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Supplementary Information

DFT and Hybrid-DFT calculations on the electronic properties of vanadate materials: theory meets experiments

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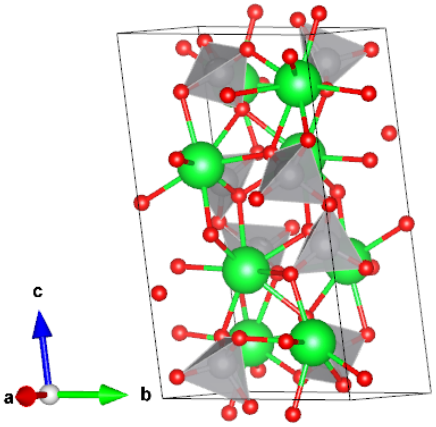
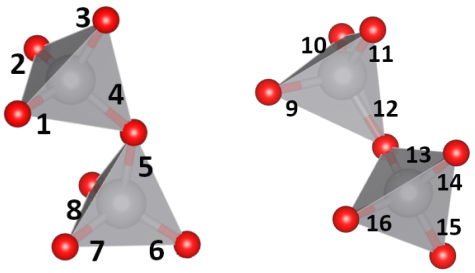
1 $Sr_2V_2O_7$



$Sr_2V_2O_7$	a	b	c	α	β	γ
Expt	7.046	7.094	12.986	99.44	93.78	90.88

Fig-SI 1: Conventional cell of $Sr_2V_2O_7$ taken from [1]. This cell contains 44 atoms. The Sr atoms are in green, the O atoms are in red, and the vanadium are represented by the gray polyhedron. The experimentally measured cell parameters and angles of the conventional cell are also given.



$Sr_2V_2O_7$	Expt	PBE	PBE+U	HSE06
1	1.667	1.699	1.702	1.675
2	1.711	1.728	1.732	1.704
3	1.669	1.693	1.696	1.670
4	1.815	1.825	1.834	1.805
5	1.822	1.834	1.845	1.823
6	1.657	1.680	1.680	1.653
7	1.696	1.720	1.726	1.695
8	1.687	1.724	1.729	1.701
9	1.695	1.731	1.737	1.709
10	1.675	1.696	1.698	1.675
11	1.670	1.693	1.695	1.661
12	1.810	1.827	1.840	1.811
13	1.819	1.821	1.832	1.805
14	1.662	1.696	1.699	1.669
15	1.683	1.703	1.705	1.681
16	1.705	1.717	1.721	1.696
Average	1.715	1.737	1.742	1.715

Fig-SI 2: Experimental and theoretical (calculated with PBE, PBE+U and HSE06) inter-atomic V-O distances in Å of V_2O_7 clusters contain in $Sr_2V_2O_7$. The reported distances are labeled by numbers and the corresponding positions are indicated by the pictures. Experimental data taken from [1].

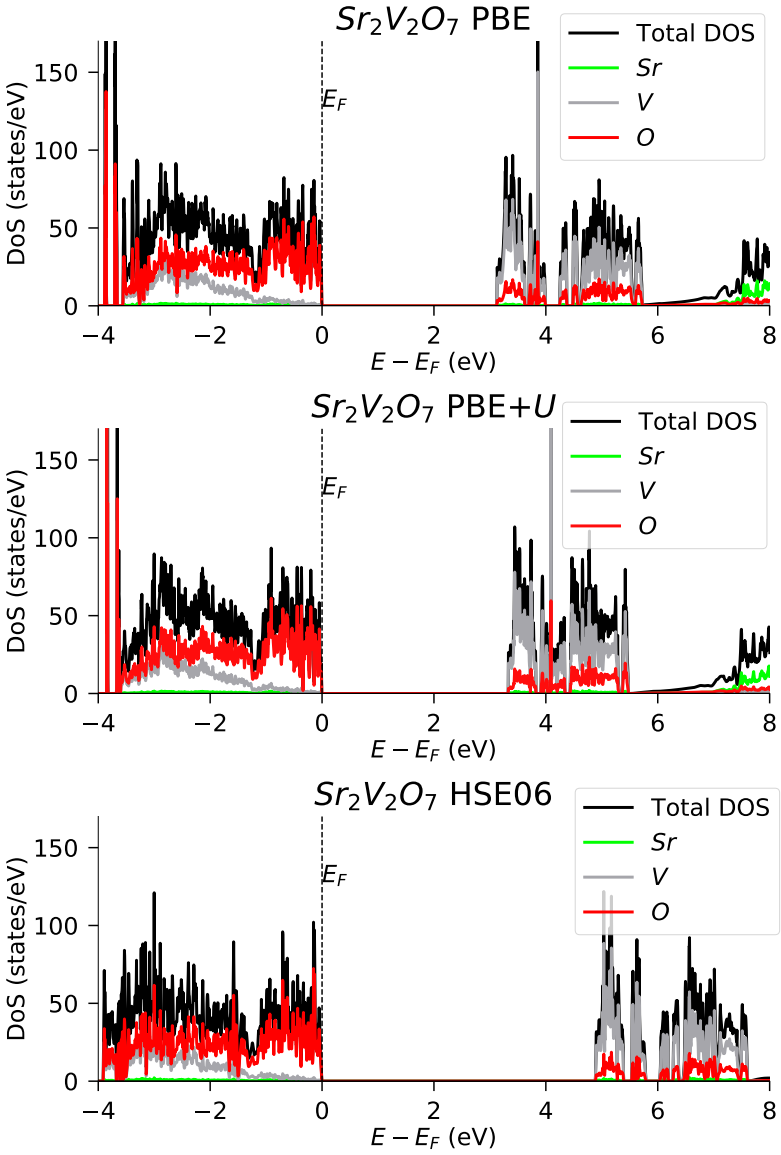


Fig-SI 3: DOS of $Sr_2V_2O_7$ calculated with PBE (top), PBE+U (middle) and HSE06 (bottom) functionals. The contribution of the strontium, vanadium and oxygen atoms are represented in green, gray and red, respectively.

