

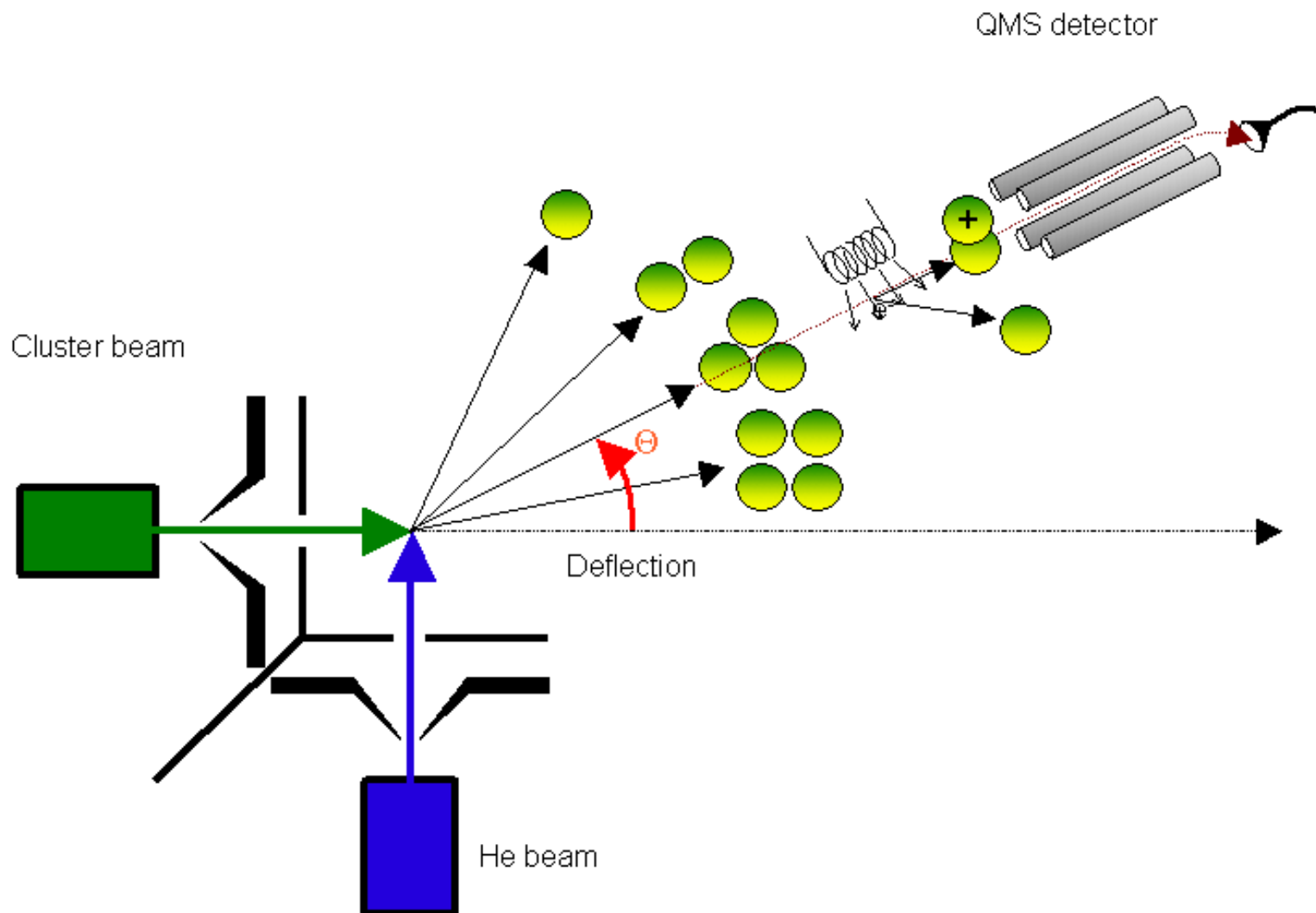


Fragmentation Dynamics of Ionized Rare-Gas Clusters: New Achievements

David Bonhommeau

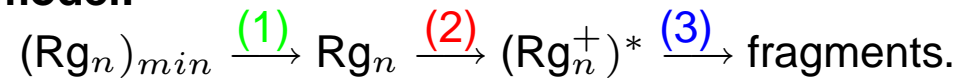
Department of Chemistry, University of Minnesota

Principle of the Experiment (U. Buck, M. Farnik)



Theoretical Model (I)

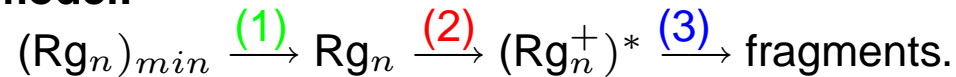
- Principle of the model:



(1) ZPE, (2) Vertical Ionization (≈ 70 eV), (3) Dissociation.

