Semiclassical modeling of an elementary chemical reaction inside helium nanodroplets

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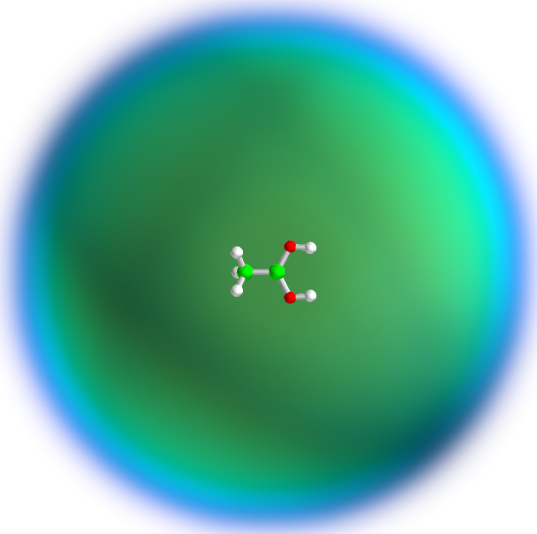
Introduction: Solvation in helium droplets

Helium binds *extremely weakly* to nearly anything
$\Longrightarrow$solvates any compound in very gentle manner, achieving ultracold ($<$1 K) temperatures



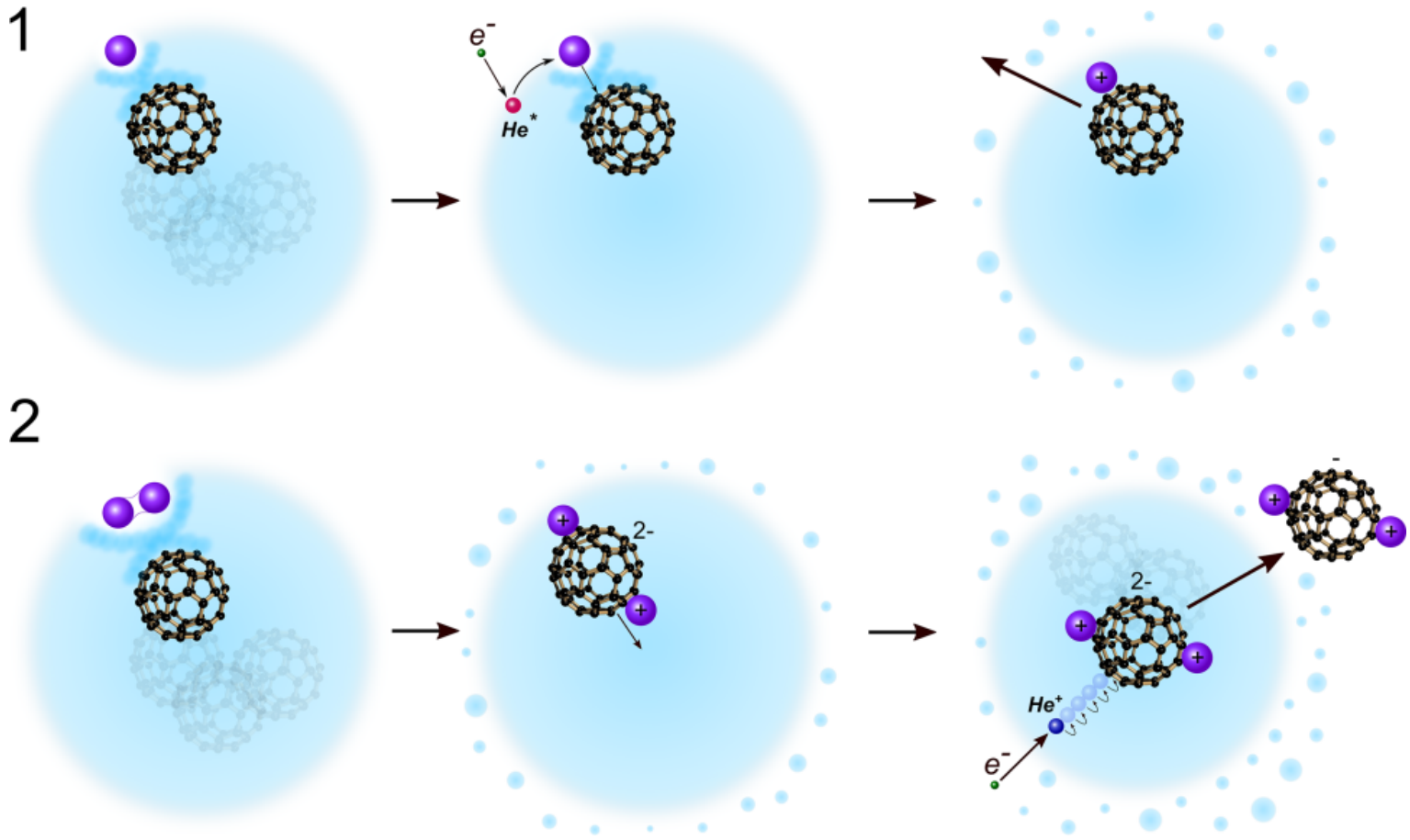
$\Longrightarrow$ideal for high-resolution spectroscopic characterization and for trapping exotic species