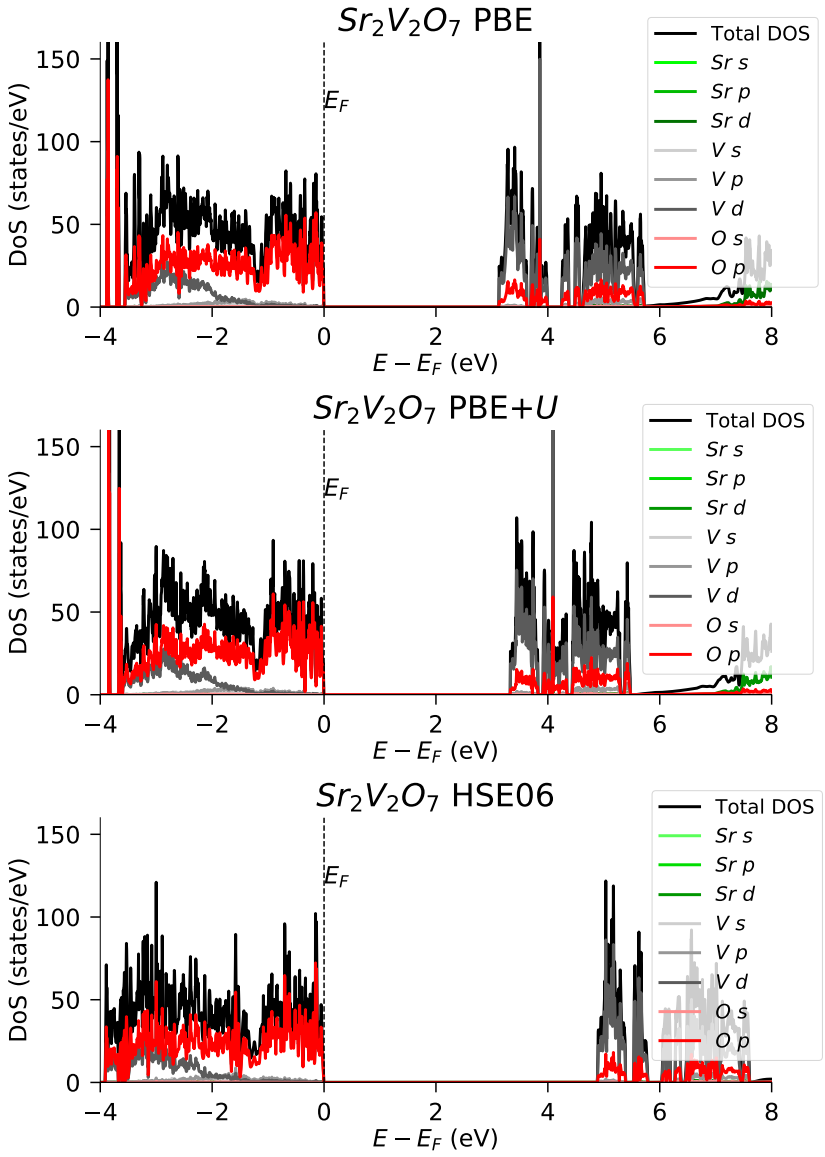


Fig-SI 4: Projected DOS of $Sr_2V_2O_7$ calculated with PBE (top), PBE+U (middle) and HSE06 (bottom) functionals. The contribution of the strontium (s, p, d), vanadium (s, p, d) and oxygen (s, p) orbitals are represented in green, gray and red, respectively.

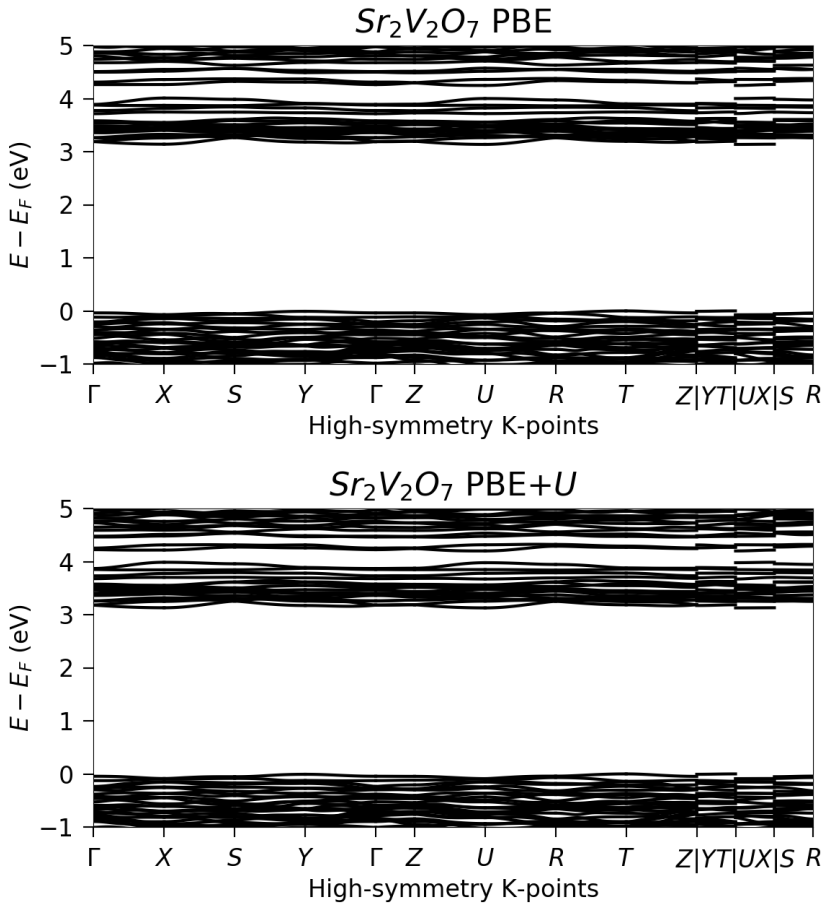


Fig-SI 5: Band structure of $Sr_2V_2O_7$ calculated with PBE (top) and HSE06 (bottom) functionals. The considered path and high symmetry K-points are defined in [2]. For technical reasons we were unable to converge the band structure of this material in HSE06.