Theoretical Model (I)

- Principle of the model:



(1) ZPE, (2) Vertical Ionization (≈ 70 eV), (3) Dissociation.

- Rg_n^+ potential-energy surfaces: The Diatomics In Molecules (DIM) model

$$H = \sum_A \sum_{B>A} H_{AB} - (N - 2) \sum_A H_A$$

- ★ Generation of $3n$ potential-energy surfaces (3 by atom) for Rg_n^+ clusters in the basis of Rg^+ effective p orbitals.
- ★ Method more realistic than pair potentials: a matrix is built, diagonalized and the charge can therefore be delocalized.
- ★ Method less time consuming than ab initio calculations.
- ★ Method proven to be suitable for rare-gas clusters (except He).
- ★ Method only based on the knowledge of Rg_2 and Rg_2^+ potentials but whose accuracy may be improved (ID-ID interactions, SO coupling).

Theoretical Model (II)

- **Multisurface Dynamics: The Molecular Dynamics with Quantum Transition (MDQT) method of Tully**

- ★ MDQT, aka MDET (Molecular Dynamics with Electronic Transition) or TFS (Tully's Fewest Switches), is a surface-hopping method.
- ★ Dynamics performed in the adiabatic representation.
- ★ Nuclei are treated classically (Hamilton equation of motion for positions and linear momenta) and moves on one adiabatic surface at a time.
- ★ Electrons (or the hole) is treated quantum mechanically (Schrödinger Equation).
- ★ Nonadiabatic transitions, or “hops”, between surfaces j and k governed by a hopping probability $g_{jk} = f(\dot{\mathbf{R}} \cdot \mathbf{d}_{jk}, c_j, c_k)$.
- ★ Velocities are adjusted at a hopping event to ensure total energy conservation.

Theoretical Model (II)

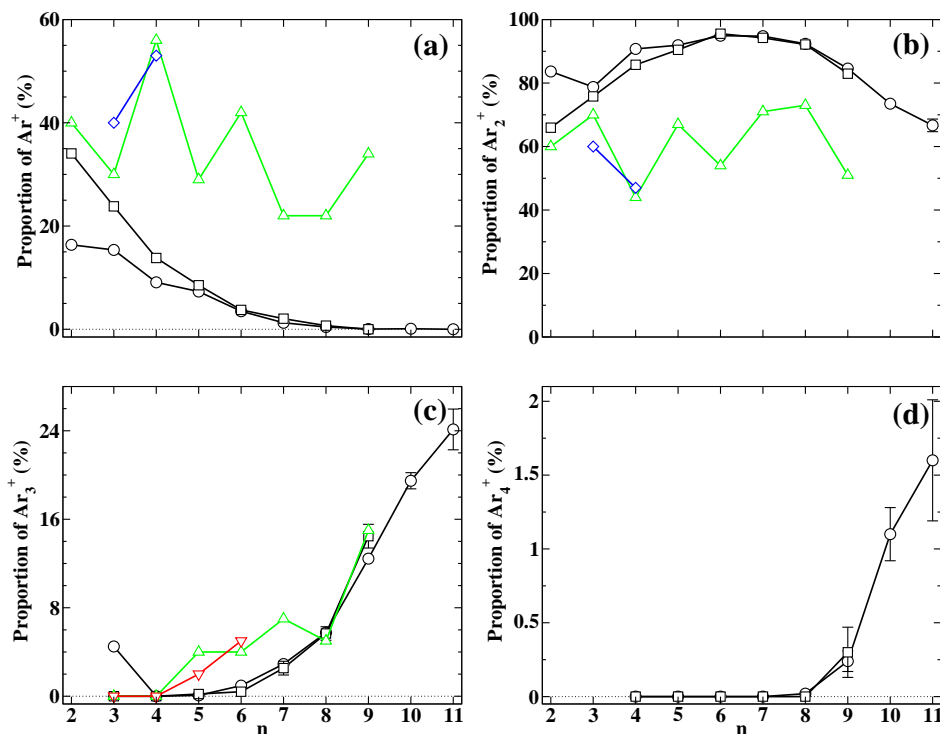
- **Multisurface Dynamics: The Molecular Dynamics with Quantum Transition (MDQT) method of Tully**

