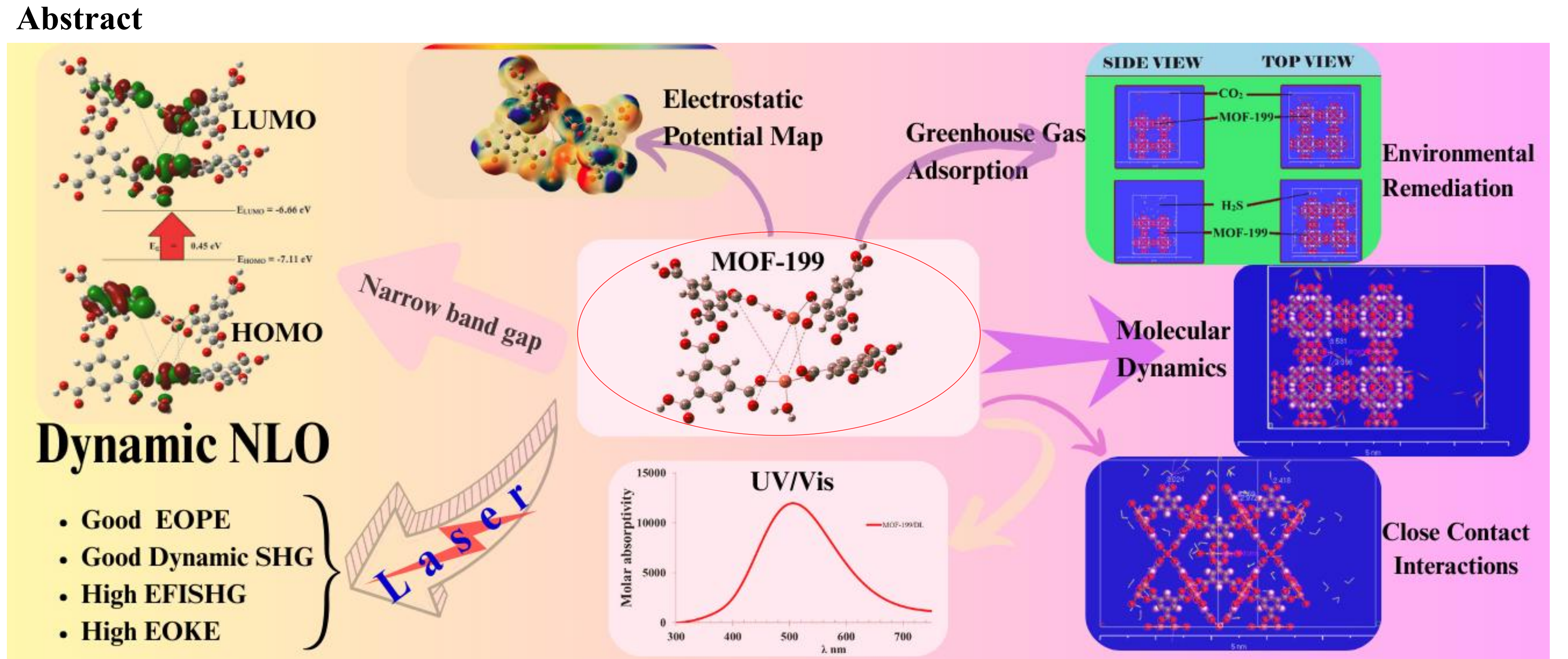


Dynamic optical behaviour and selective adsorptive properties of MOF-199: insights from the DFT, Monte Carlo and molecular dynamics simulations

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INTRODUCTION

The demand on clean and affordable energy is both global and ever-increasing. Recent report by international energy agency shows a rising shift towards exploitation of renewable energy sources in the last decade [1]. Although fossil fuel contributes a large percentage to energy source globally, its fast depletion and negative impact on the environment spur research on renewable alternatives.

