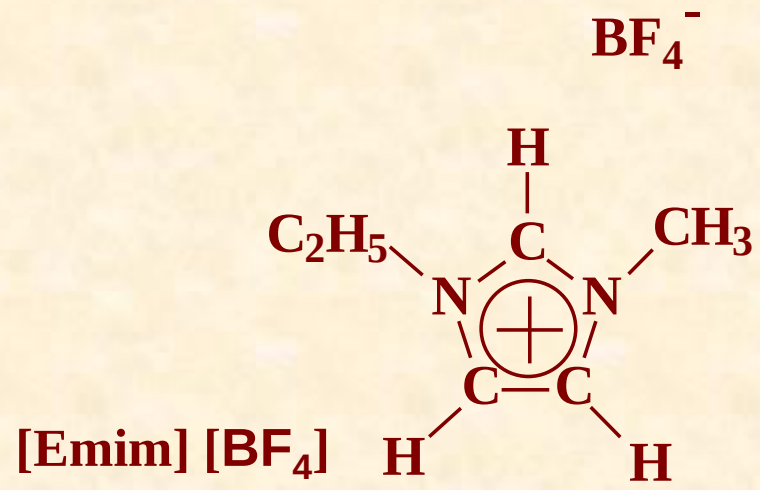
Solvation of Palladium Nanoparticles in Ionic Liquid: a QM/MM Study

Elena Zvereva, Sergey Katsyuba (IOPC)

Paul Dyson (EPFL)

Alexey Aleksandrov (EPU Paris-Saclay)

Ионные жидкости:



[Emim] $[BF_4]$

+ остаются жидкими в широком интервале температур ☺;

+ термически стабильны ☺;

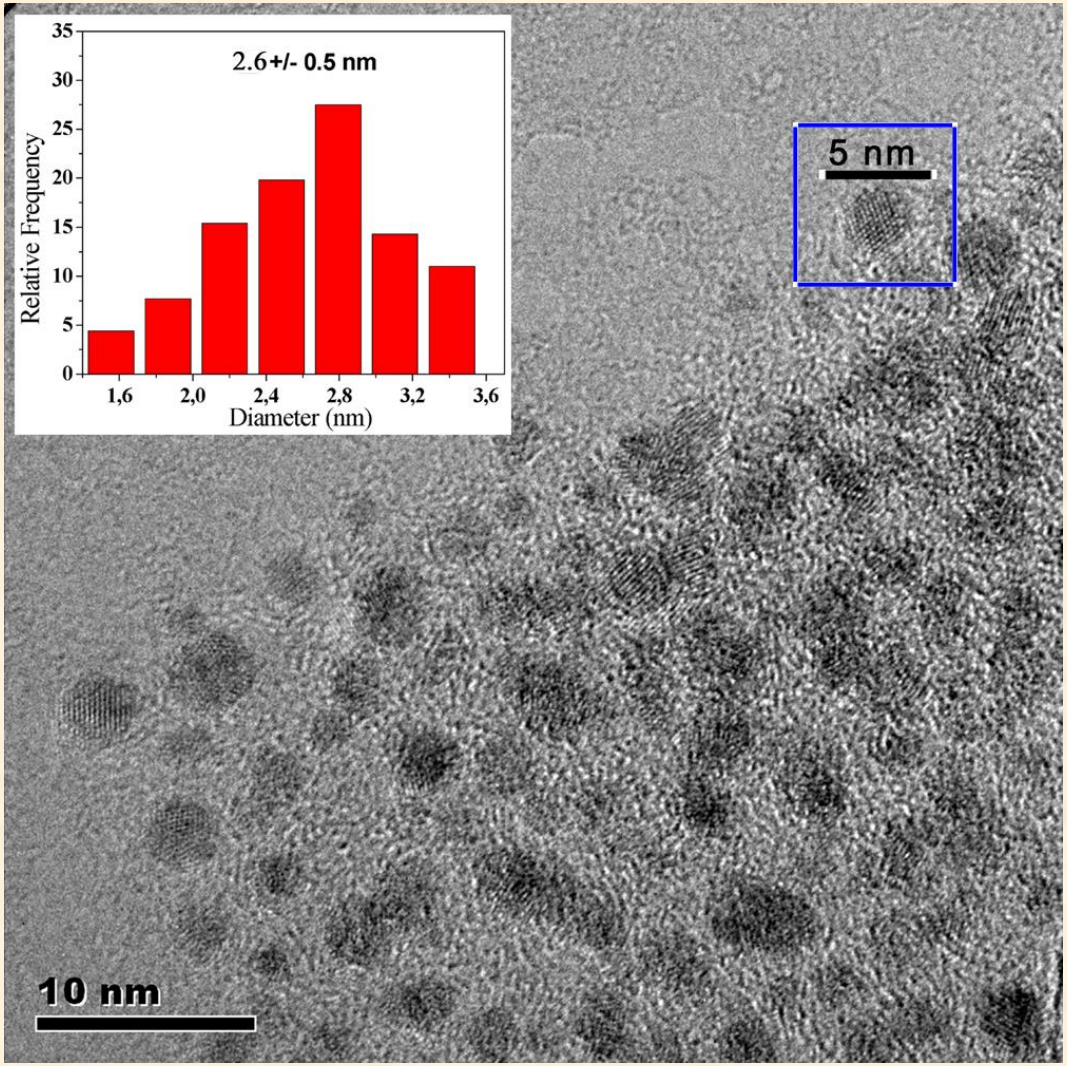
+ как правило, не воспламеняются ☺;

+ практически не испаряются ☺;