- ★ MDQT, aka MDET (Molecular Dynamics with Electronic Transition) or TFS (Tully's Fewest Switches), is a surface-hopping method.
- ★ Dynamics performed in the adiabatic representation.
- ★ Nuclei are treated classically (Hamilton equation of motion for positions and linear momenta) and moves on one adiabatic surface at a time.
- ★ Electrons (or the hole) is treated quantum mechanically (Schrödinger Equation).
- ★ Nonadiabatic transitions, or “hops”, between surfaces j and k governed by a hopping probability $g_{jk} = f(\dot{\mathbf{R}} \cdot \mathbf{d}_{jk}, c_j, c_k)$.
- ★ Velocities are adjusted at a hopping event to ensure total energy conservation.

- **Results:**

- ★ That can be compared to experiments: Ionic fragment abundances, cluster internal energies.
- ★ That cannot be experimentally obtained: parent ion or transient species lifetimes, neutral fragment abundances, percentage of long-lived trajectories, effect of the SO coupling.

Ar_n^+ clusters: comparison to experiments



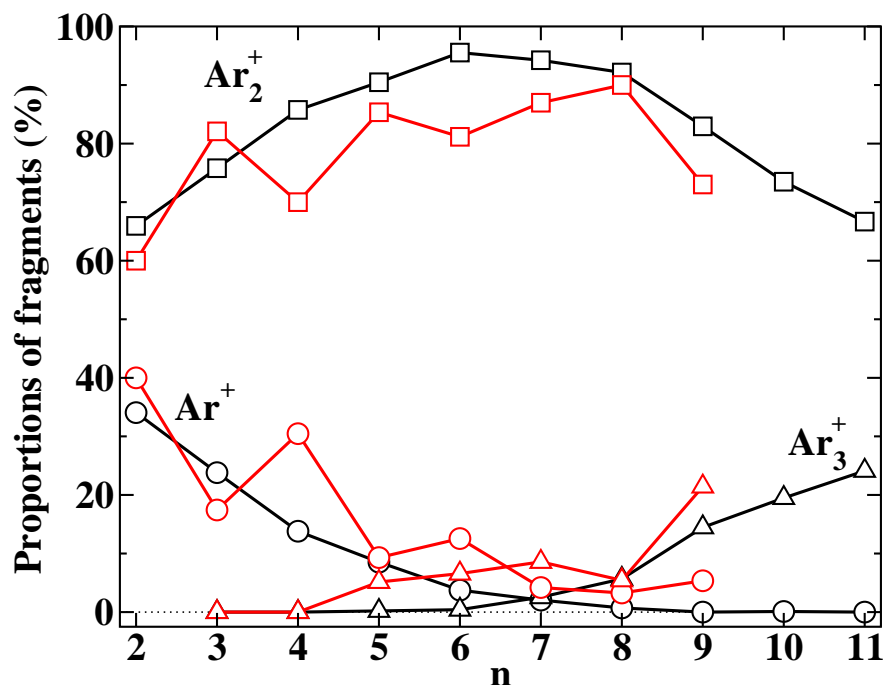
- Circles/Squares: our work without/with SO coupling (2006).
- Upward triangles: Lohbrandt et al. (2000).
- Downward triangles: Buck et al. (1986).
- Diamonds: Bastida et al. (1996).

Ref: D. Bonhommeau et al., J. Chem. Phys., **124** (18), 184314 (2006).

Possible source of discrepancies

- **Heating of the neutral precursor: No**, since such a heating has almost no effect on fragment abundances.
- **Contribution of long-lived trajectories: No**, since they are too rare for $n \leq 9$ to explain the discrepancy to experiment.
- **Selective ionisation of some highly excited electronic states: No**, since a selective ionization would not lead to as many Ar^+ fragments for $n = 9$ and the electron-impact ionization cross section of s orbitals is 20 to 30 times lesser than for p orbitals.
- **Secondary ionisation of neutral fragments: Possible**, since characteristic times of the dynamics are of the order of the picosecond whereas neutral clusters remain $\approx 1 \mu\text{s}$ in ionization chamber.
- **Experimental resolution and/or theoretical approximations: Possible**. In particular, old experiments were found not to be sufficiently resolved.

