IX Workshop on Novel Methods for Electronic Structure Calculations

10th – 19th November 2021
La Plata – Argentina

UNIVERSIDAD NACIONAL DE LA PLATA

FACEN

CIFTA
FACEN-UNCA

Centro de Investigaciones Fisicoquímicas Teóricas y Aplicadas

DECOMPOSITION OF Li2S IN EXPLICIT SOLVENT

Costello Verónica Viviana[1], Lobo Maza Flavia[1], López María Beatriz[1], Zoloff Michoff Martín[2]

[1] Centro de Investigaciones Fisicoquímicas Teóricas y Aplicadas (CIFTA), Facultad de Ciencias Exactas y Naturales, Universidad Nacional de Catamarca.
[2] Instituto de investigaciones en Fisicoquímica de Córdoba (INFIQC), Facultad de Ciencias Químicas, Universidad Nacional de Córdoba.

INTRODUCTION

One of the most promising technologies for *the next generation of Li* batteries is rechargeable lithium-sulfur (Li-S) batteries. These are based on a cathode of a sulfur composite, an organic electrolyte and metallic lithium as the active material for the anode. However, the implementation of Li-S batteries in everyday applications still presents several technical drawbacks that must yet be overcome.

One possible solution with great potential is the use of lithium sulfide (Li_2S) as the cathode material, since it is possible to couple it to Li-free anodes, such as graphite, Si or Sn. However, Li_2S like S_8 are electronic and ionic insulators, with a high activation potential for their initial oxidation step. To overcome this problem, different strategies have been explored, such as the use of catalytic surfaces. However, it has been suggested that another important factor that governs the reactions in organic solvents is the so called "donor number" (DN), which is a measure of the ability of the solvent to form complexes with ions in solution. This implies that to improve the description of the effect of the solvent in the decomposition reaction of Li_2S, it is necessary to include explicit solvent molecules to properly describe the first sphere of solvation of the species along the reaction pathway.

In the present work, through DFT calculations, the interaction of Li_2S with different explicit solvent molecules is characterized: DOL (1) (1,3-dioxolane), DME (2) (dimethyl ether) and DMF (3) (dimethylformamide) (Fig. 1).
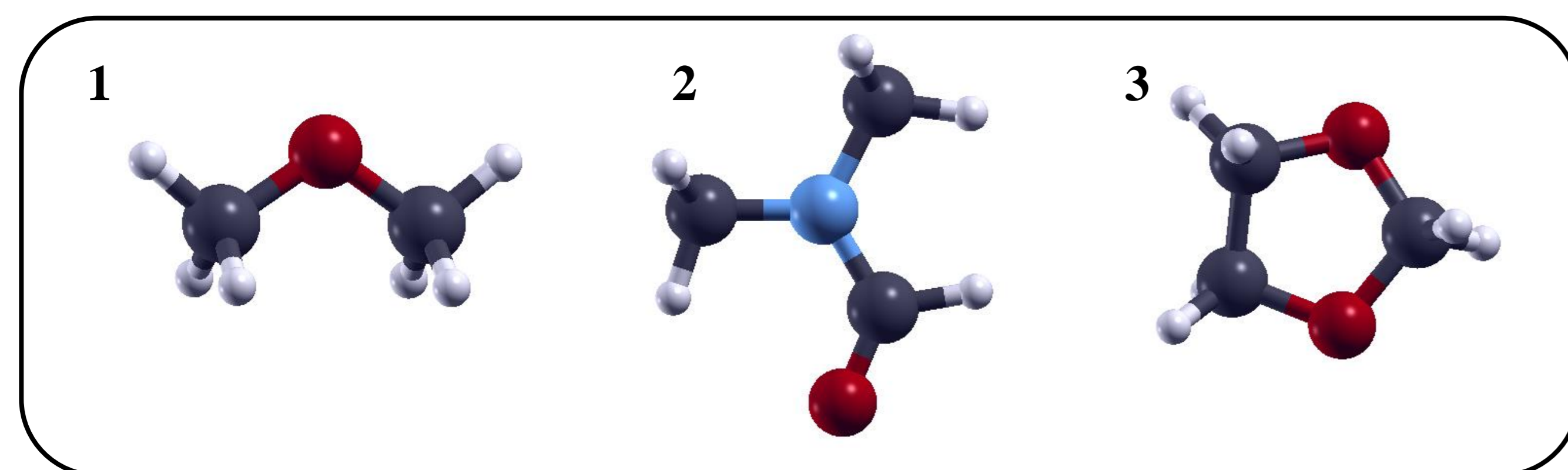

Figure 1: solvent molecules

METHODOLOGY

Computational DFT calculations were performed using Quantum Espresso (QE), employing the generalized gradient approximation (GGA) of the PBE function to describe the exchange and correlation effects. The central electrons were modeled by pseudopotentials in the projected augmented wave (PAW) method. Van der Waals interactions were considered by Grimme's DFT-D2 semi-empirical correction. All calculations were made taking into account the spin polarization.