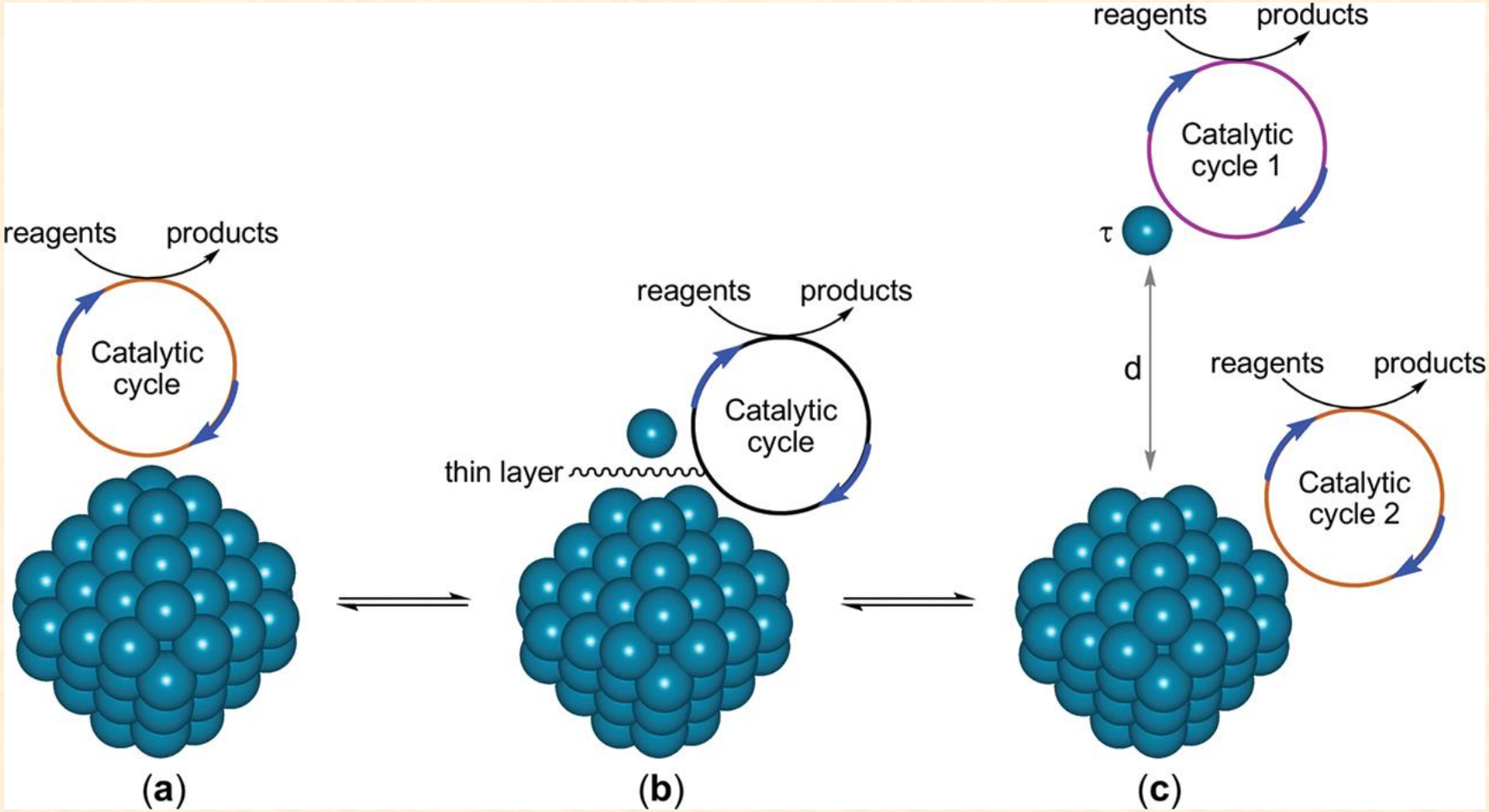
+ проводят электрический ток ☺;

…

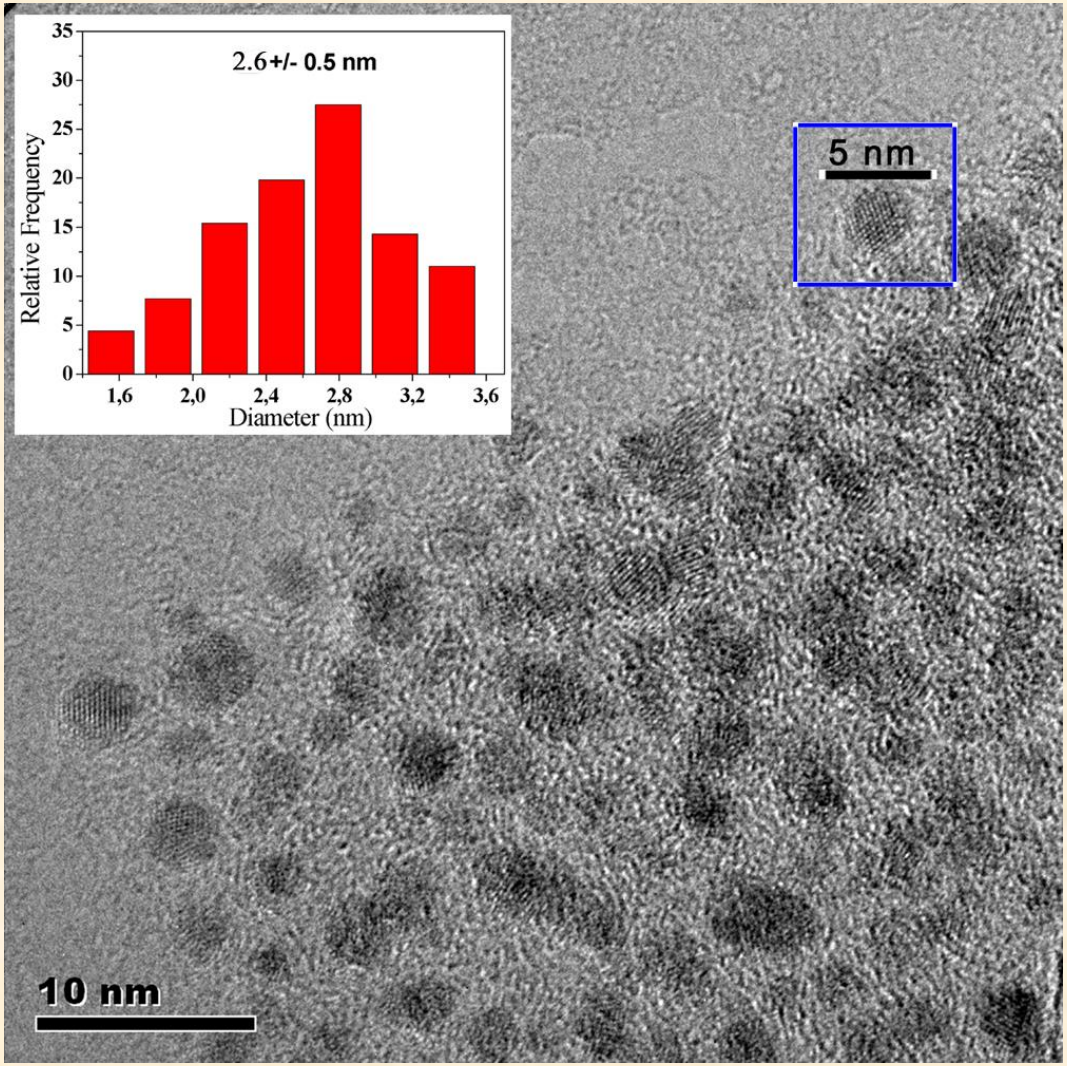
- обладают высокой вязкостью ☹



Typical TEM and HRTEM images of the Pd nanoparticles in [Emim][BF_4] and a size histogram of the Pd-NPs.
Katsyuba et al., *Chem. Phys. Chem*. **2012**, *13*, 1781



Organometallics, **2012**, 31, 1595.