Helium nanodroplets of the bosonic element ^{4}He are also superfluid. *However*, enhanced localization near ionic impurities and possible formation of snowballs ($\simeq$1st shell is frozen)

Long-range electron transfer in HNDs

Alkali atoms and dimers M_k *resist solvation* in helium droplets

Experimental evidence for long-range electron transfer upon ionization of M_kC_{60} in helium droplets [Scheier group, JCP 145 (2016)]:



Outline of this presentation

→ *Carry out a detailed atomistic modeling* of the much simpler reaction,

$$(\mathrm{Na}^0 + \mathrm{Cl}^0)@\mathrm{He}_n \longrightarrow (\mathrm{Na}^+\mathrm{Cl}^-)@\mathrm{He}_k + (n-k)\mathrm{He},$$

→ *describe* the correct electronic states of the reactants (neutral) and products (ionized)

as well as nuclear delocalization effects

and, as far as possible, as a function of explicit time

In this purpose we

1. Design a reactive force field built upon the empirical valence-bond framework for NaCl embedded in the helium environment
2. Investigate the reaction triggered by some collision energy or upon partial evaporation of the solvent

Empirical valence-bond (EVB) modeling

The NaCl diatomic is modeled as a combination of its neutral (V_n) and ionized (V_i) states, a coupling term (V_c) being introduced to allow for both states to coexist continuously. Matrix of the simplified 2-state EVB model:

$$V_{\mathrm{NaCl}} = \begin{pmatrix} V_i & V_c \\ V_c & V_n \end{pmatrix},$$

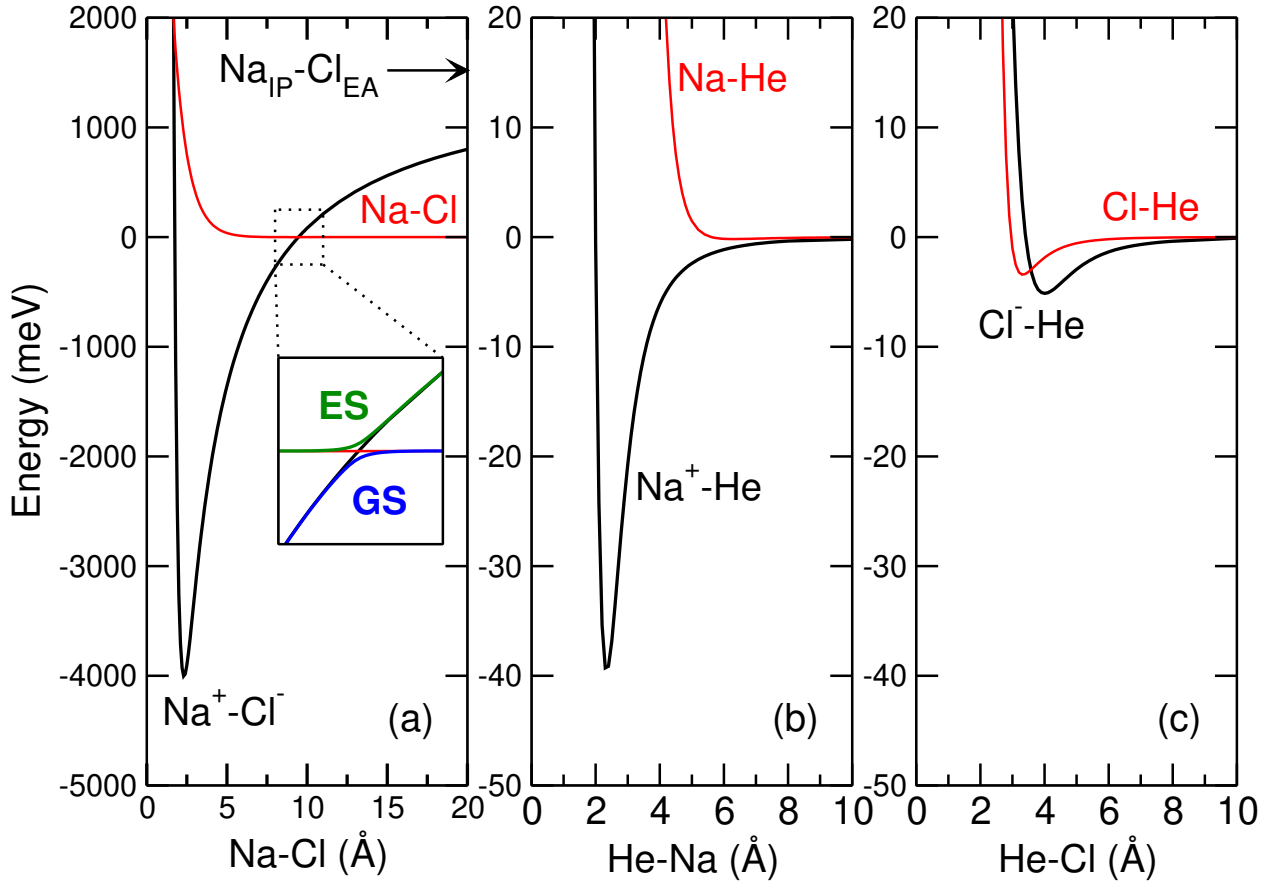
with V_i and V_c potentials shifted in the limit of infinite Na–Cl separation by 1.52 eV [IP(Na)-EA(Cl) difference]

In the presence of helium atoms, both states V_i and V_n are dressed by appropriate pairwise repulsion-dispersion terms, including those corresponding to He-He interactions. In the ionic state a polarizable contribution on helium atoms due to the charges on Na^+ and Cl^- ions is also added

The dynamics of Na, Cl embedded in helium nanodroplets is addressed through path-integral and ring-polymer molecular dynamics simulations

Potential energy curves

SCS-MP2 calculations at the complete basis set limit:

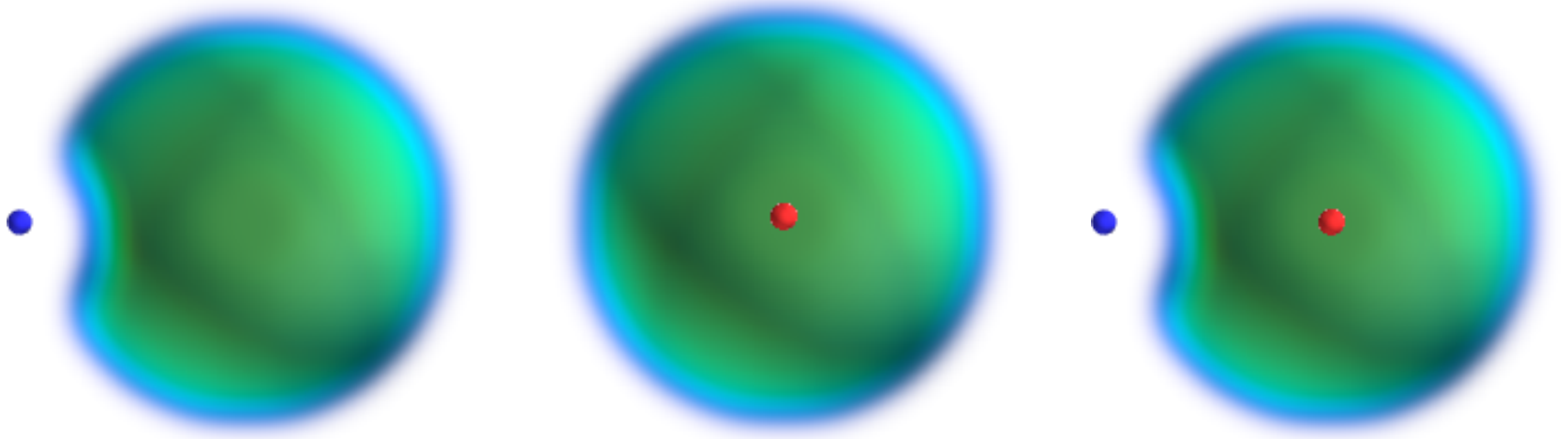


$\Longrightarrow$NaCl binds about 100 times more strongly than Na^+He, which binds about 100 times more strongly than NaHe

$\Longrightarrow$Of all interactions, NaHe is the weakest (about 1 cm^{-1}), followed by He_2 (7 cm^{-1}) [*but He_2 indeed exists*]

Equilibrium structures in the neutral state

Given the energetics, He_{1000} droplets doped with the (radical) Na^0 and Cl^0 atoms look like



