

BI 09 Density functional studies of $[\text{Ag}(\text{CN})_2]^-$ doped in alkali halide crystals



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Nano-clusters of closed-shell d^{10} metal cyanide complexes are found to be good candidates in a wide range of technological applications such as in energy transfer, optical memory and emission tunability. These interesting photophysical phenomena are due to metal-metal interactions which depend on cluster sizes, compositions and orientations. Among those cyanide complexes, recent experimental studies show energy tunability of dicyanoargentate(I) complexes, $\{[\text{Ag}(\text{CN})_2]^- \}_n$, in alkali halide crystal. In our study, we simulated three potential dimeric configurations of $[\text{Ag}(\text{CN})_2]^-$ doped in NaCl host using Density Functional Theory (DFT) with Becke, three-parameter, Lee-Yang-Parr (B3LYP) exchange-correlation functional and Stuttgart/Dresden (SDD) basis set. We used $4 \times 4 \times 4$ and $4 \times 4 \times 5$ super cell models to enclose the monomeric and dimeric configurations in NaCl, respectively. In dimeric configuration, considered three types were differed according to the two bridging ions between two Ag atoms; both CN $[(\mu^2-\text{CN})_2]^-$, or both Cl $[(\mu^2-\text{Cl})_2]^-$ or a mix of two $[(\mu-\text{CN})(\mu-\text{Cl})]$. Calculated Raman spectral peak for $[(\mu^2-\text{CN})_2]^-$ structure appeared at 2140 cm^{-1} showing an excellent agreement with experimentally observed peak around 2150 cm^{-1} . According to our spectral analysis, we herewith report that $(\mu^2-\text{Cl})_2$ dimerization has taken place within NaCl crystal and experimentally observed different emission bands are due to formation of cluster compounds.

Keywords: tunability, nano-clusters, luminescent, super cell