) Abundances of electronic states of Kr$^+$ (left columns) and Xe$^+$ (right columns) after the dark dynamics simulation step ($t_{DD} = 600$ ps) starting from levels L09–L12.
weak non-adiabatic couplings with the lower electronic states. Clearly, assuming the efficiency of the internal conversion leads to a wrong physical picture. We got similar results also for xenon. Radiative decay has a huge effect on fragments abundances, as illustrated for krypton in fig. 3. The time scales are now three or more orders of magnitude larger since the radiative decay is much slower than initial dark dynamics, nevertheless, convergence is almost reached here at about 10 µs. Noteworthy, the ionic monomer fragments largely prevail now, in a qualitative agreement with the experiment, with the dominating radiative transition going from the lowest state of the upper group of states (L09) to the highest states of the lower group (L08 and L07).

Let us now discuss the range of applicability of our method to other cases. Three factors contribute to make the method work well here: a) there is little internal conversion during the initial dark dynamics and metastable species are massively formed; b) the radiative decay is orders of magnitude slower than the dark dynamics, so there is no strong competition between non-radiative and radiative processes; and c) the post-radiative fragmentation is fast and even simple energetic considerations suffice to predict fragmentation ratios. Concerning the first point, if metastable species are not involved, obviously there is no need to consider the radiative decay. However, metastable species and radiative decay are rather important in ionic rare-gas clusters and a wide variety of molecular systems where internal conversion is not achieved. The time scales are the major difficulty. They are often very different for the dark processes and radiative decay. Taking benefit of this difference, we propose a sequential approach here: for a large number of trajectories the dark dynamics is stopped at a sufficiently long time \( t_{DD} \) at which the radiative decay starts as a purely electronic evolution. However, if radiative and non-radiative decay times are comparable and internal conversion competes with the radiative decay, the situation may be more involved and the present approach may meet difficulties. In that case, a natural, but computationally expensive extension of the method can be found among strategies combining radiative and non-radiative electronic transitions in dynamical simulations. Another difficulty with the present approximation is that, for larger systems, evaporative cooling could take place after radiative decay instead of a rapid fragmentation typical for the systems investigated in this work. Then, the present method can be combined with the recently proposed multiscale dynamics scheme where the description over long time scale for the final evaporative cascade is effectively taken into account via a kinetic Monte Carlo approach [10].

Conclusions. – In conclusion, we propose here a multiscale dynamics approach combining sequentially non-radiative and radiative dynamics and allowing an efficient modeling of processes involving electronically metastable species over a very long time. The approach gives rather encouraging results if applied to the fragmentation of krypton and xenon tetramers after ionization by taking into account metastable states with radiative lifetimes of the order of microseconds in addition to the non-radiative non-adiabatic dynamics with typical times of more than three orders of magnitude shorter (tens of picoseconds). Agreement with the experimental finding that mostly monomer ions are produced has been obtained for the first time for Kr\(_4^+\) (all considered levels) and to some extent also for Xe\(_4^+\) (the highest level).
More generally, the presented multiscale scheme can be used for various systems evolving through fast non-radiative processes into metastable products. The necessary condition for such modeling is that a reliable interaction model providing a sufficiently large manifold of excited electronic states is available as well as an appropriate model for transition dipole moment evaluation. The model can be further improved by combining non-radiative and radiative electronic transitions during dynamical calculations or in evaluation of slow phase and including the treatment of evaporative cooling.

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