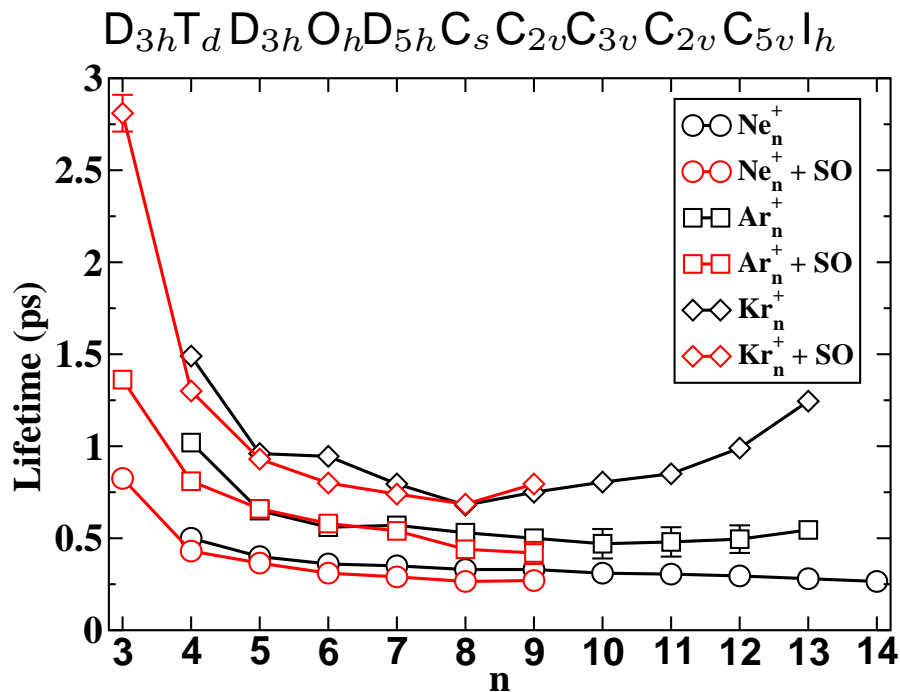
New investigation of Ar_n^+ dissociation



- Our work (2006) and **experiment by Buck (2006)**.
- Qualitative and quantitative agreement for all the cluster and fragment sizes.
- Extension to krypton and xenon clusters: discrepancies to experiment are much more marked for krypton and xenon clusters with a propensity to form monomers ($\geq 90\%$) that is not theoretically found.

Ref: D. Bonhommeau et al., Int. Rev. Phys. Chem., **26** (2), 353-390 (2007).