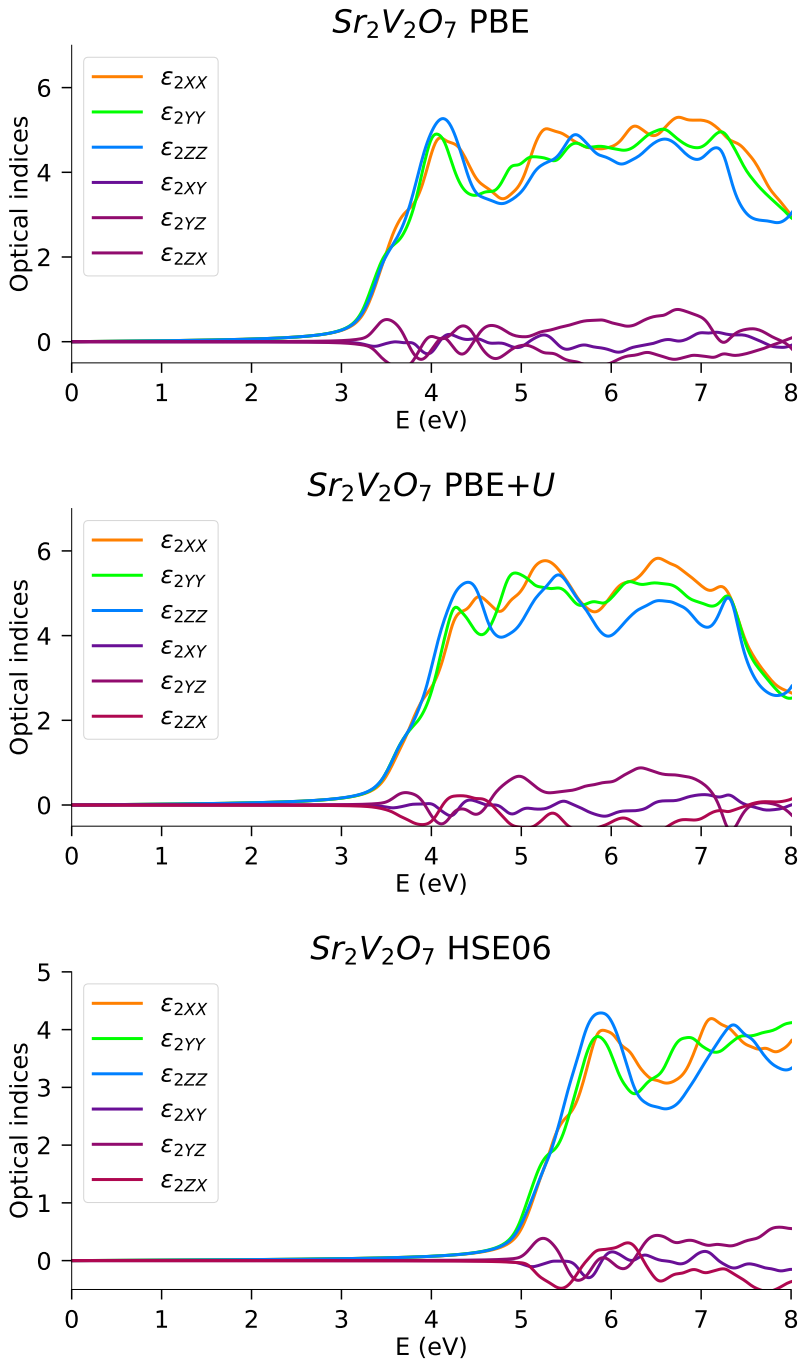


Fig-SI 6: Imaginary part of the dielectric tensor ϵ_2 of $Sr_2V_2O_7$ calculated with PBE (top), PBE+U (middle) and HSE06 (bottom) functionals. The components ϵ_{2xx}, ϵ_{2yy} and ϵ_{2zz} are in orange, green and blue, respectively.

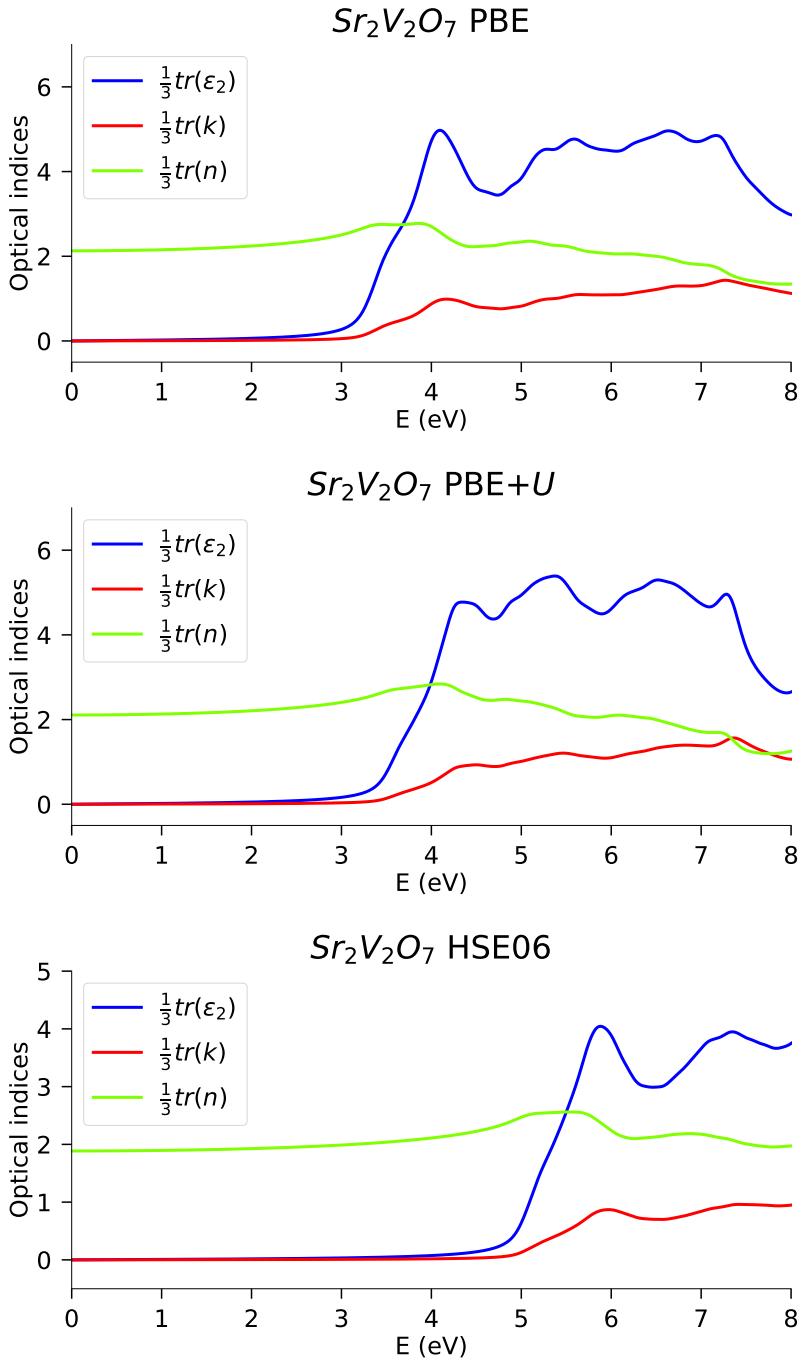
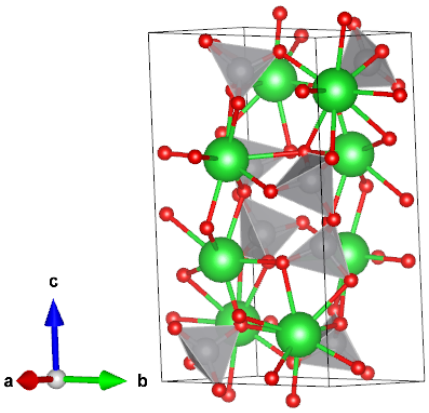


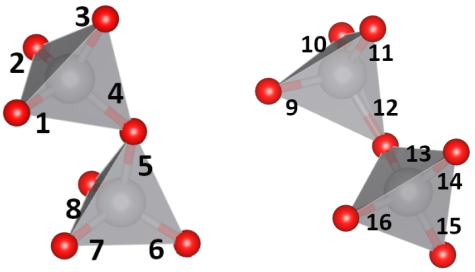
Fig-SI 7: Trace of the imaginary part of the dielectric tensor ϵ_2 (blue), of the refractive index n (green), and of extinction coefficient k (red) of $Sr_2V_2O_7$, calculated with PBE (top), PBE+U (middle) and HSE06 (bottom) functionals.