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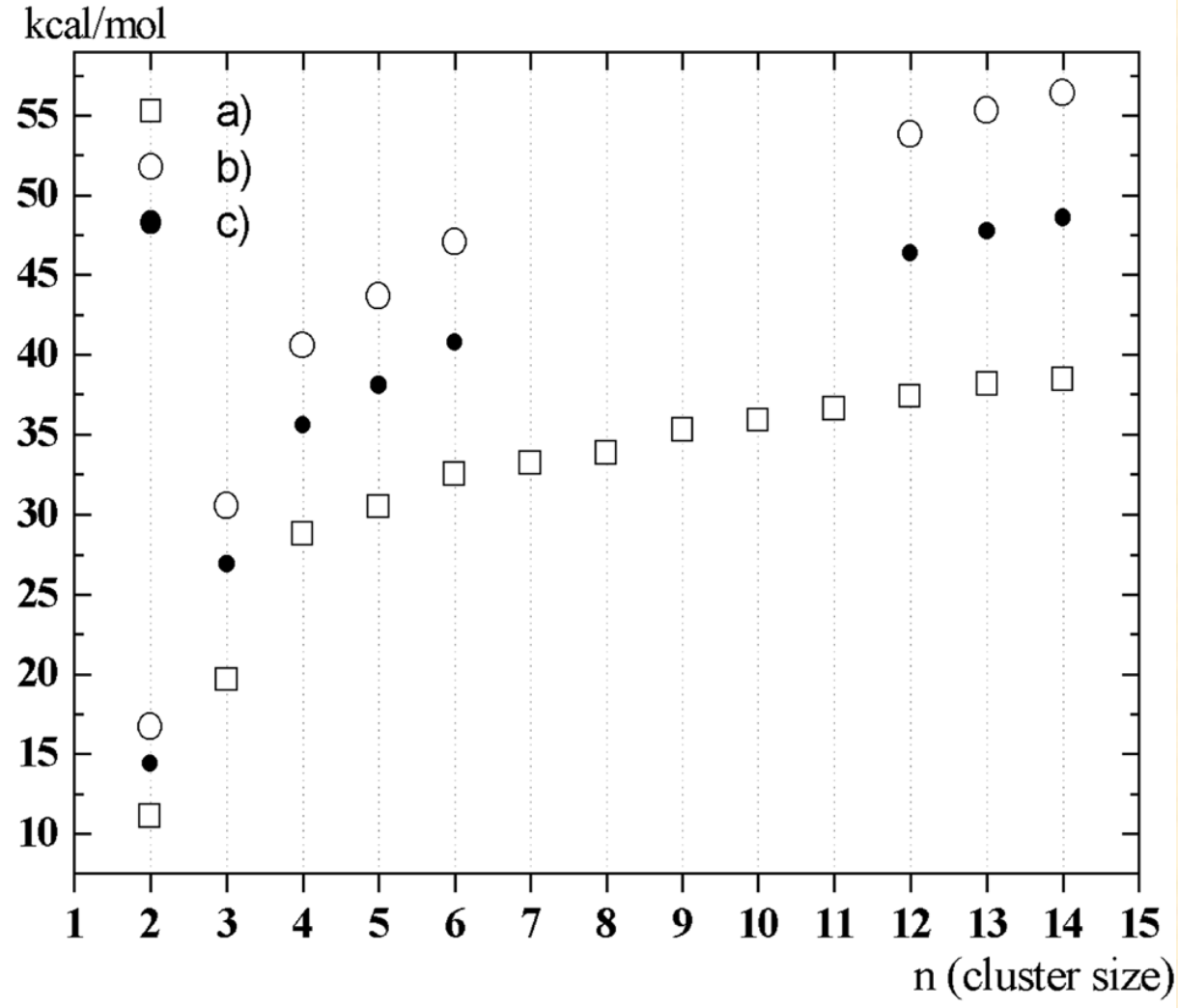
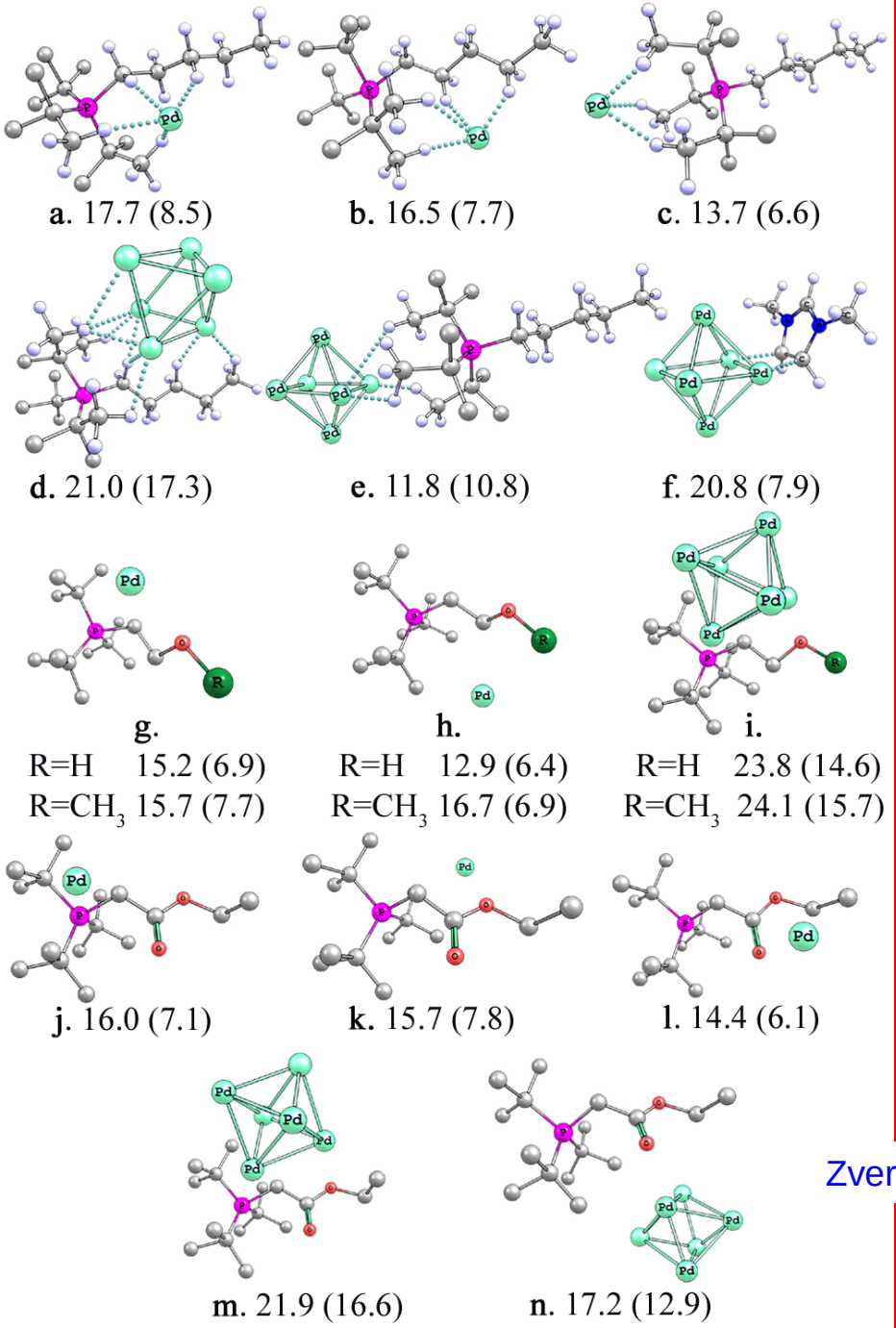
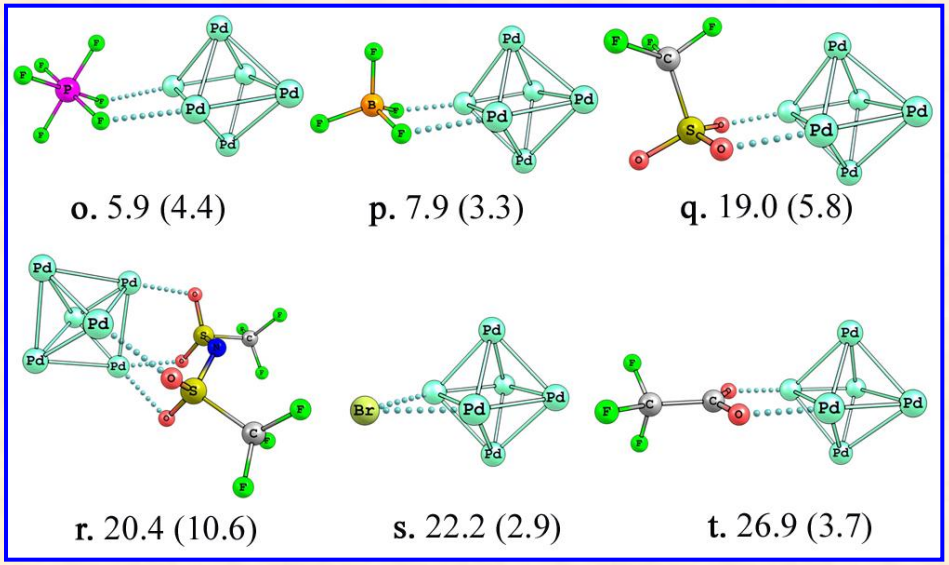
Energy of cohesion EC = [E(Pd_n) – nE(Pd)]/n