Rg⁺ clusters: parent ion lifetimes



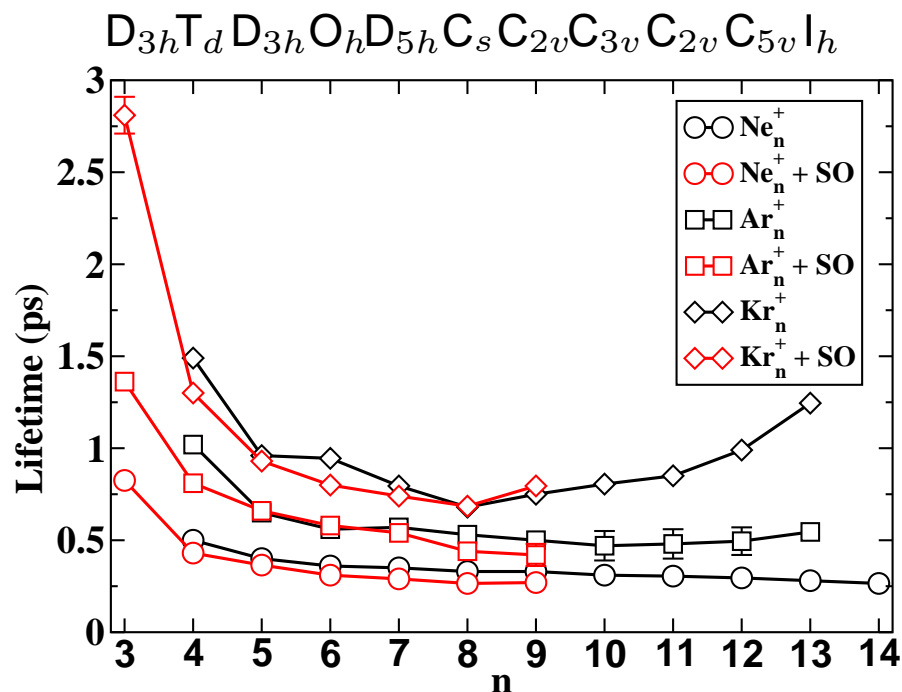
- ***n*-dependence:**

- ★ Decrease for Ne_{*n*}⁺, decrease and increase for Ar_{*n*}⁺ and Kr_{*n*}⁺.

- ★ Kr_{*n*}⁺: minimum for Kr₈⁺, maximum for Kr₄⁺ and Kr₁₃⁺, local maximum for Kr₆⁺.

- ★ Origin: symmetry of Kr_{*n*} neutral clusters, small ZPE of these clusters.

Rg⁺ clusters: parent ion lifetimes



- ***n*-dependence:**

- ★ Decrease for Ne_{*n*}⁺, decrease and increase for Ar_{*n*}⁺ and Kr_{*n*}⁺.

- ★ Kr_{*n*}⁺: minimum for Kr₈⁺, maximum for Kr₄⁺ and Kr₁₃⁺, local maximum for Kr₆⁺.

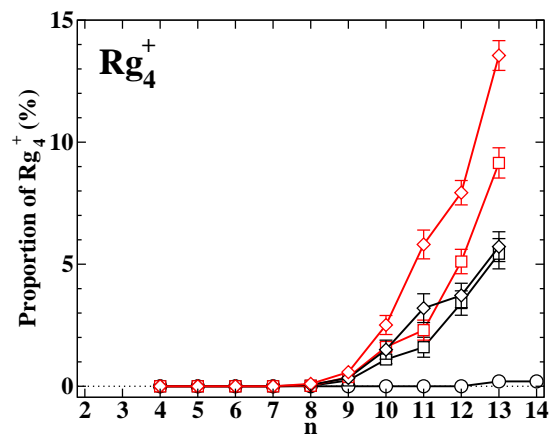
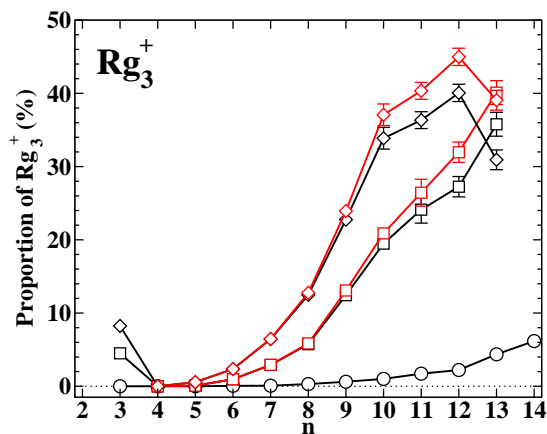
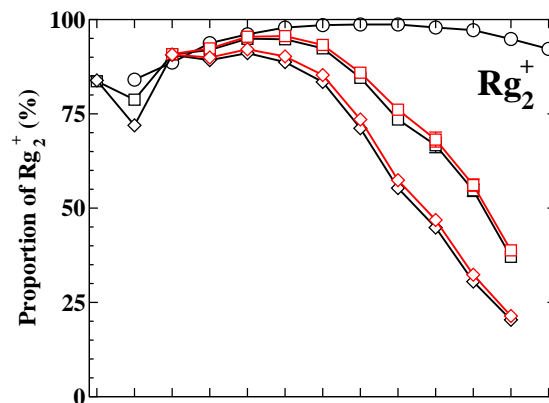
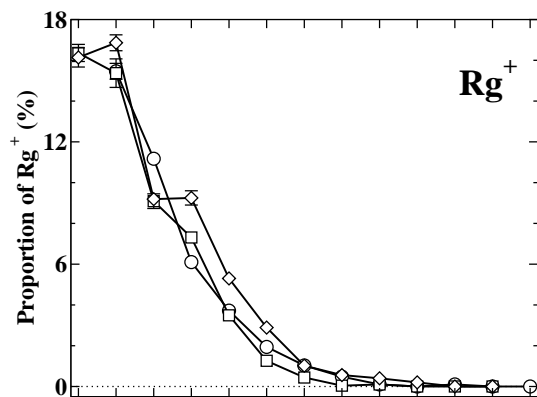
- ★ Origin: symmetry of Kr_{*n*} neutral clusters, small ZPE of these clusters.