RESEARCH PROBLEM

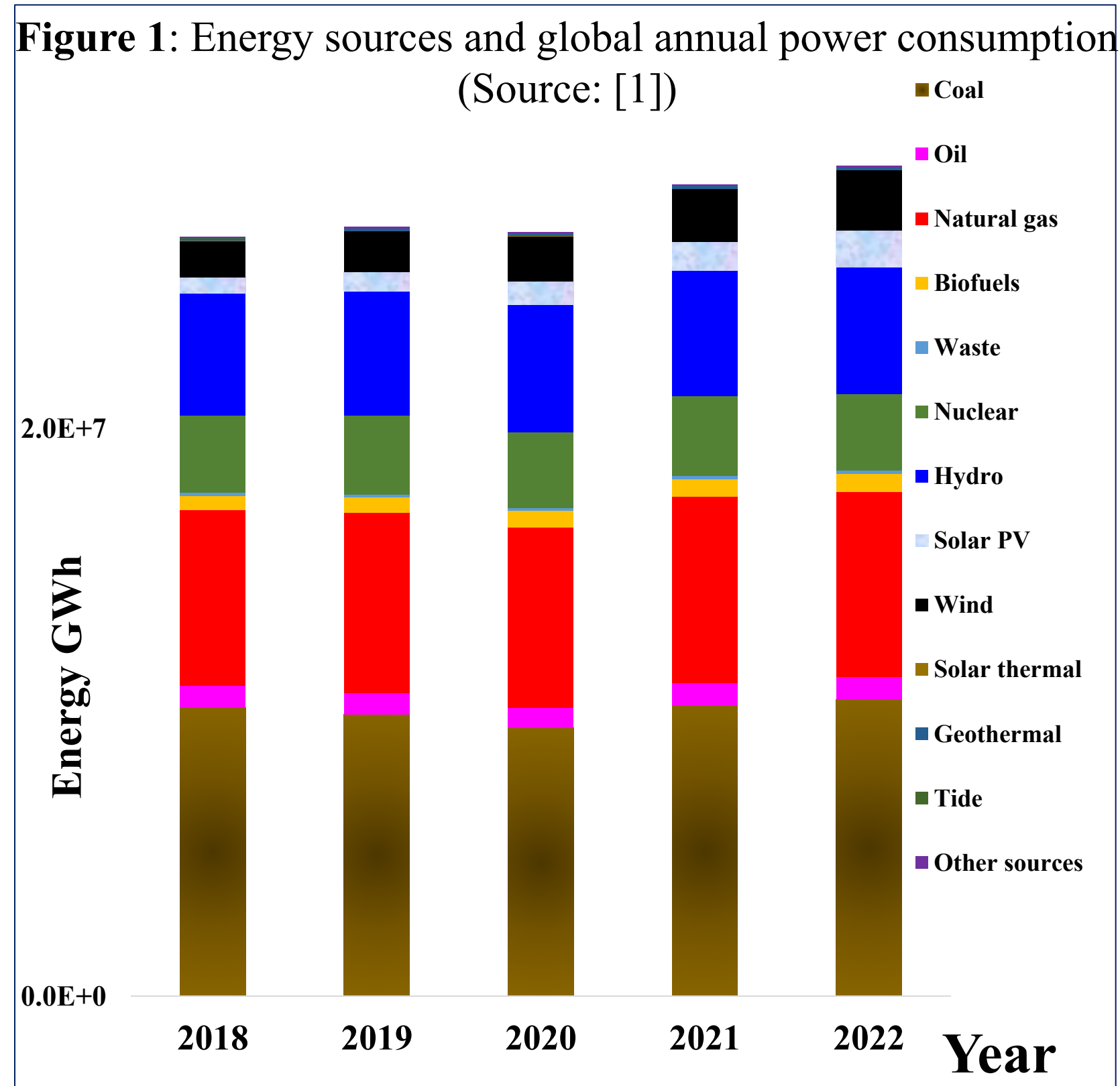
- Fossil fuel depletion
- Greenhouse gas (GHG) emission from fossil fuel
- Need for systems that can interconvert light energy and adsorb greenhouse gases
- Metal organic framework (MOF) is a potential nonlinear optical (NLO) and GHG adsorbing material [2-4]

Aim of Research

- Design and study of the adsorption and NLO properties of MOF-199 for optoelectronic applications

Research Objectives

- Model ground state geometry of MOF-199
- Conduct optical study on MOF-199 using DFT
- Investigate adsorption properties using Monte Carlo method
- Study the stability of MOF-199/GHG configuration using Molecular Dynamics simulation