a) B3LYP; b) PBE; c) PBE – Gibbs free energy of cohesion



Katsyuba et al., *Chem. Phys. Chem*. **2012**, *13*, 1781





Binding energies in kcal·mol^{-1}:

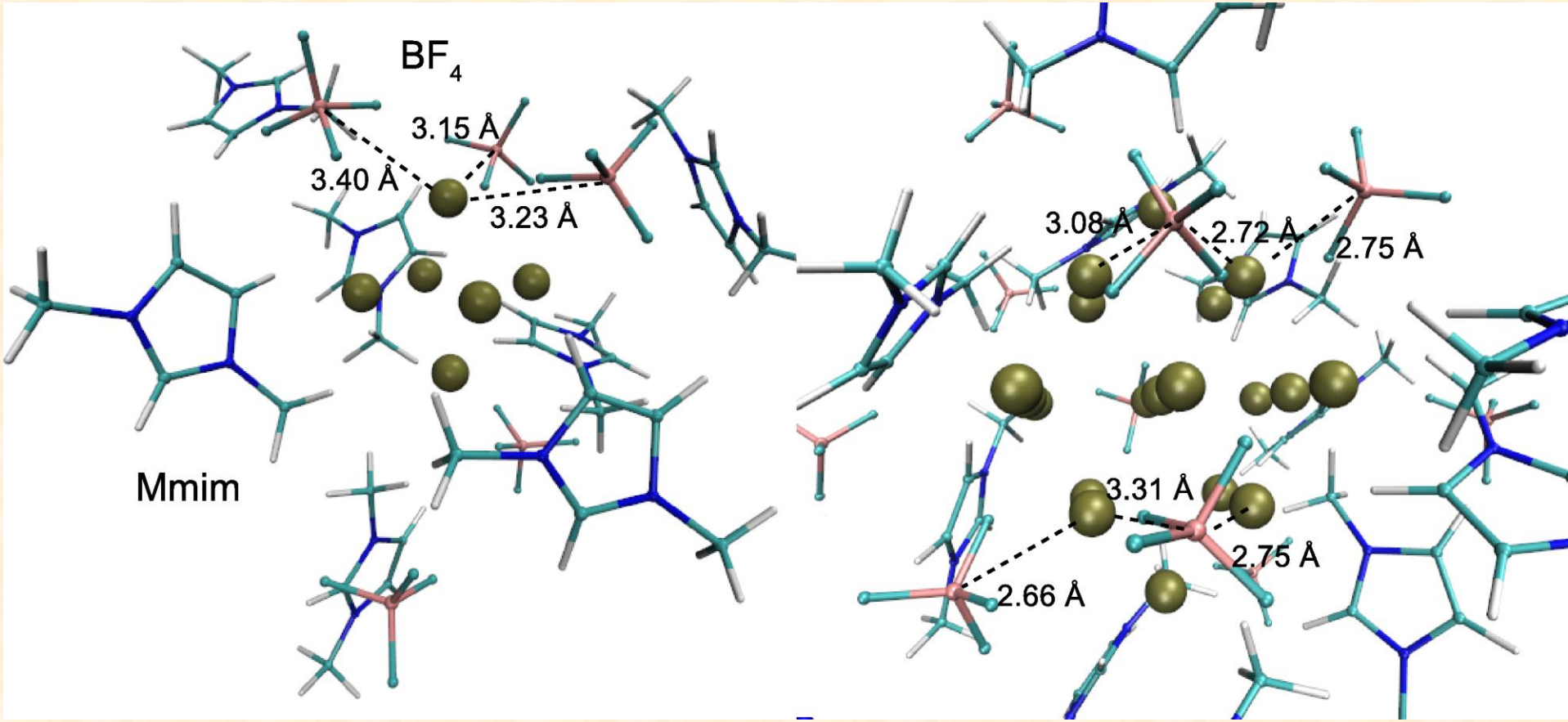
BE = E(substrate) + E(Pd$_n$)
- E(substrate/Pd$_n$ adduct)

(in parenthesis - the computed London dispersion energy contribution, D3(BJ))