RESULTS AND DISCUSSION

The solvation of lithium sulfide was studied, analyzing its interaction with different solvents. The interaction energy and the total atomic charges for the Li_2S and solvent molecules (ΔQ) were calculated (Table 1). Then, the electron density differential (Fig. 2) and the projected density of states (pDOS) of the isolated solvent molecules (Fig. 3) were performed.

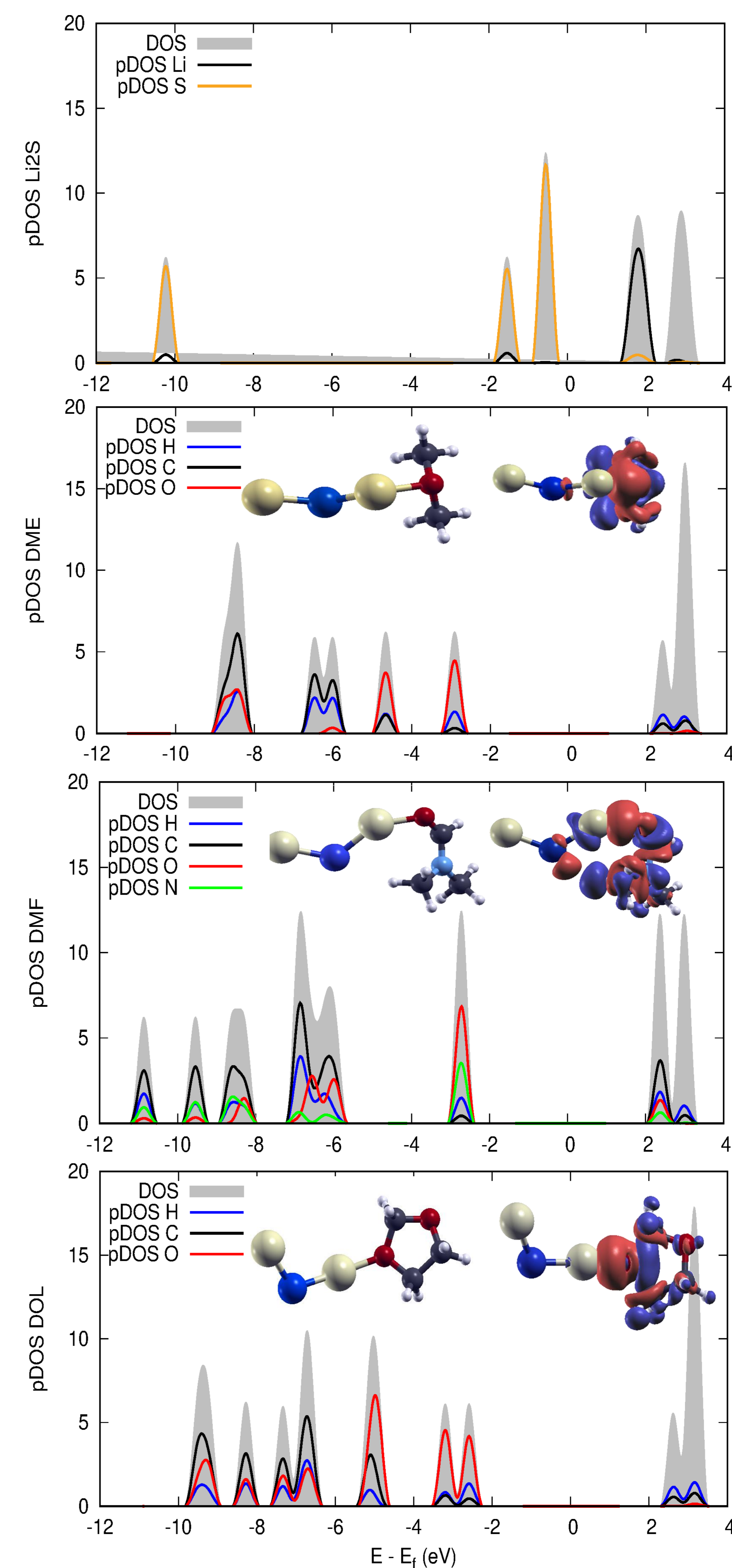| Aducts	Interaction energy (eV)	Fragmentation energy (eV)	ΔQ Li2S	ΔQ Solvent
Li2S+DME	-0.88	-3.58	0,1027	-0,1029
Li2S+DMF	-1.15	-3.64	0.1111	-0.1112
Li2S+DOL	-0,78	-3.40	0.1135	-0.1133

Table 1: comparative table of the interaction energies, fragmentation energies and Li_2S with the different solvent molecules

Figure 3: isosurface electron density (+0.001 red / -0.001 blue). Projected density of states (pDOS) of the isolated solvent molecules.

CONCLUSION AND FUTURE PROJECTION

It was observed that Li interacts strongly with O_2, where there is a greater energy of interaction with DMF, followed by DME and finally with DOL, as with charge transfer, checking with: the electron density differential where the region red is where charge accumulates, that is, where the bond is formed (positive part) and blue where there is a depletion (negative part); and with pDOS where it is observed that O_2 contributes mainly to the orbitals. Work is underway to determine the barriers to decomposition of isolated Li_2S (in the absence of a catalytic surface) and subsequently combine it with an implicit description of solvents, in which the system is embedded in a continuous dielectric.