Theoretical study of small calcium fluoride nanoparticles

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Abstract. CaₙF₂ₙ nanoclusters for n ranging from 2 to 10 were calculated with B3LYP/6-31G ab initio method. For n=5 and n=7 no stable configurations were found. The energy parameters, symmetries and stability of the nanoclusters is discussed. The results of ab initio calculations are then compared to pair potentials (PP) classical calculation.

1. Introduction

The calcium fluoride crystal has a rather low refractive index, is characterized by a wide range of spectral transparency 120-10000 nm. This makes it possible to use it as lenses, prisms, windows in various spectral devices operating in a wide optical region.

It has long been known that the presence of defects in the crystal lattice of CaF₃, even in a small concentration, leads to a significant change in the optical properties both in the visible and in the UV region [1]. The defects, as well as nanoclusters of small size have a structure different from the crystal [2, 3]. It can be assumed that calcium fluoride nanoparticles CaₙF₂ₙ, where n is the number of formula units, can have unique optical properties. There are many studies dedicated to calcium fluoride nanoparticles. Tahvildari and co-authors [4] demonstrate the method of obtaining clean CaF₂ nanoparticles with a size of about 20 nm, this material is considered promising for use in medicine and optics.

It has been shown experimentally that spatial structure of CaF₂ nanoparticles exceeding 5 nm in diameter becomes similar to crystalline [5]. To the present moment no systematic study of CaF₂ nanoparticles can be found in the literature. However, for more complicated fluorides like LaF₃ the structure of nanoparticles was studied theoretically [3].

This work is devoted to a theoretical study of calcium fluoride nanoparticles, in order to establish mechanically stable nanoparticles CaₙF₂ₙ, (n=1-10). The obtained configurations are later to be used to study their electronic and optical properties.

2. Method

We started with manually constructed structures of CaF₂·n nanoparticles, which was followed by geometry optimization procedure. The total energy of the nanoclusters was calculated within DFT using B3LYP exchange-correlation functional. The 6-31G basis sets was used, as implemented in the PCGAMESS/Firefly code[6].
It was convenient to characterize the mechanical stability by the value of $\Delta E(n)$, the energy per one formula unit:

$$\Delta E(n) = \frac{E(n)}{n} - E(1)$$

where $E(n)$ is the total energy of the nanocluster for a given $n$. If $\Delta E(n) > 0$ we will assume that the given structure is not stable.

However, for larger nanoclusters we will have to use the molecular mechanics with pair potentials (PP) because ab initio calculations are not feasible with large $n$. For molecular mechanics calculations we use the potentials obtained by Catlow et al. [7]. In order to show that these pair potentials adequately predict the spatial structure of the cluster, we compare the results from molecular mechanics method with the results of the DFT calculations. To calculate the total energy using the pair potentials we applied the GULP software [8].

3. Results and discussion

Fourteen mechanically stable configurations of $\text{Ca}_n\text{F}_{2n}$ nanoclusters were constructed manually for $n$ ranging from 2 to 10 and their geometries were optimized at DFT level of theory. For $n=5$ and $n=7$ no stable configurations could be obtained. The value of the band gap for the nanoclusters was estimated from one-electron spectrum of Kohn-Sham energies as the difference between lowest unoccupied (LUMO) and highest occupied (HOMO) molecular orbitals. The geometries of calculated nanoclusters are shown on figure 1.

After that obtained configurations of nanoclusters were recalculated with pair potentials with geometry optimization. All obtained characteristics of the nanoclusters are summarized in table 1. It has
to be noted that some nanoclusters underwent a considerable distortion when recalculated with pair potentials compared to their DFT geometries. Such configurations are marked in “distortion” column of table 1. We have also determined symmetry groups for all considered configurations.

Table 1. The energy parameters of calculated \( \text{Ca}_n\text{F}_{2n} \) nanoclusters.

| Nanocluster | \( E_g \), eV | \( \Delta E(n) \), eV (DFT) | \( \Delta E(n) \), eV (PP) | Distortion | Symmetry |
|-------------|---------------|--------------------------|--------------------------|------------|---------|
| 2           | 7.83          | -1.24                    | -0.19                    | D\(_{4h}\)  |
| 3           | 8.28          | -2.44                    | -1.40                    | D\(_{3h}\)  |
| 4           | 9.19          | -2.80                    | -1.81                    | D\(_{3h}\)  |
| 6a          | 10.93         | -3.62                    | -2.57                    | D\(_{3h}\)  |
| 6b          | 9.03          | -2.94                    | -2.58                    | *           | S\(_6\)  |
| 6c          | 7.93          | -3.12                    | -2.29                    | *           | D\(_{2h}\) |
| 8a          | 7.89          | -3.60                    | -2.56                    | *           | C\(_s\)  |
| 8b          | 9.85          | -3.95                    | -2.83                    | *           | C\(_s\)  |
| 8c          | 4.09          | -3.55                    | -2.55                    | *           | D\(_{3d}\) |
| 8d          | 10.48         | -3.91                    | -2.79                    | C\(_i\)  |
| 9a          | 9.69          | -3.92                    | -2.73                    | *           | C\(_s\)  |
| 9b          | 10.05         | -3.98                    | -2.84                    | C\(_1\)  |
| 10a         | 5.28          | -3.89                    | -2.67                    | *           | C\(_{2v}\) |
| 10b         | 6.61          | -3.98                    | -2.83                    | D\(_{2h}\) |

The \( \Delta E(n) \) values calculated \textit{ab initio} and with pair potentials for most configurations show systematic difference of about 1 eV with \textit{ab initio} being lower. That would be more reliable to use the crystal cohesive energy instead of \( E(1) \) in definition (1), but for molecular calculations it is impossible to obtain this value. According to \textit{ab initio} calculated \( \Delta E(n) \) values all considered configurations are stable not only mechanically, but they are also stable with respect to the decay into two smaller clusters. It can be observed also from Table 1 that the configurations with larger value of estimated band gap do not change significantly upon the geometry optimization with pair potentials. This can be understood if one recalls that pair potentials from [7] were optimized to reproduce crystalline \( \text{CaF}_2 \) with purely ionic electronic structure and large band gap.

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