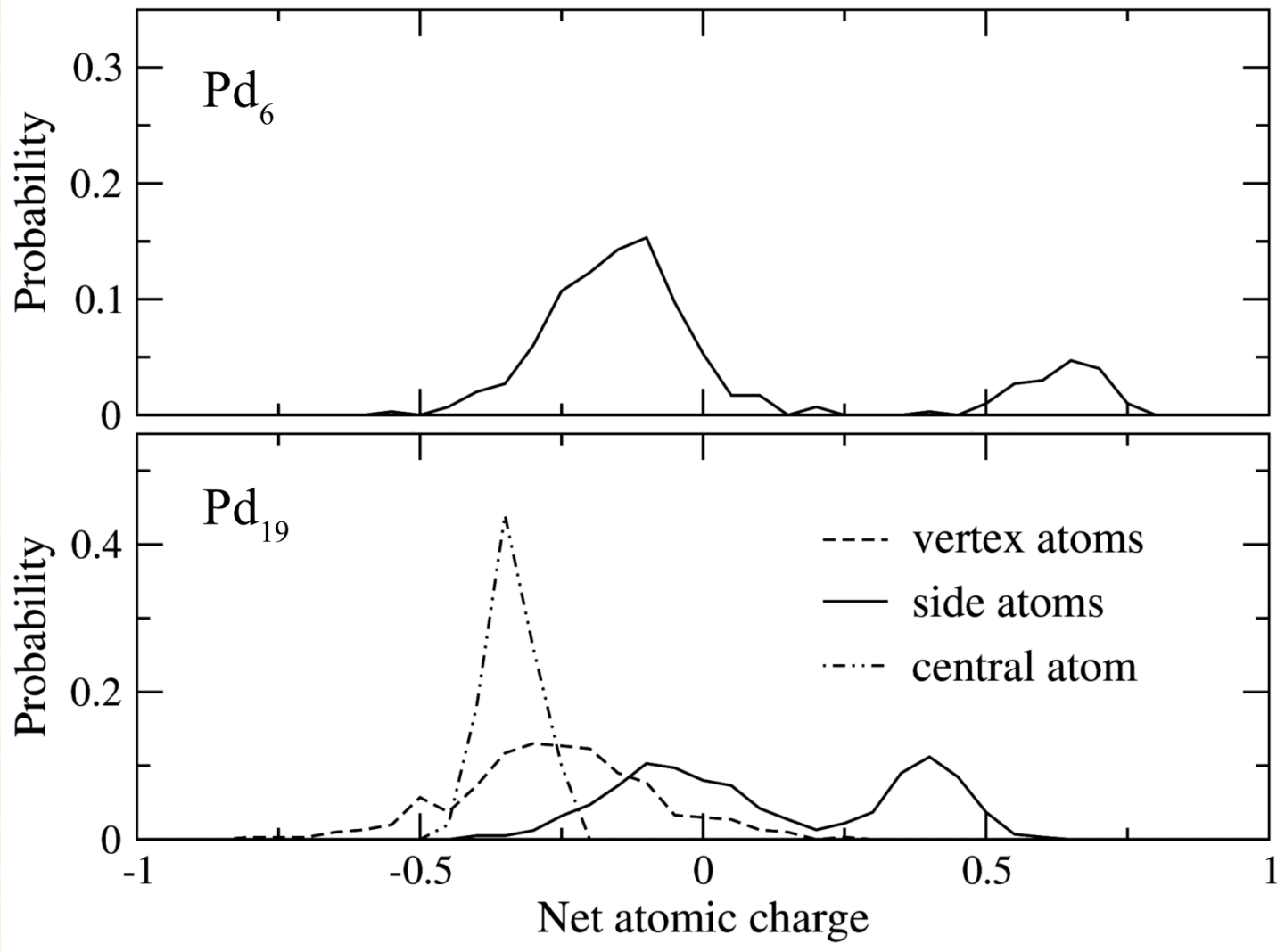
PBE0-D3(BJ)/def2-TZVP//TPSS-D3(BJ)/def2-TZVP COSMO

Zvereva et al., *Phys. Chem. Chem. Phys.* **2014**, *16*, 20672

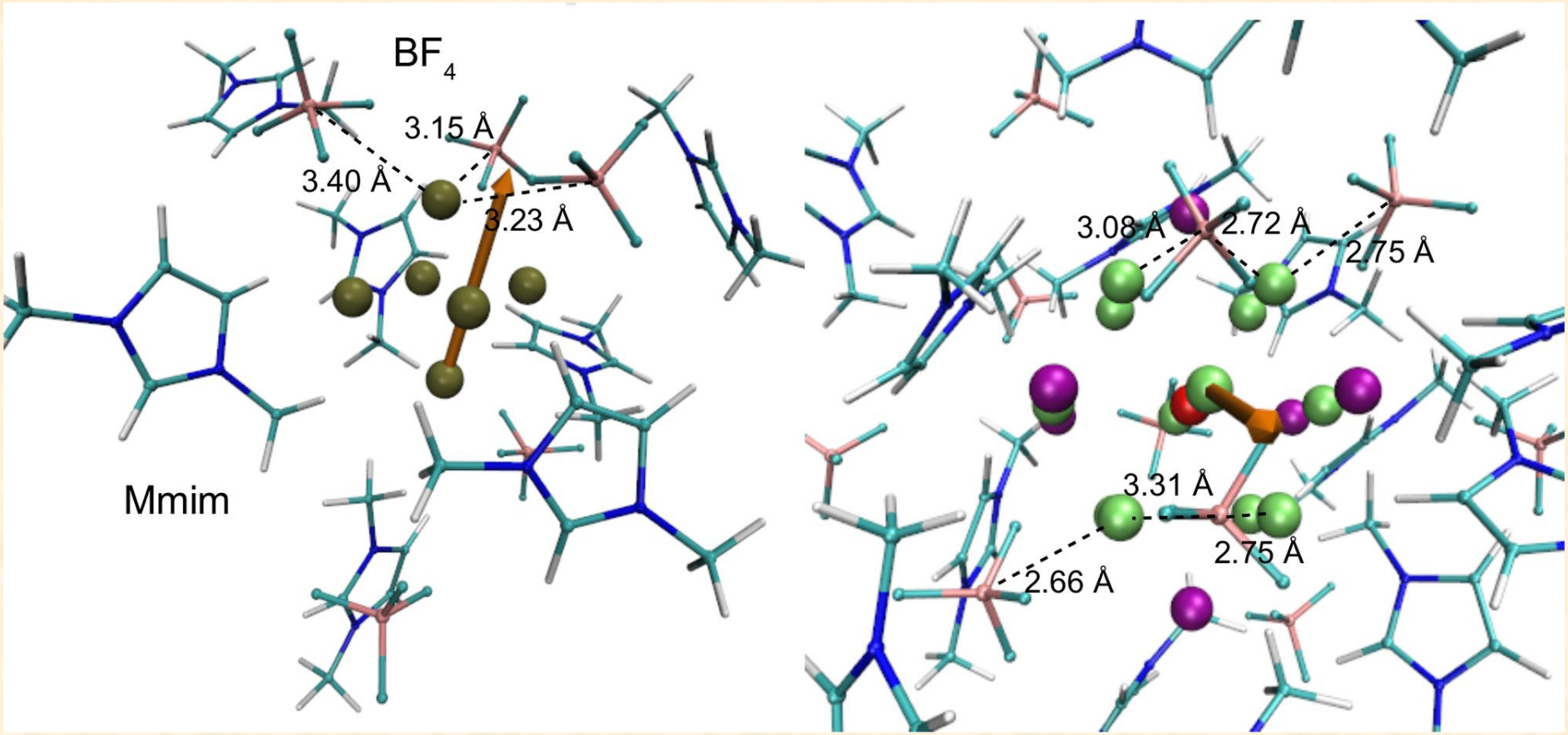
- QM/MM
- QM: TPSS-D3/def2-TZVP or PM6
- MM: CL&P force field [Canongia Lopes, J.; Pádua, A. H., *Theor. Chem. Acc.* **2012,** *131* (3), 1-11]. The simulations included a 30 Å cubic box of 125 [Mmim][BF_4] ion pairs.