METHOD

Computational Method

- Geometry optimization: DFT/B3LYP/LANL2DZ/6-311++G(d,p)
- Frequency calculation: No imaginary frequency
- NLO calculations: CPHF/DFT/B3LYP/LANL2DZ/6-311++G(d,p)
- Electronic calculation: TD-DFT/B3LYP/LANL2DZ/6-311++G(d,p)
- Energy calculation: electronic and optoelectronic properties
- GHG Adsorption simulation: Monte Carlo (MC), Molecular Dynamics (MD), Close Contact (CC) calculations, Pair Distribution Function (PDF) analysis [5,6]

RESULTS AND DISCUSSIONS

Figure 2: Optimized structure of MOF-199

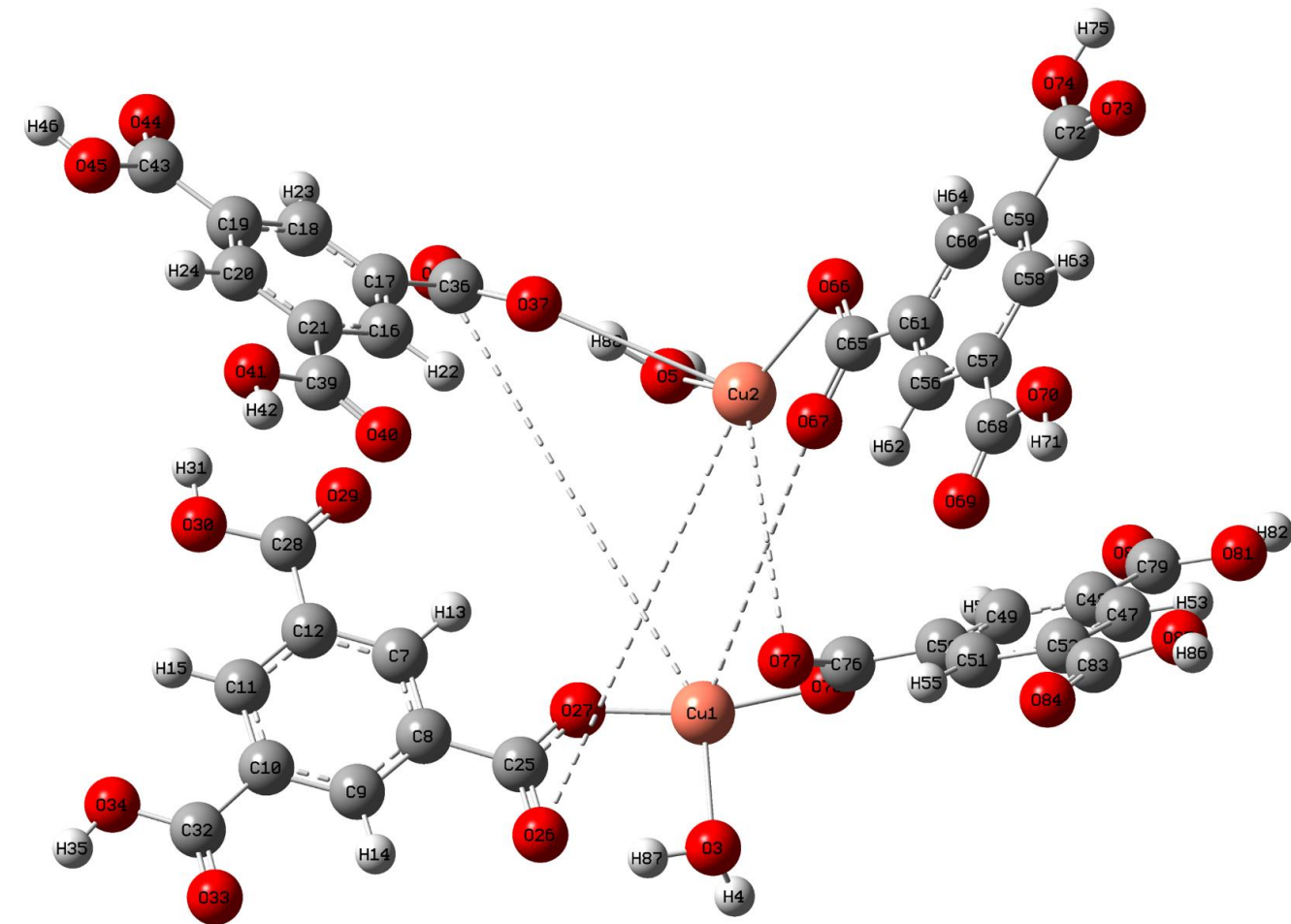


Table 1: Chemical reactivity parameters of MOF-199

	E _H	E _L	E _g	IP	EA	χ	S	ω	ω ⁻	ω ⁺	
MOF-199	-7.11	-6.66	0.45	7.11	6.66	6.89	4.35	52.7	108.8	101.9	Present study
CuMOF	-7.19	-4.55	2.74	7.19	4.55	5.87	0.73	12.4	15.4	9.6	Ref [7]