2 $Ba_2V_2O_7$



$Ba_2V_2O_7$	a	b	c	α	β	γ
Expt	7.306	7.320	13.571	87.32	80.52	89.91

Fig-SI 8: Conventional cell of $Ba_2V_2O_7$ taken from [3]. This cell contains 44 atoms. The Ba atoms are in green, the O atoms are in red, and the vanadium are represented by the gray polyhedron. The experimentally measured cell parameters and angles of the conventional cell are also given.



$Ba_2V_2O_7$	Expt	PBE	PBE+U	HSE06
1	1.705	1.722	1.727	1.702
2	1.666	1.699	1.701	1.666
3	1.687	1.700	1.703	1.679
4	1.824	1.833	1.845	1.816
5	1.818	1.831	1.842	1.816
6	1.686	1.711	1.715	1.689
7	1.692	1.714	1.718	1.690
8	1.663	1.695	1.697	1.669
9	1.669	1.689	1.691	1.663
10	1.698	1.720	1.725	1.698
11	1.700	1.717	1.721	1.693
12	1.833	1.837	1.849	1.820
13	1.815	1.824	1.836	1.803
14	1.666	1.698	1.700	1.674
15	1.677	1.704	1.706	1.681
16	1.700	1.724	1.729	1.701
Average	1.719	1.739	1.744	1.716

Fig-SI 9: Experimental and theoretical (calculated with PBE, PBE+U and HSE06) inter-atomic V-O distances in Å of V_2O_7 clusters contain in $Ba_2V_2O_7$. The reported distances are labeled by numbers and the corresponding positions are indicated by the pictures. Experimental data taken from [3].

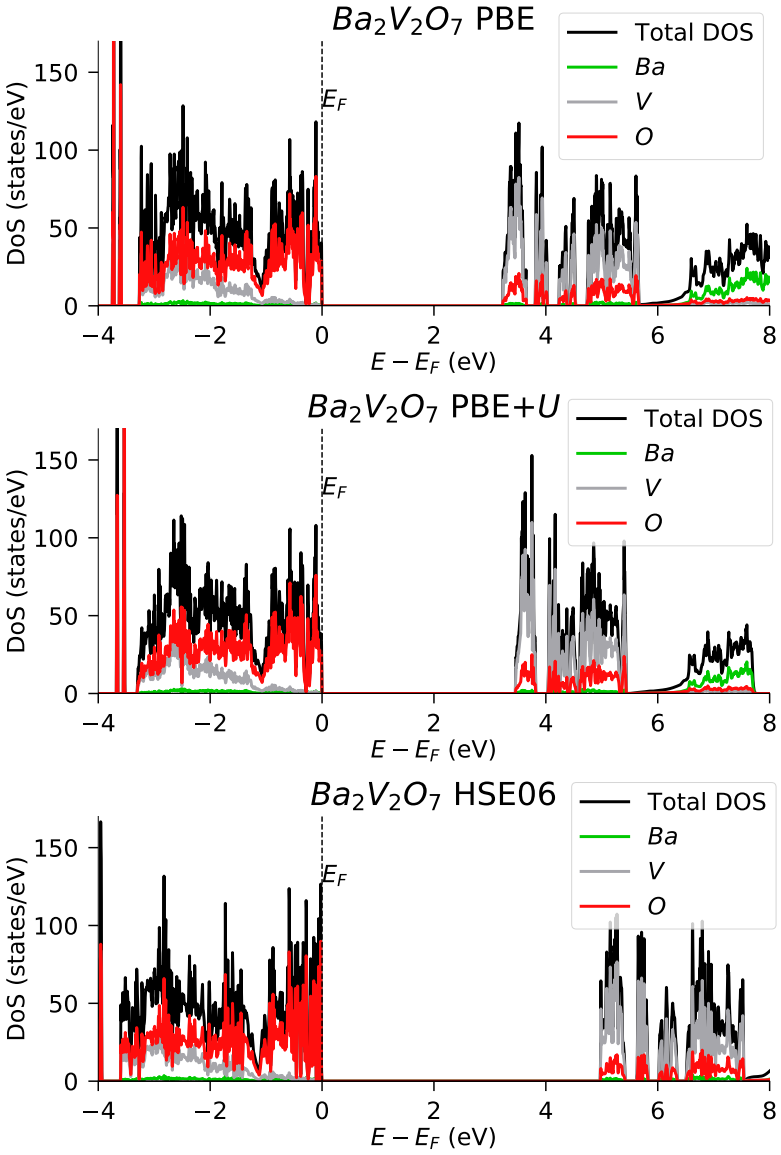


Fig-SI 10: DOS of $Ba_2V_2O_7$ calculated with PBE (top), PBE+U (middle) and HSE06 (bottom) functionals. The contribution of the barium, vanadium and oxygen atoms are represented in green, gray and red, respectively.