Zvereva et al., *J. Phys. Chem*. C **2016**, *120*, 4596



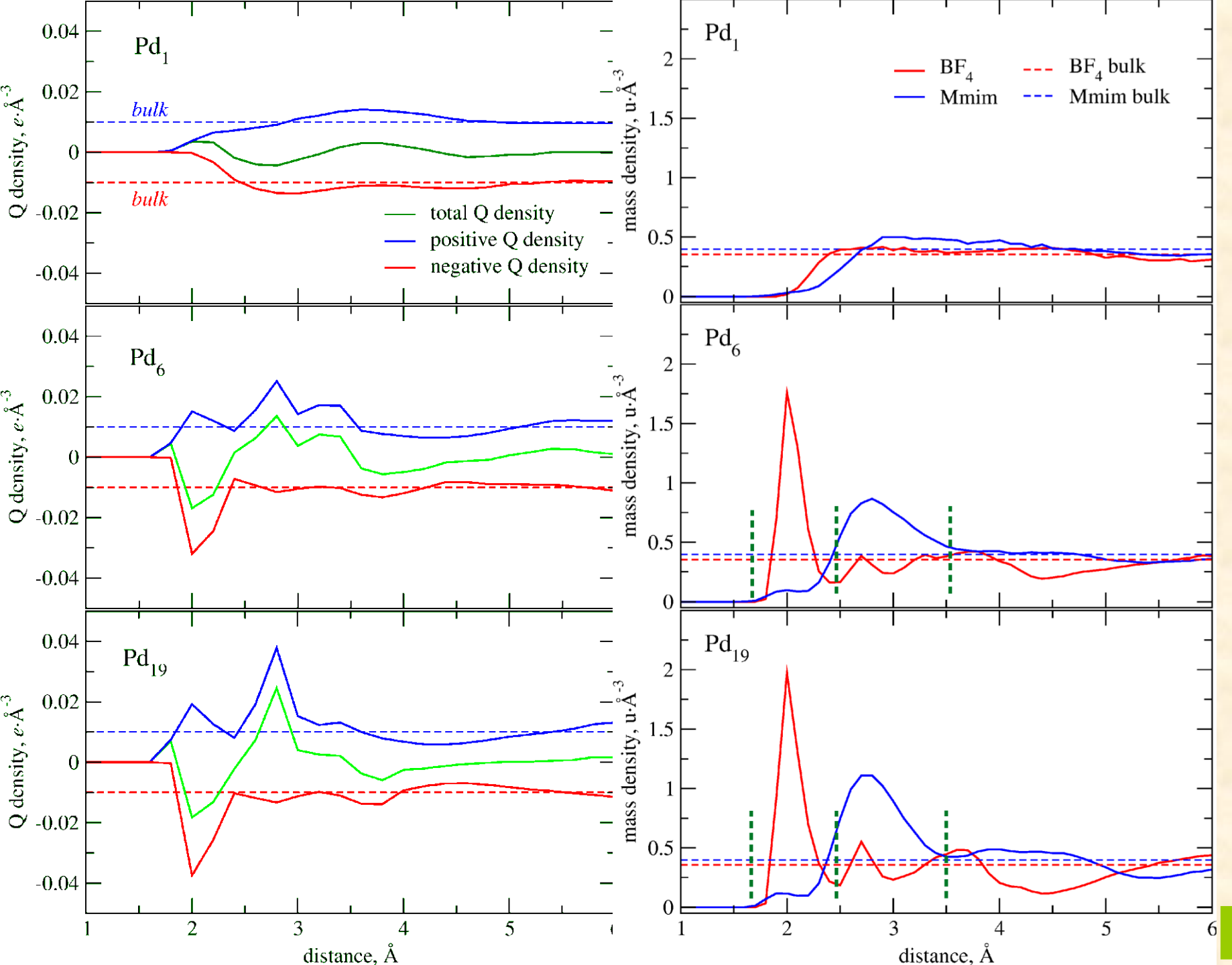
Zvereva et al., *J. Phys. Chem.* C **2016**, *120*, 4596

