Electronic and Optical Properties of Small Metal Fluoride Clusters: Supporting Information

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This Supporting Information contribution is made by the two different parts you find in the following:

1) ADDITIONAL MATERIAL I: Configurational Effects on the Spectra
2) ADDITIONAL MATERIAL II: Energy stability of the ground state

**ADDITIONAL MATERIAL I : Configurational Effects on the Spectra**

![Absorption spectra for SrF$_2$ monomers](image)

**Figure S1:** Absorption spectra for the SrF$_2$ monomers for two different point group symmetries, $D_{\infty h}$ and $C_{2v}$.

To evaluate the consequences of different geometries on the absorption spectra, we also performed symmetry-constrained DFT and TDDFT calculations for the linear geometry $D_{\infty h}$ of the SrF$_2$ monomer as an example. Fig. S1 compares the optical spectra of linear ($D_{\infty h}$) and fully-optimized bent ($C_{2v}$) structures. Important differences are present in the region 5-6.5 eV both in position and in oscillator strength of the peaks, while in the region above 7.2
eV the spectra are qualitatively similar with a significant redistribution of spectral strength between the peaks. Moreover, in the case of the linear SrF$_2$ monomer with $D_{\infty h}$ symmetry a transparency region appears between 5.5 eV and 7.2 eV. In addition, while for the bent geometry the onset energy is 5.26 eV, in the case of the linear cluster it is reduced to 5.05 eV. In Tab. S1 some physical observables for the two SrF$_2$ clusters in the studied symmetries are compared. It is clear from that table that beside the onset energy also the other observables show differences in the two different geometries. The present results confirm therefore the need and importance of the correct evaluation of the ground state and its geometry as a necessary prerequisite for the calculation of excited states and absorption spectra.

Table S1: Ground-, excited-state and optical properties for the SrF$_2$ cluster in the $D_{\infty h}$ and $C_2v$ symmetries. The average distance between metal and fluorine atoms $R'_{M-F}$, the vertical ionization energy $I_{E_V}$, the quasiparticle energy gap ($E_{gap}$), the optical onset($E_{opt}$) and the binding energy of the exciton($E_b$) are reported.

| Monomer       | $R'_{M-F}$ | $I_{E_V}$ | $E_{gap}$ | $E_{opt}$       | $E_b$               |
|---------------|------------|-----------|-----------|-----------------|--------------------|
| SrF$_2$ ($D_{\infty h}$) | 2.164      | 10.71     | 10.08     | **5.05** (1.3 $\times 10^{-3}$; H $\rightarrow$ L) | 5.03               |
| SrF$_2$ ($C_2v$)    | 2.130      | 10.94     | 10.16     | **5.26** (7 $\times 10^{-4}$; H $\rightarrow$ L) | 4.9                |
ADDITIONAL MATERIAL II: Energy stability of the ground state

It is well known from the literature\textsuperscript{1,2} that \((\text{MF}_2)_n\), for \(n=2,3\), show many different local minima at energies as low as few tenths of eV over the ground state (global minimum), so we have performed a search for the lower energy isomers as outlined below, in order to correctly identify the true ground state.

To perform this task we have used the ABCluster software package\textsuperscript{3,4} based on the artificial bee colony algorithm, which is inspired by the foraging behavior of a bee colony.\textsuperscript{5} The algorithm has been applied by its authors to various clusters of different chemical nature. In all the cases the authors obtained results in agreement with previous experimental and theoretical studies.\textsuperscript{4}

Table S2: Ground state (GS) and next lower energy isomer (I1) for dimers and trimers. First column: energy separation \(\Delta E\) between I1 and GS. Second column: I1 point group symmetry. Third column: GS point group symmetry.

|        | \(\Delta E\) (eV) | I1 symmetry | GS symmetry |
|--------|-------------------|-------------|-------------|
| dimers |                   |             |             |
| \((\text{MgF}_2)_2\) | 0.70 | \(C_{3v}\) | \(D_{2h}\) |
| \((\text{CaF}_2)_2\) | 0.07 | \(C_{2h}\) | \(C_{3v}\) |
| \((\text{SrF}_2)_2\) | 0.19 | \(C_{2h}\) | \(C_{3v}\) |
| \((\text{BaF}_2)_2\) | 0.15 | \(C_{2h}\) | \(C_{3v}\) |
| trimers |                   |             |             |
| \((\text{MgF}_2)_3\) | 0.39 | \(C_s\) | \(D_{2d}\) |
| \((\text{CaF}_2)_3\) | 0.25 | \(C_s\) | \(C_{2v}\) |
| \((\text{SrF}_2)_3\) | 0.44 | \(C_s\) | \(C_{2v}\) |
| \((\text{BaF}_2)_3\) | 0.48 | \(C_s\) | \(C_s\) |

Here we have used the ABCluster package in conjunction with Gaussian16 to search for the lower energy isomers of the fluoride dimers and trimers. The outcomes of this procedure are reported in Tab. S2 both for the ground state (GS) and the next lower energy isomer (I1). The first important result is that all the ground-state geometries and symmetries presented in section Ground state and morphological properties of the main text have been confirmed.
In Tab. S2 we report the relative energy of I1 with respect to GS (first column), the point group symmetry for I1 (second column) and for GS (third column).

In the case of dimers, the relative energy goes from a minimum of 70 meV for (CaF$_2$)$_2$ to a value ten times greater for (MgF$_2$)$_2$, with the other energies in between.

In the case of trimers, the relative energy is on the average around 0.4 eV.

References

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