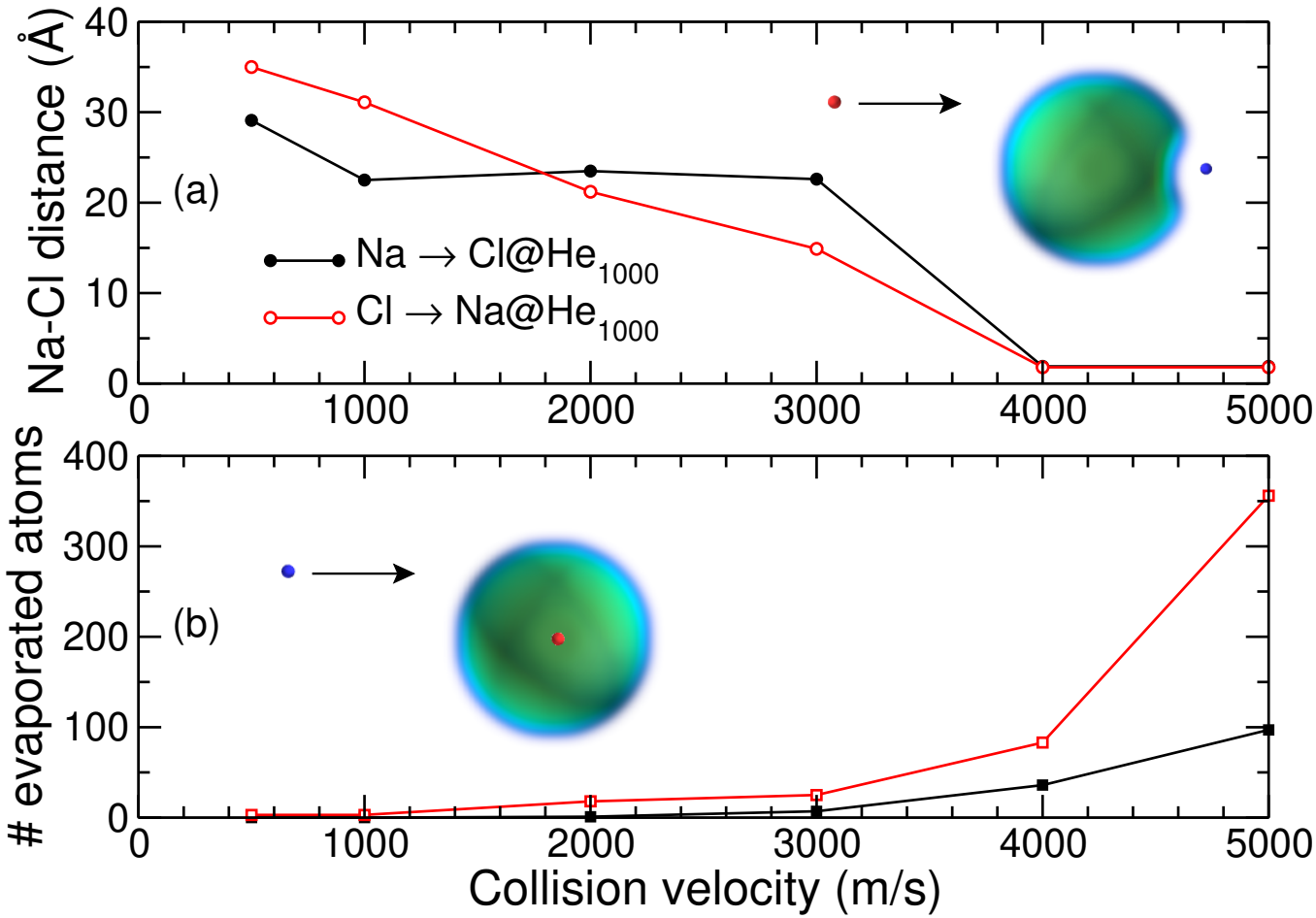
$Na^0@He_{1000}$ $Cl^0@He_{1000}$ $(Na^0+Cl^0)@He_{1000}$

$\Longrightarrow$Helium is a decent solvent for chlorine, but *very poor* for sodium

$\Longrightarrow$Ionic bond formation requires bringing the two atoms closer to each other, which we attempt to achieve through *collisions* or *solvent evaporation*, staying on the EVB ground state