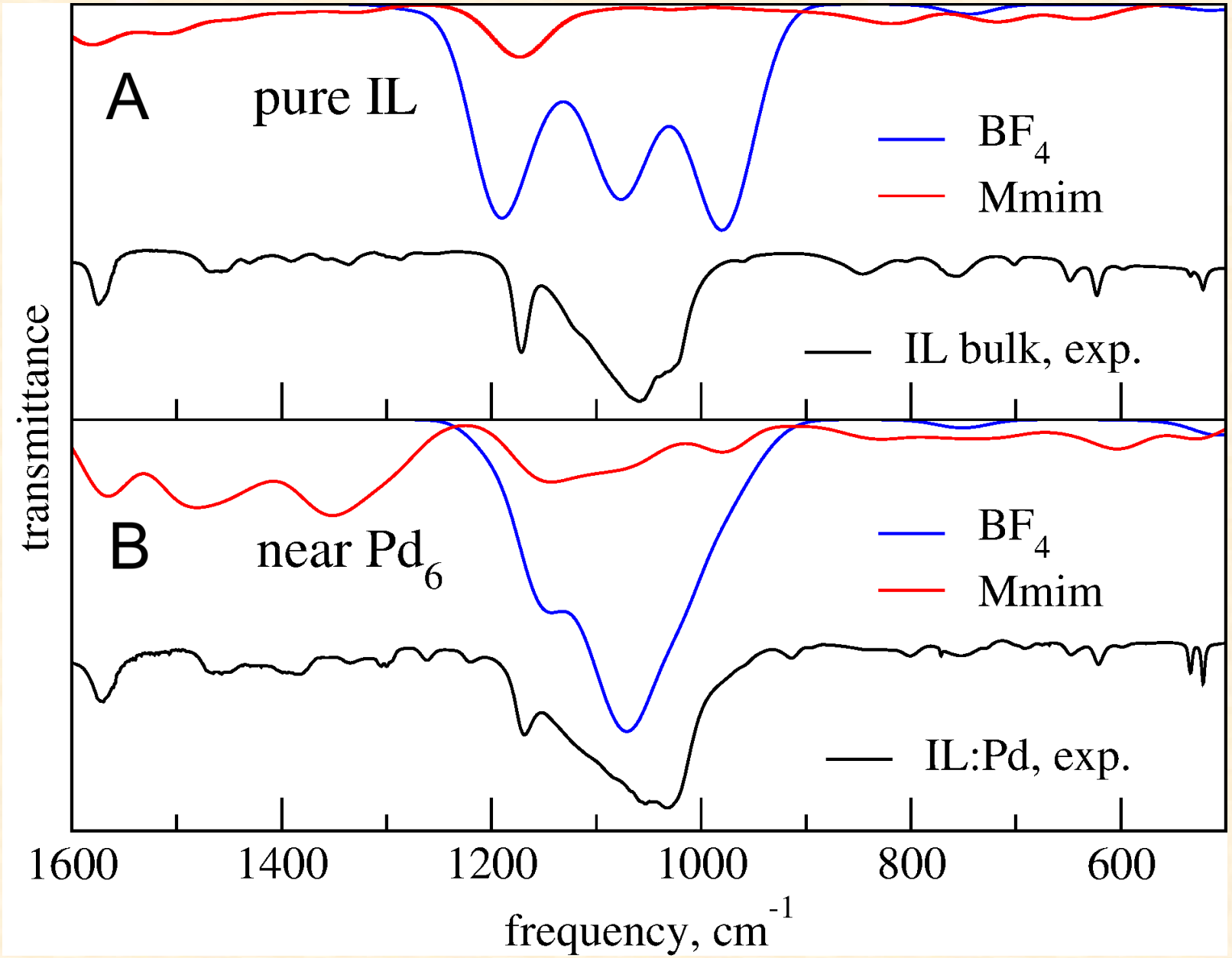


μ = **13.4 ± 1.6 D** **27.8 ± 9.7 D**

μ (Pd) = **0.5 ± 0.2 D**

Zvereva et al., *J. Phys. Chem*. C **2016**, *120*, 4596

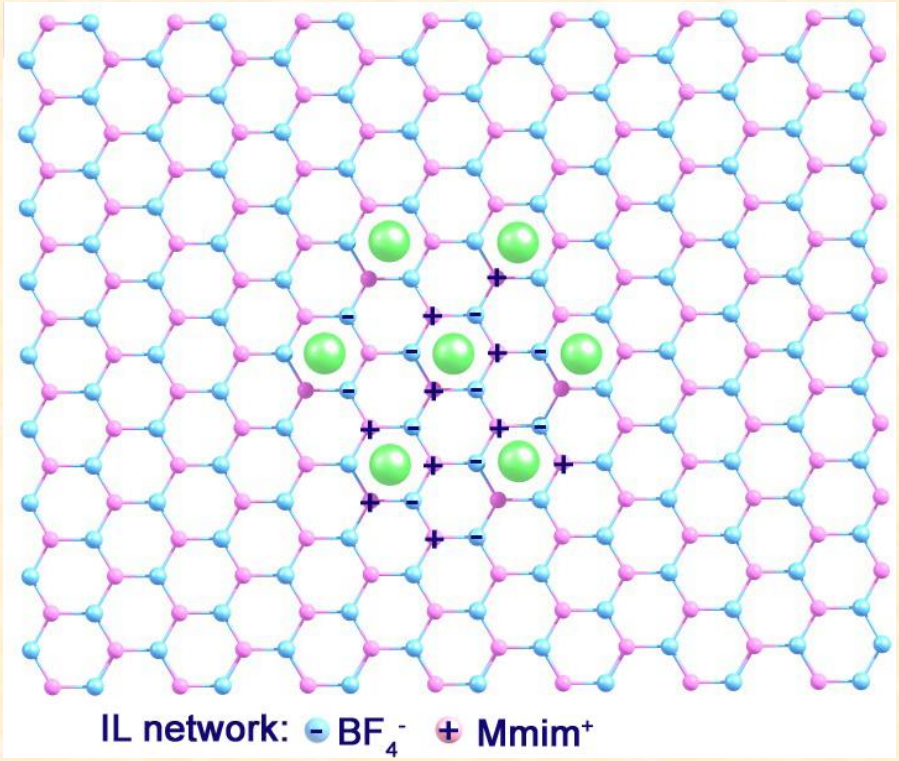

Pd1
bulk
bulk
total Q density
positive Q density
negative Q density
Q density, e·Å-3
Pd6
Pd19
distance, Å
Pd1
BF4
Mmim
BF4 bulk
Mmim bulk
mass density, u·Å-3
Pd6
Pd19
distance, Å

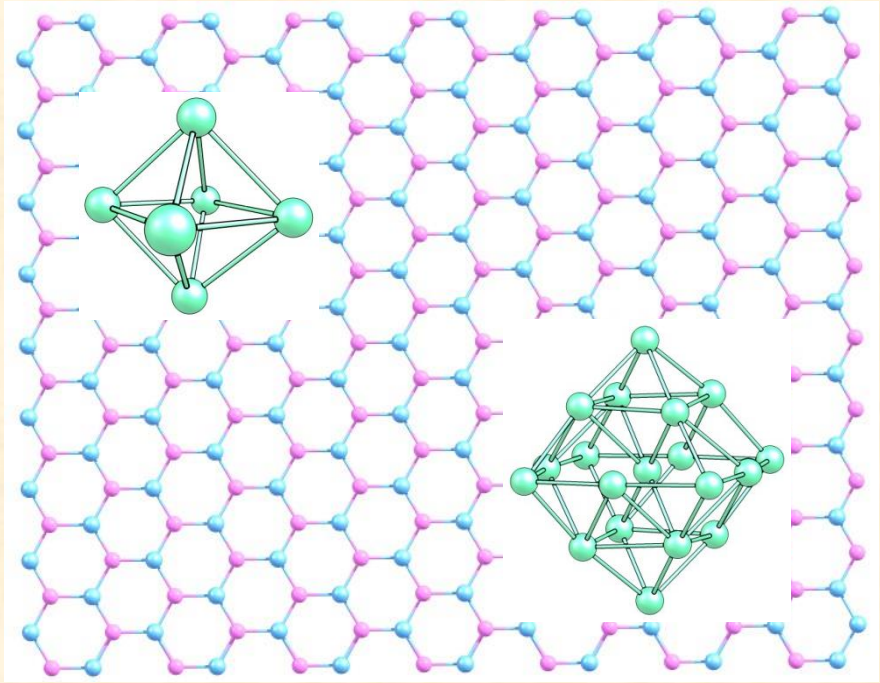

A
pure IL
BF4
Mmim
IL bulk, exp.
B
near Pd6
BF4
Mmim
IL:Pd, exp.
transmittance
1600
1400
1200
1000
800
600
frequency, cm-1