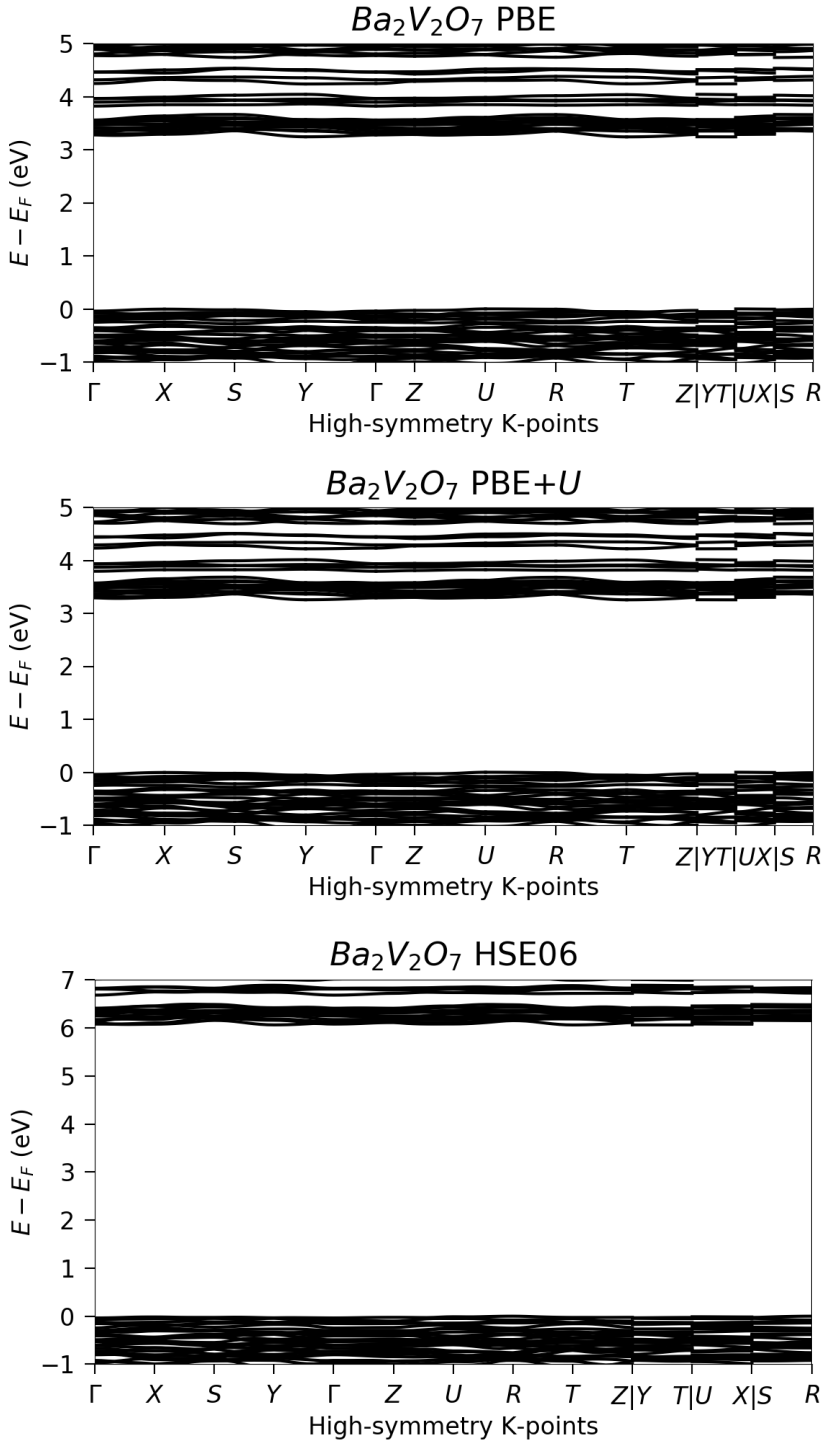


Fig-SI 11: Band structure of $Ba_2V_2O_7$ calculated with PBE (top), PBE+U (middle) and HSE06 (bottom) functionals. The considered path and high symmetry K-points are defined in [2].

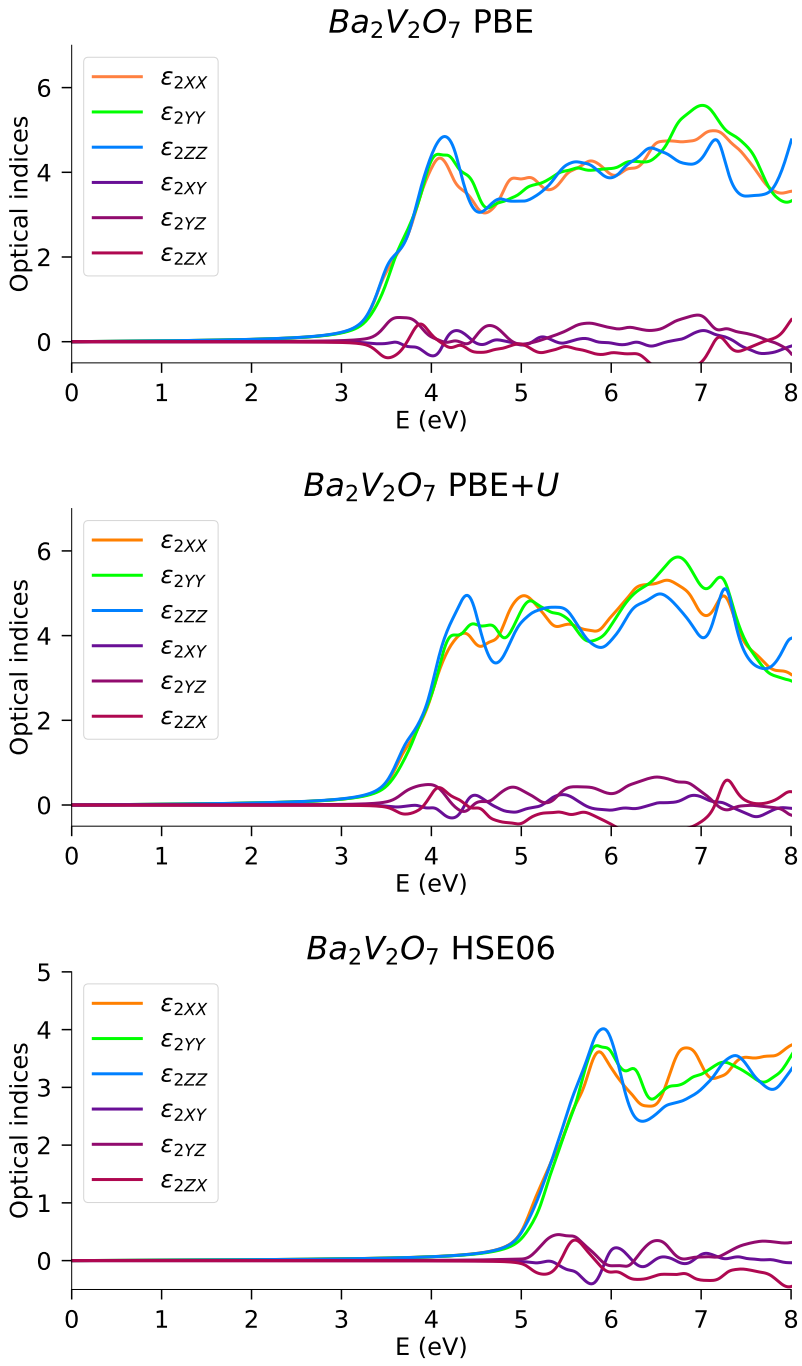


Fig-SI 12: Imaginary part of the dielectric tensor ϵ_2 of $Ba_2V_2O_7$ calculated with PBE (top), PBE+U (middle) and HSE06 (bottom) functionals. The components ϵ_{2xx}, ϵ_{2yy} and ϵ_{2zz} are in orange, green and blue, respectively.