Forming NaCl through collisions

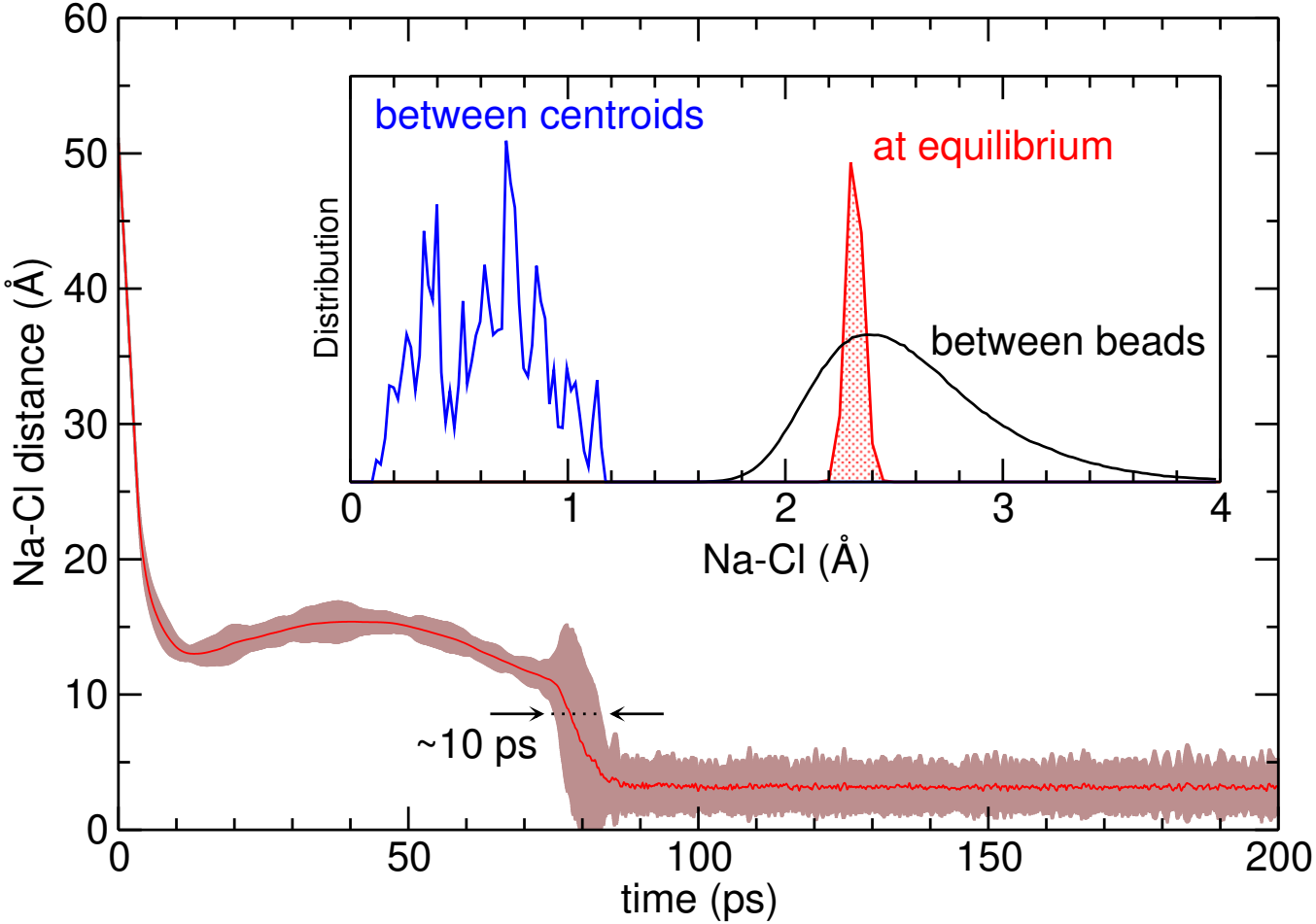
Landau-Zener criterion for adiabaticity satisfied for collision velocities below 16 km/s