All units are in eV except S (in eV⁻¹)

Table 2: Electronic absorption properties of MOF-199

	λ _{max} nm	E _{ex} eV	f	LHE (%)	Orbital	Orbital contribution
MOF-199/SL	421	2.95	0.35	55	H-4 → L	61%
MOF-199/DL	515	2.41	0.17	32	H-30 → L	41%

SL: single-layered; DL: double-layered; LHE: Light-harvesting efficiency

Table 3: Static Optical properties of MOF-199 (ħω = 0)

MOF	μ	α	Δα	β _x	β _y	β _z	β _{tot}	γ
MOF-199	1.82	313	286	1.76	1829	2422	3035	40
CuMOF	8.25	266	184	5800	5400	12900	15100	78

α in a.u.; β in C³m³J⁻²/10⁻⁵³; γ in C⁴m⁴J⁻³10⁻⁶¹

Figure 3:(a) Orbital energies and (b) computed absorption spectra of MOF-199

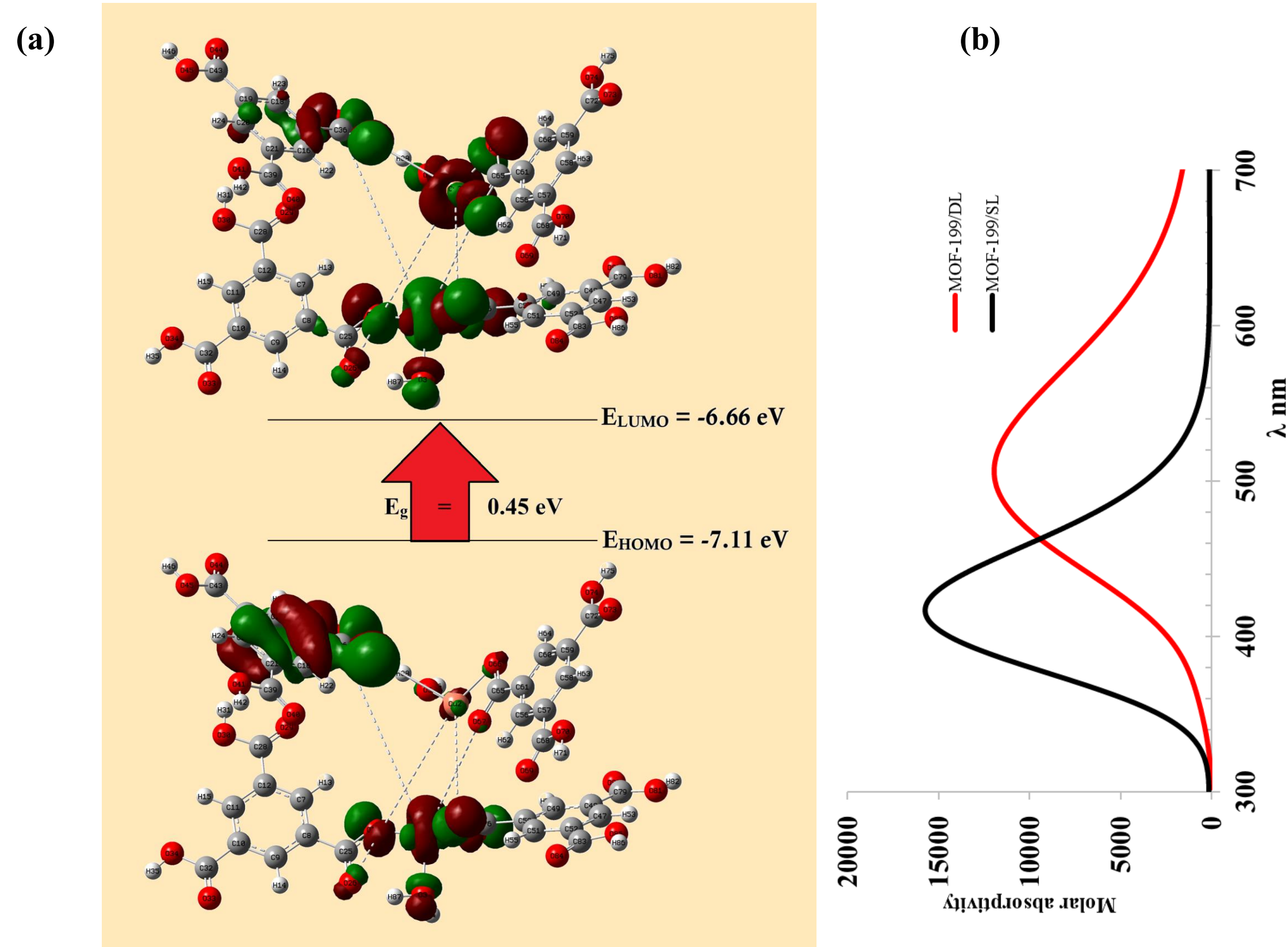


Table 4: Dynamic Optical properties of MOF-199

MOF	β (-2ω;ω,ω)	β (-ω;ω,0)	β (0;0,0)	γ _I (-2ω;ω,ω,0)	γ _{II} (-ω;ω,0,0)	γ _{III} (0;0,0,0)	
MOF-199*	1740	13290	3035	625	77	40	Present
MOF-199**	6806	2736	3035	28	42	40	Present
CuMOF**	4100	4900	15100	141	164	78	Ref [7]

*: laser frequency 532 nm (ħω = 0.085645 au); **: laser frequency 1064 nm (ħω = 0.042823 au)

Table 5: Monte Carlo adsorption properties of MOF-199 on selected greenhouse gases.

Structure	E _{Tot}	E _{Ads}	E _{Rigid-ads}	E _{Def}	dE _{ad} /dN _i
MOF-199-CH ₄	-271	-271	-299	28	-0.98
MOF-199-CO ₂	-773	-773	-784	11	-0.99
MOF-199- H ₂ S	-778	-778	-785	7	-2.64
MOF-199- NH ₃	-1,250	-1,250	-1,310	62	-0.52