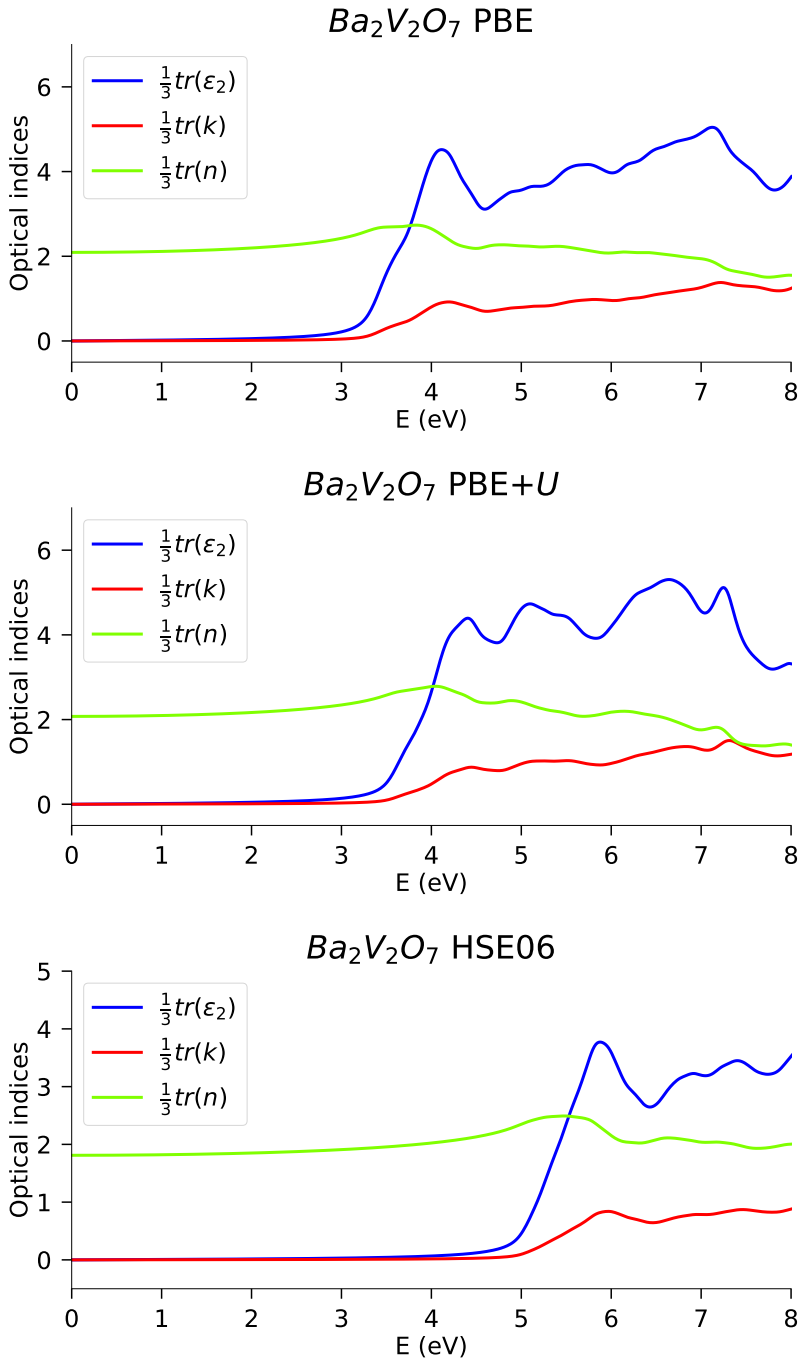
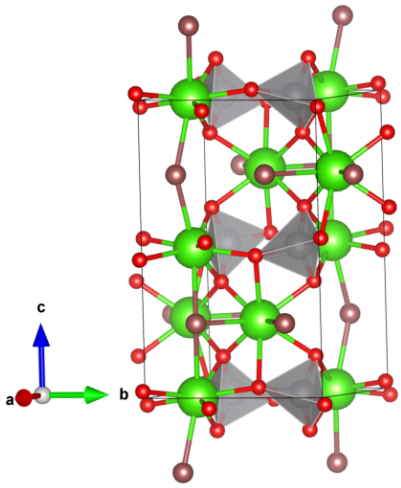


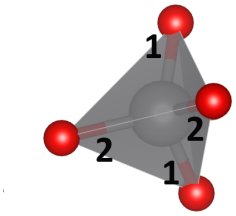
Fig-SI 13: Trace of the imaginary part of the dielectric tensor ϵ_2 (blue), of the refractive index n (green), and of extinction coefficient k (red) of $Sr_2V_2O_7$, calculated with PBE (top), PBE+U (middle) and HSE06 (bottom) functionals.

3 Ca_2VO_4Cl



Ca_2VO_4Cl	a	b	c	α	β	γ
Expt	6.311	7.140	11.052	90.00	90.00	90.00

Fig-SI 14: Conventional cell of Ca_2VO_4Cl taken from [4]. This cell contains 32 atoms. The Ca atoms are in green, the O atoms are in red, the Cl atoms are in brown, and the vanadium are represented by the gray polyhedron. The experimentally measured cell parameters and angles of the conventional cell are also given.



Ca_2VO_4Cl	Expt	PBE	PBE+U	HSE06
1	1.710	1.732	1.737	1.711
2	1.703	1.725	1.729	1.702
Average	1.706	1.728	1.733	1.706

Fig-SI 15: Experimental and theoretical (calculated with PBE, PBE+U and HSE06) inter-atomic V-O distances in Å of the VO_4 cluster contain in Ca_2VO_4Cl. The reported distances are labeled by numbers and the corresponding positions are indicated by the pictures. Experimental data taken from [4].

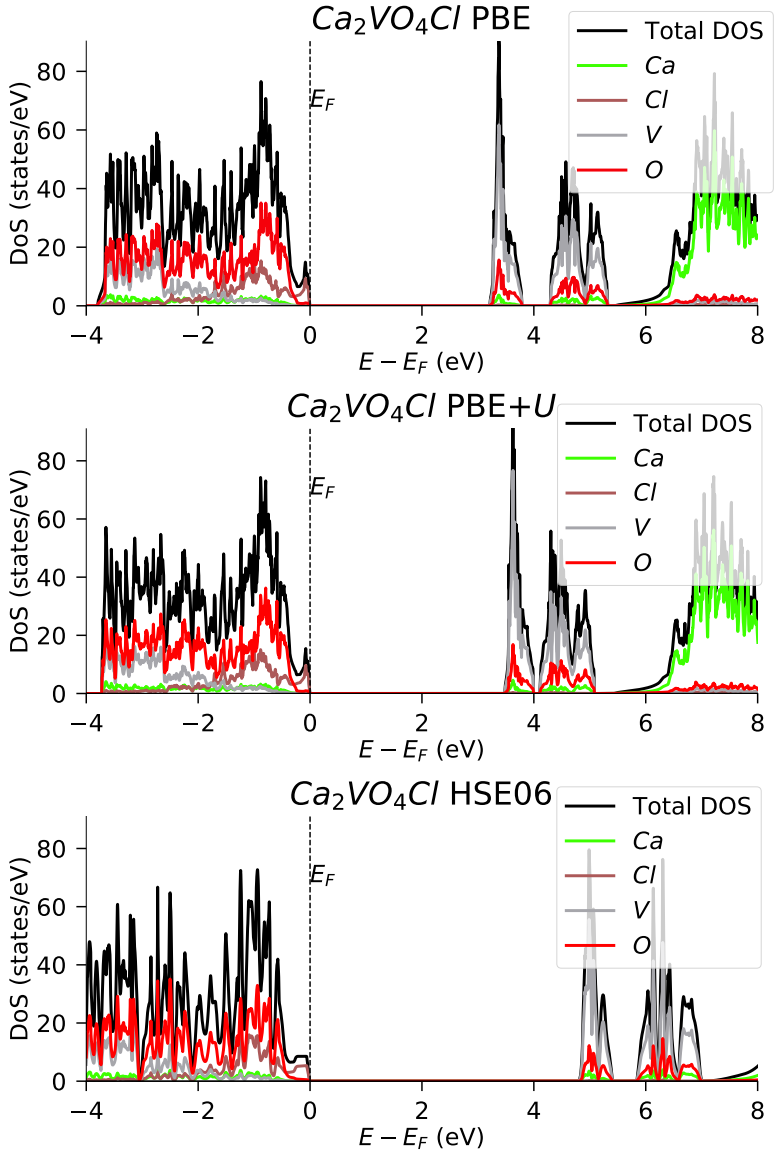


Fig-SI 16: DOS of Ca_2VO_4Cl calculated with PBE (top), PBE+U (middle) and HSE06 (bottom) functionals. The contribution of the calcium, vanadium, chlorine and oxygen atoms are represented in green, gray, brown and red, respectively.