$\Longrightarrow$significant velocities needed to pierce through the droplet

A CASE STUDY: $Na \rightarrow Cl@He_{1000}$

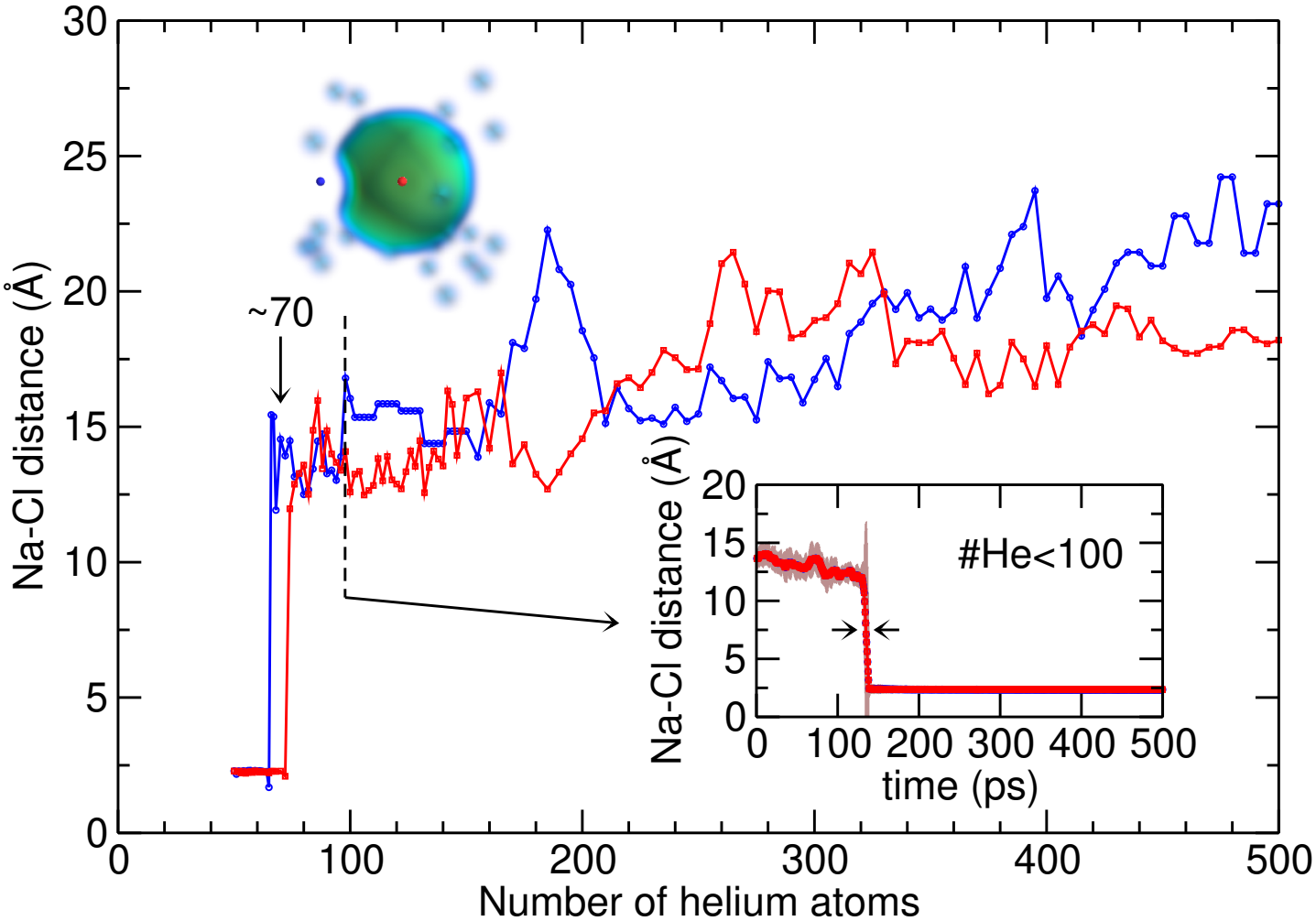
Analysis of a trajectory at 4000 m/s: distance fluctuations among the RPMD beads, in the final state and as a function of time:



$\Longrightarrow$*significant delocalization* enhanced by the solvent

$\Longrightarrow$the reaction takes about 10 ps but is initiated at the curves crossing (no evidence for long-range electron transfer)

Forming NaCl through solvent evaporation



$\Longrightarrow$without excess energy, NaCl is formed spontaneously once the droplet has shrunk enough down to 70 He atoms

$\Longrightarrow$the reaction appears also rather slow ($\sim$10 ps)

Concluding remarks

1. *Preliminary attempt* at characterizing a chemical reaction involving electron transfer, a quantum solvent and for two reaction partners with different solvation behaviors
2. Nuclear delocalization seems important even for NaCl, although no evidence for long-range transfer was identified in the path-integral simulations

Future directions

- Need for explicit electrons?
- Closer look at the transition toward the ionic state and the possible influence of snowballs
- Combine with TDDFT-fluid for the helium description, allowing to account for *exchange statistics*

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Thank you for your attention!