


Ab initio Dynamics of Metal Nanoparticles: Structure and Properties

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Ab-initio assignments of IR and Raman bands of bulk Ba species relevant in the NO_x storage and reduction

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NO_x storage and reduction (NSR) process is one of the most important technologies for the reduction of NO_x components in automotive exhaust. There are numerous vibrational spectroscopic studies aimed at elucidating the NSR mechanism; however long-standing controversy exists in the band assignment of Ba species (NO_x storage component) present in the catalyst, existing as nitrates, carbonates, and possibly oxides.¹

Based on DFT framework, the fundamental modes of bulk Ba(NO₃)₂ and BaCO₃ are calculated using the PBE functional by Quantum Espresso² and compared to experimentally obtained mid-/far-IR and Raman spectra.³ Crystal symmetry has been taken into account to achieve accurate calculation of lattice modes and to explain the spectral features observed in far-IR spectra. A clear and firm assignment of IR- and Raman bands of Ba(NO₃)₂ and BaCO₃ could be given, evidently showing incorrect, but widely accepted band assignments, highlighting the importance of reevaluation of band assignments by *ab initio* methods. This study serves as a reference for IR and Raman spectra of bulk barium species relevant in NSR.

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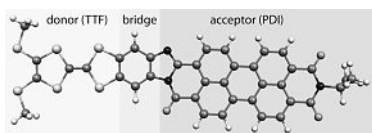
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The failure of the time-dependent DFT and CC2 methods to predict the absorption spectrum of a donor-acceptor dyad

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Electron donor-acceptor (D-A) molecules are of prime interest on account of their potential applications in molecular electronic devices. The tetrathiafulvalene donor (TTF) was fused to the acceptor perylene-tetracarboxydiimide (PDI) via a π -bridge [1]. The TTF-PDI dyad shows several charge transfer (CT) transitions as well as a PDI localized $\pi\pi^*$ -excitation in the UV/vis spectrum.



Time-dependent DFT (TD-DFT) gives accurate predictions for valence excited states at low computational cost. However, it has been reported that TD-DFT shows serious problems with CT transitions of extended π -systems [2]. As an alternative, we have employed the second-order approximate coupled cluster singles and doubles method (CC2), which gives very accurate electronic excitation energies, albeit with much higher computational cost. CC2 correctly reproduces the CT transitions, but fails for the PDI-localized $\pi\pi^*$ -excitation. The long-range corrected density functional method [3] (LC-BLYP) is the only approach to correctly predict both CT and $\pi\pi^*$ transitions of TTF-PDI.

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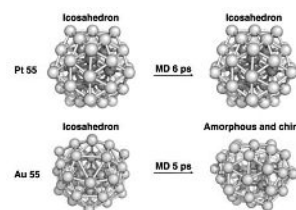
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Ab initio dynamics of metal nanoparticles: structure and propertiesAngelo Vargas¹, Gianluca Santarossa¹, Marcella Iannuzzi² and Alfons Baiker^{1,*}

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The study of the electronic properties of metal nanoparticles is of great relevance for the tailoring of new materials in general, and in particular for catalysis. It is well known that in the nano-size range metal particles have distinct features from bulk properties. Improved computational techniques and highly parallel computational resources allow performing *ab initio* molecular dynamics of metal nanoparticles, and the theoretical study of their chemical behavior [1][2]. In particular the structure and electronic properties of gold nanoparticles is investigated in order to uncover the marked change of reactivity between the unreactive bulk and the catalytically active gold nanoparticles [3].



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Path integral evaluation of equilibrium isotope effects

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A general and rigorous methodology to compute the quantum equilibrium isotope effect is described. Unlike standard approaches, ours does not assume separability of rotational and vibrational motions and does not make the harmonic approximation for vibrations or rigid rotor approximation for the rotations. In particular, zero point energy and anharmonicity effects are described correctly quantum mechanically. The approach is based on the thermodynamic integration with respect to the mass of the isotopes and on the Feynman path integral representation of the partition function. An efficient estimator for the derivative of free energy is used whose statistical error is independent of the number of imaginary time slices in the path integral [1], speeding up calculations by a factor of ~ 100 at 500 K and more at room temperature. We describe the implementation of the methodology in the molecular dynamics package AMBER 10. The method is tested on three [1,5] sigmatropic hydrogen shift reactions. Because of the computational expense, we use *ab initio* potentials to evaluate the equilibrium isotope effects within the harmonic approximation, and then the path integral method together with semiempirical potentials to evaluate the anharmonicity corrections. Our calculations show that the anharmonicity effects amount up to 30% of the symmetry reduced reaction free energy. Numerical results are compared with recent experiments of Doering and coworkers [2,3].

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