- **Effect of the Spin-Orbit coupling:**

- ★ Decrease of lifetimes, especially for highly symmetric parent ions like Kr₆⁺.

- ★ Origin: some degeneracies are lifted, so more couplings, faster relaxation, and smaller lifetimes.

Rg_n^+ clusters: long-lived trajectories



- Ne (circles), Ar (squares) and Kr (diamonds) clusters.
- without SO coupling ($t_{lim} = 100$ ps).
- without SO coupling but the future of long-lived trajectories is considered ($t_{lim} = 10$ ns).

Multiscale dynamics: The case of Ar_n^+ (n=20-30)

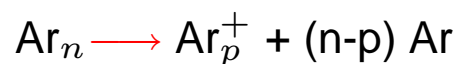
- **Method:**

1. Nonadiabatic dynamics (TFS method) for the internal conversion ($t \sim 1$ ps).
2. Molecular dynamics (MD) on the ground electronic state ($t \sim 1$ to 100 ps).
3. Phase Space Theory (PST) to model the production of monomers ($t \sim 1$ ms), collaboration with F. Calvo and P. Parneix.

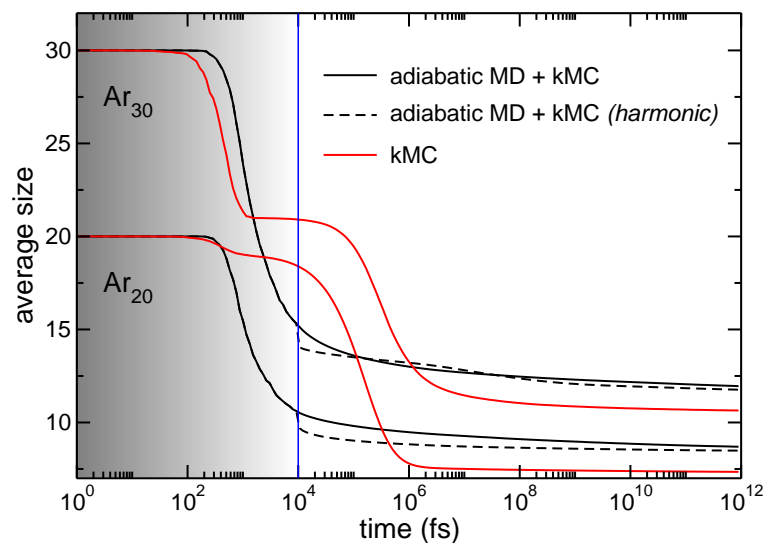
Multiscale dynamics: The case of Ar_n^+ ($n=20-30$)

- **Method:**

1. Nonadiabatic dynamics (TFS method) for the internal conversion ($t \sim 1$ ps).
2. Molecular dynamics (MD) on the ground electronic state ($t \sim 1$ to 100 ps).
3. Phase Space Theory (PST) to model the production of monomers ($t \sim 1$ ms), collaboration with F. Calvo and P. Parneix.



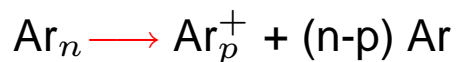
$n = 20, 30$ and $p = 9$ (for instance)