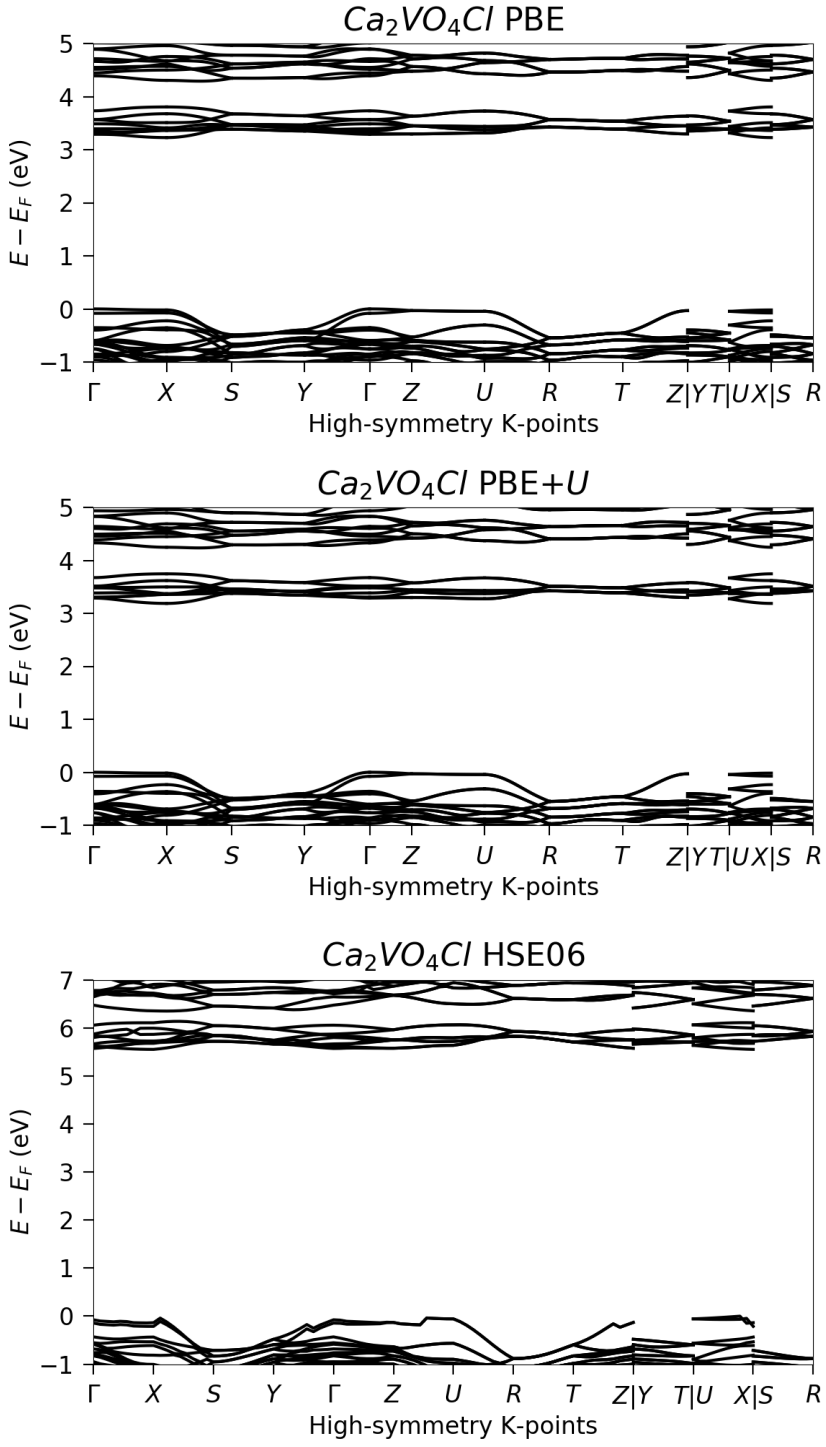


Fig-SI 17: Band structure of Ca_2VO_4Cl calculated with PBE (top), PBE+U (middle) and HSE06 (bottom) functionals. The considered path and high symmetry K-points are defined in [2].

