

# Characterization of Optical Spectra of Interacting Systems: Application to Oxide-Supported Metal Clusters

Miquel Huix-Rotllant,<sup>1</sup> Ajanta Deka,<sup>1,2</sup> Sergey I. Bosko,<sup>1</sup> Alexei V. Matveev,<sup>1</sup>  
Lyudmila V. Moskaleva,<sup>1</sup> and Notker Rösch<sup>1</sup>

<sup>1</sup> *Department Chemie, Theoretische Chemie, Technische Universität München,  
85747 Garching, Germany, roesch@ch.tum.de*

<sup>2</sup> *Department of Chemical Sciences, Tezpur University, 784028 Assam, India*

We present a general strategy for interpreting optical spectra of systems which comprise two partitions that interact relatively weakly. To characterize the transitions obtained from linear-response time-dependent density functional (TDDFT) calculations, we combined an analysis on the basis of natural transition orbitals (NTO) [1] with a fragment molecular orbital (FMO) analysis. The NTO transformation allows one to identify leading contributions of particle-hole excitations in the spectral bands, whereas the FMO analysis yields a characterization of each particle-hole pair in terms of (leading) contributions of the corresponding fragments.

We applied this procedure to assign and characterize optical transitions of coinage metal dimers  $M_2$  ( $M = \text{Cu}, \text{Ag}, \text{Au}$ ) adsorbed on  $\text{MgO}(001)$ , at ideal oxygen sites or at oxygen vacancies,  $F_s$  and  $F_s^+$ . The TDDFT calculations were carried out at the generalized-gradient level on structures [2] that had been obtained with cluster models embedded in an extended elastic polarizable environment [3]. We analyzed the spectra in comparison with those of the corresponding gas-phase species, both qualitatively and quantitatively. The qualitative analysis obtained with the new procedure agrees very well with the previous assignment [4]. Furthermore, the quantitative results furnish a straightforward and transparent characterization of the main spectral bands.

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