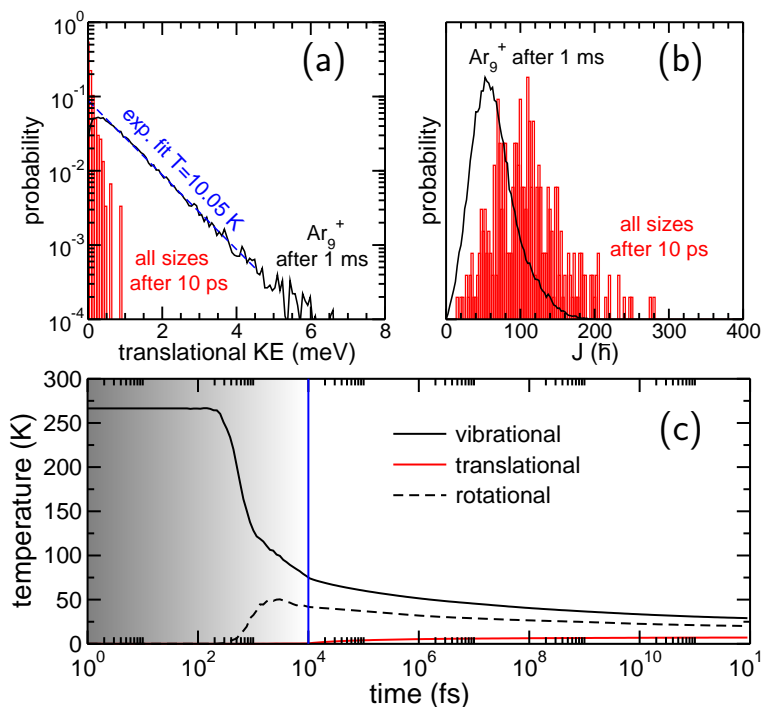
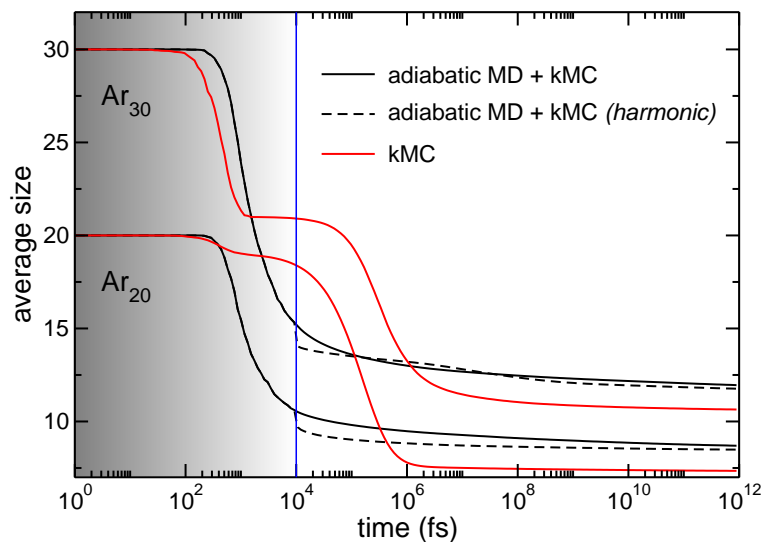
Multiscale dynamics: The case of Ar_n^+ ($n=20-30$)

• Method:

1. Nonadiabatic dynamics (TFS method) for the internal conversion ($t \sim 1$ ps).
2. Molecular dynamics (MD) on the ground electronic state ($t \sim 1$ to 100 ps).
3. Phase Space Theory (PST) to model the production of monomers ($t \sim 1$ ms), collaboration with F. Calvo and P. Parneix.



$n = 20, 30$ and $p = 9$ (for instance)



Ref: F. Calvo et al., Phys. Rev. Lett., **99** (8),083401 (2007).

Conclusion

- **The DIM/MDQT model used for rare-gas clusters allows to**

- ★ Find several results in qualitative agreement with experiments (extensive fragmentation, n value for the appearance of the first trimer fragments, etc...), and even in quantitative agreement for argon clusters.
- ★ Predict some results not experimentally reachable (parent ion lifetimes, effect of long-lived trajectories).
- ★ Model the internal conversion in multiscale fragmentation models that can be applied to large clusters and whose results can be directly compared to experiments.

- **Future work**

- ★ More carefully studying discrepancies between theory and experiments obtained for Kr and Xe clusters.
- ★ Using the multiscale model for other systems, other kind of excitation (photoionisation), etc ...

Acknowledgements

- **Collaborators:**

- ★ Dr Nadine Halberstadt (Université Paul Sabatier, Toulouse 3, France),
- ★ Dr Florent Calvo (Université Claude Bernard, Lyon 1, France),
- ★ Dr Pascal Parneix (Université Paris-Sud, Orsay, France),
- ★ Pr Udo Buck (Max-Planck Institut für Dynamik und Selbstorganisation, Göttingen, Germany),
- ★ Dr Michal Fárník (J. Heyrovský Institute of Physical Chemistry, Prague, Czech Republic).

- **Institutions:**

- ★ French government (grant),
- ★ IDRIS national supercomputing center (grant of computer time, France),
- ★ CALMIP regional supercomputing center (grant of computer time, Midi-Pyrénées, France).