Energy of cohesion EC = $[E(Pd_n) - nE(Pd)]/n$

Pd_6: -57.9±0.5 kcal·mol^{-1}

Pd_{19}: -68.0±1.0 kcal·mol^{-1}





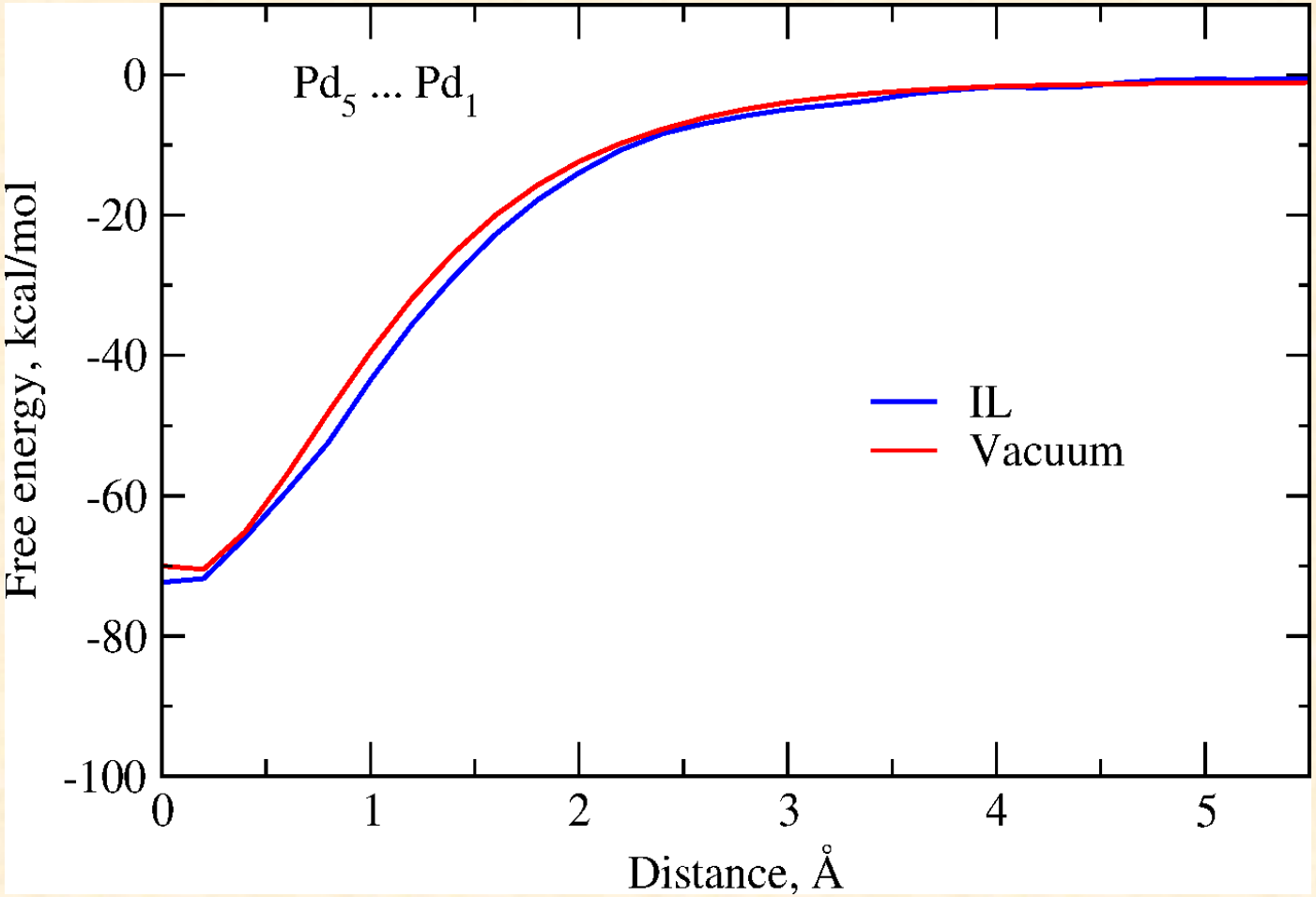
Interaction energy with IL ($E_{QM/MM} - E_{MM} - E_{QM}$):

Pd_1: -3.5±1.9 kcal·mol^{-1}

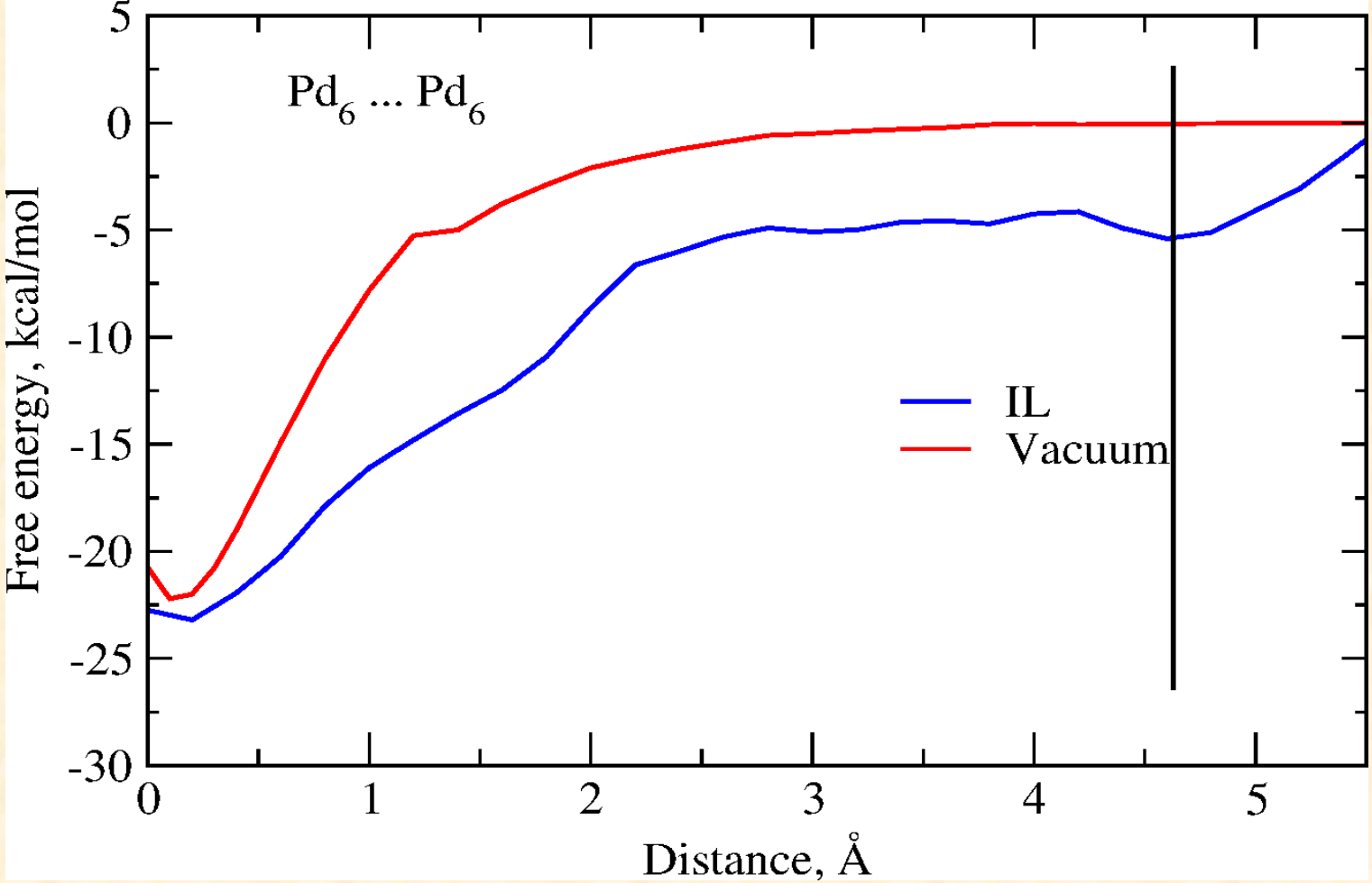
Pd_6: -79.2±7.4 kcal·mol^{-1}

$[Mmim][BF_4]$: -146.4±20.0 kcal·mol^{-1}

Pd_{19}: -180.2±7.3 kcal·mol^{-1}



Potential of mean force to displace a palladium atom from the Pd_6 cluster in vacuum and the ionic liquid. Distances are given relative to the minimum energy interaction distance



Potential of mean force to displace two Pd_6 clusters in vacuum and in the ionic liquid. Distances are given relative to the minimum energy interaction distance

Conclusions

- The IL induces a strong polarization in palladium clusters
- The clusters have large induced dipole moments and, as a result, interact strongly with the IL.
- This results in an accumulation of the IL layer of high density around the clusters. The interface layer of *ca*. 3.5 Å thickness has a negative charge on the inner surface composed mainly of anions and an outer positive charge provided by the cations.
- A single palladium atom does not show any noticeable preference for the positive or negative ions and interacts only very weakly with the IL
- The absolute energy of aggregation of the clusters is larger than the difference in the interaction energies of smaller clusters which implies that stabilisation of Pd-NPs in the IL is due to kinetic stabilisation rather than thermodynamic stabilisation

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