Figure 4: CC of (a) CO₂ and (b) H₂S on MOF-199

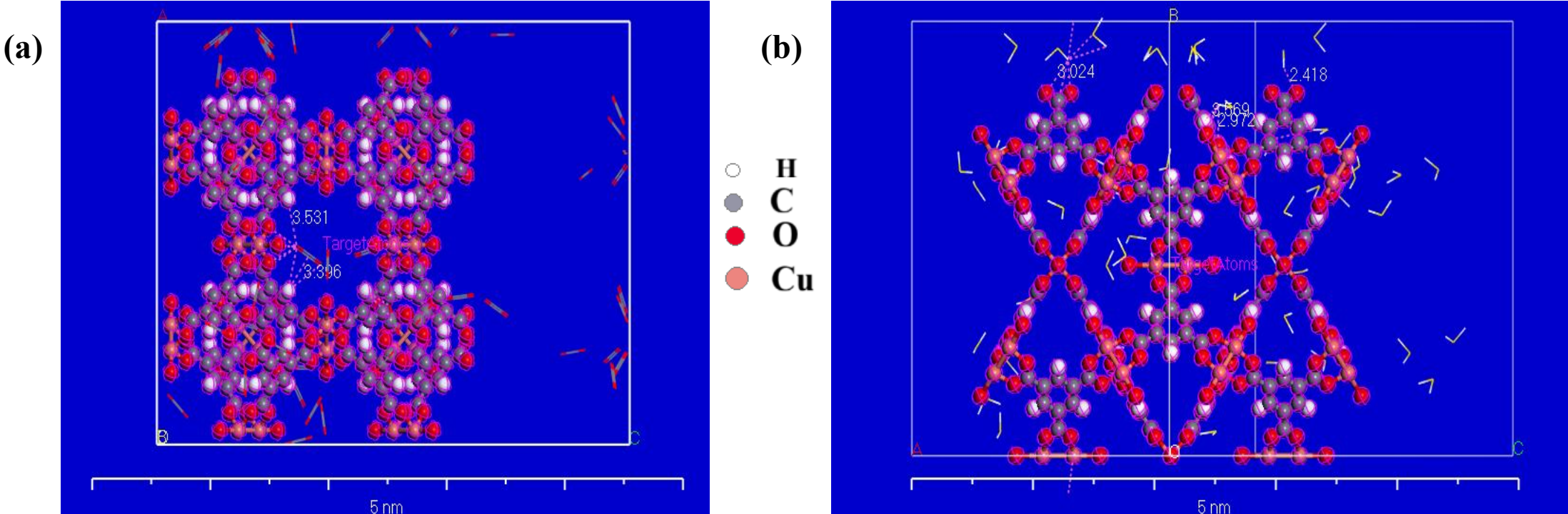


Figure 5: PDF of CO₂ on MOF-199

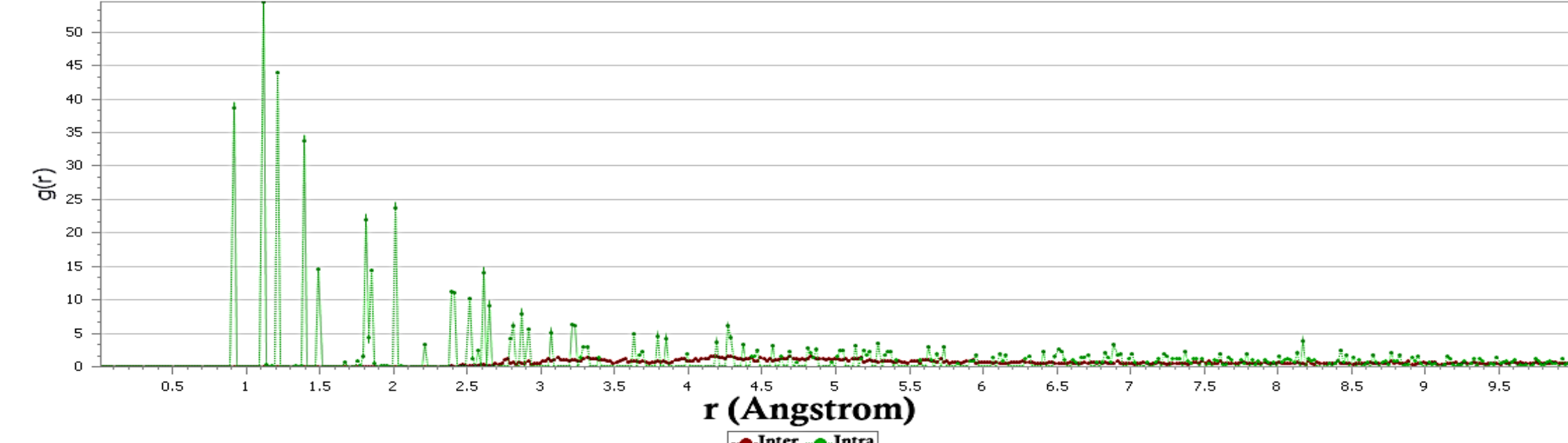


Table 6: Molecular dynamics simulation of adsorbates in MOF-199 pore at 200 ps

	Total energy (kcal/mol)			
Simulation time (ps)	MOF-199-CH ₄	MOF-199-CO ₂	MOF-199- H ₂ S	MOF-199- NH ₃
0	12,323.87	12,038.00	12,146.73	11,667.00
40	11,550.68	11,298.77	11,305.19	11,388.98
80	11,558.67	11,288.94	11,293.12	11,390.38
120	11,549.36	11,248.16	11,293.64	11,396.11
160	11,529.18	11,257.55	11,290.11	11,355.83
180	11,533.21	11,259.00	11,287.12	11,359.28
200	11,543.40	11,270.83	11,281.22	11,350.56

CONCLUSIONS

- The optical response of MOF-199 changed on application of different laser frequencies.
- Apart from SHG [β(-2ω;ω,ω)], other NLO parameters (EOPE, EOKE, EFISHG) were enhanced under high-energy laser frequency (ħω = 0.085645 au).
- The light harvesting efficiency is 32% with λ_{max} of 515 nm.
- MOF-199 displayed strong binding interactions with NH₃, CH₄, CO₂ and H₂S.
- The MOF displayed special affinity for H₂S and CO₂ gases.
- Close contact and pair distribution function analyses confirmed physical and chemical adsorption of the gases on the MOF.
- MOF-199 is a NLO material for optoelectronic applications (SDG 7) such as optical data storage technology, ultrafast communication, and optical switching, and a potential GHG adsorbent (SDG 13).

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