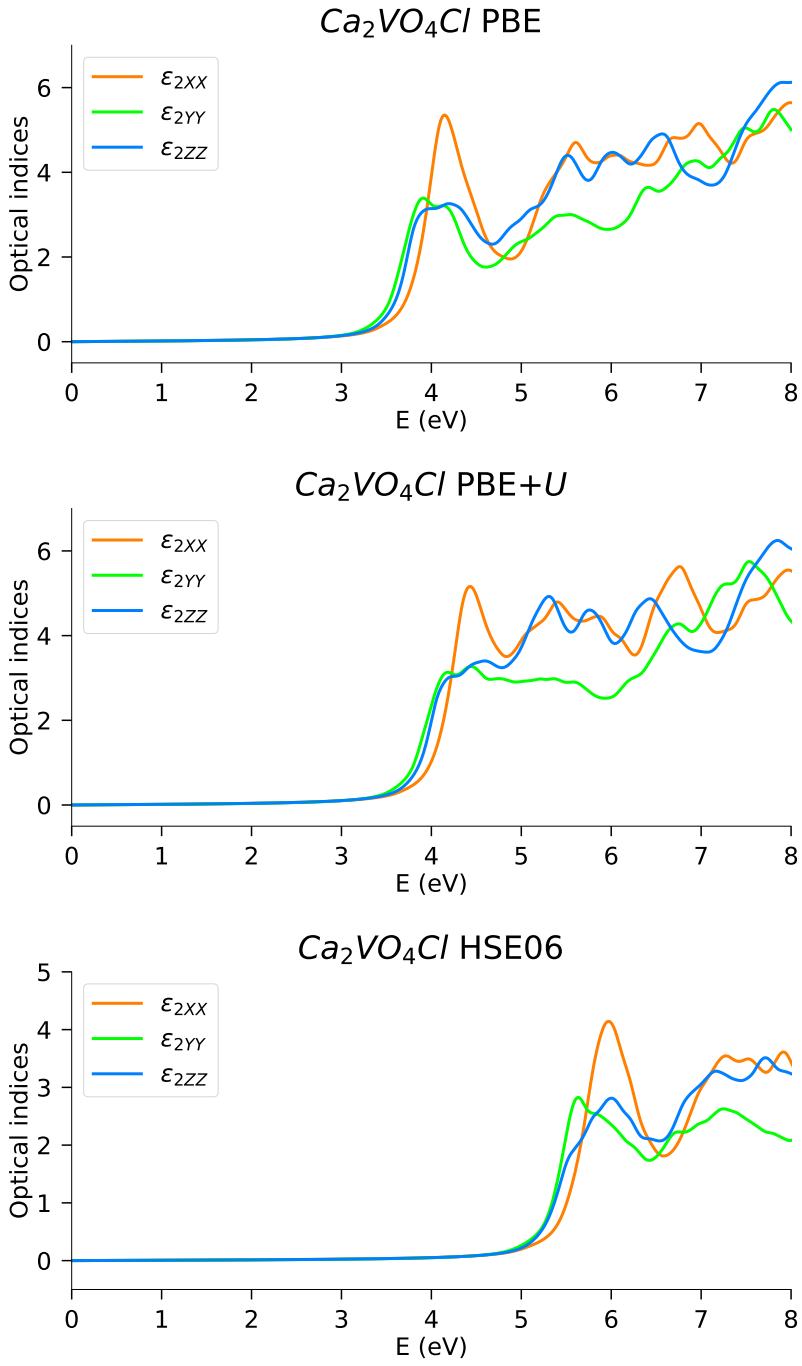


Fig-SI 18: Imaginary part of the dielectric tensor ϵ_2 of Ca_2VO_4Cl calculated with PBE (top), PBE+U (middle) and HSE06 (bottom) functionals. The components ϵ_{2xx}, ϵ_{2yy} and ϵ_{2zz} are in orange, green and blue, respectively.

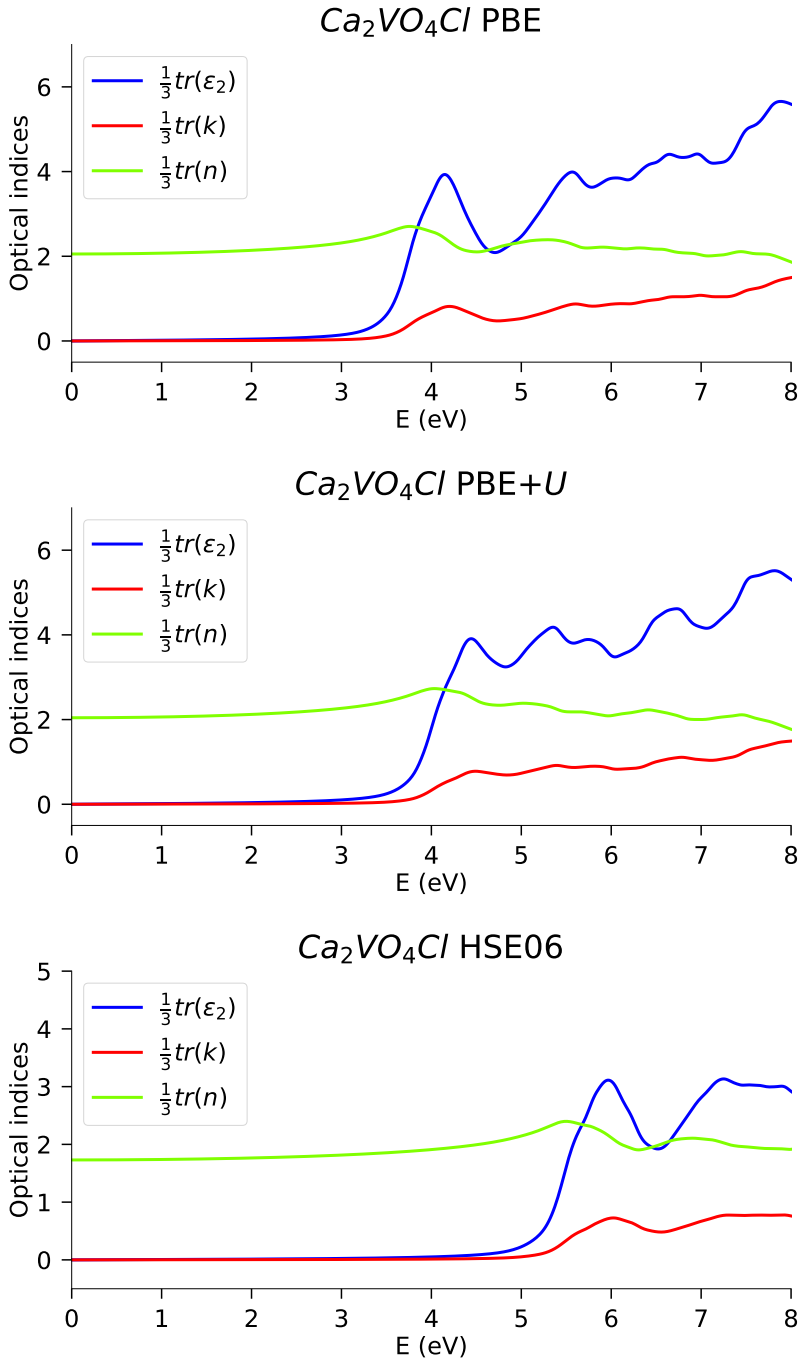
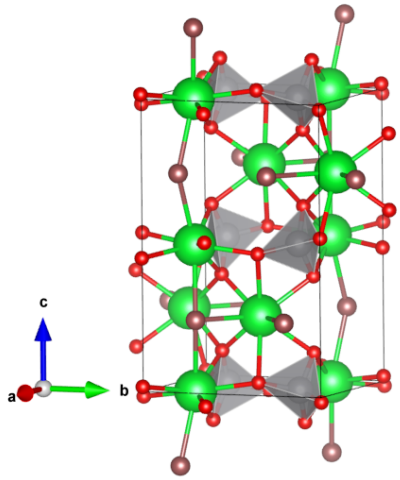


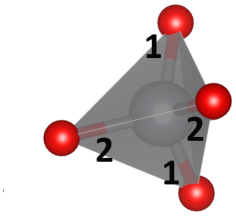
Fig-SI 19: Trace of the imaginary part of the dielectric tensor ϵ_2 (blue), of the refractive index n (green), and of extinction coefficient k (red) of Ca_2VO_4Cl, calculated with PBE (top), PBE+U (middle) and HSE06 (bottom) functionals.

4 Sr_2VO_4Cl



Sr_2VO_4Cl	a	b	c	α	β	γ
Expt	6.570	7.520	11.527	90.00	90.00	90.00

Fig-SI 20: Conventional cell of Sr_2VO_4Cl taken from [5]. This cell contains 32 atoms. The Sr atoms are in green, the O atoms are in red, the Cl atoms are in brown, and the vanadium are represented by the gray polyhedron. The experimentally measured cell parameters and angles of the conventional cell are also given.



Sr_2VO_4Cl	Expt	PBE	PBE+U	HSE06
1	1.726	1.737	1.742	1.715
2	1.715	1.728	1.733	1.706
Average	1.720	1.732	1.738	1.710

Fig-SI 21: Experimental and theoretical (calculated with PBE, PBE+U and HSE06) inter-atomic V-O distances in Å of the VO_4 cluster contain in Sr_2VO_4Cl. The reported distances are labeled by numbers and the corresponding positions are indicated by the pictures. Experimental data taken from [5].

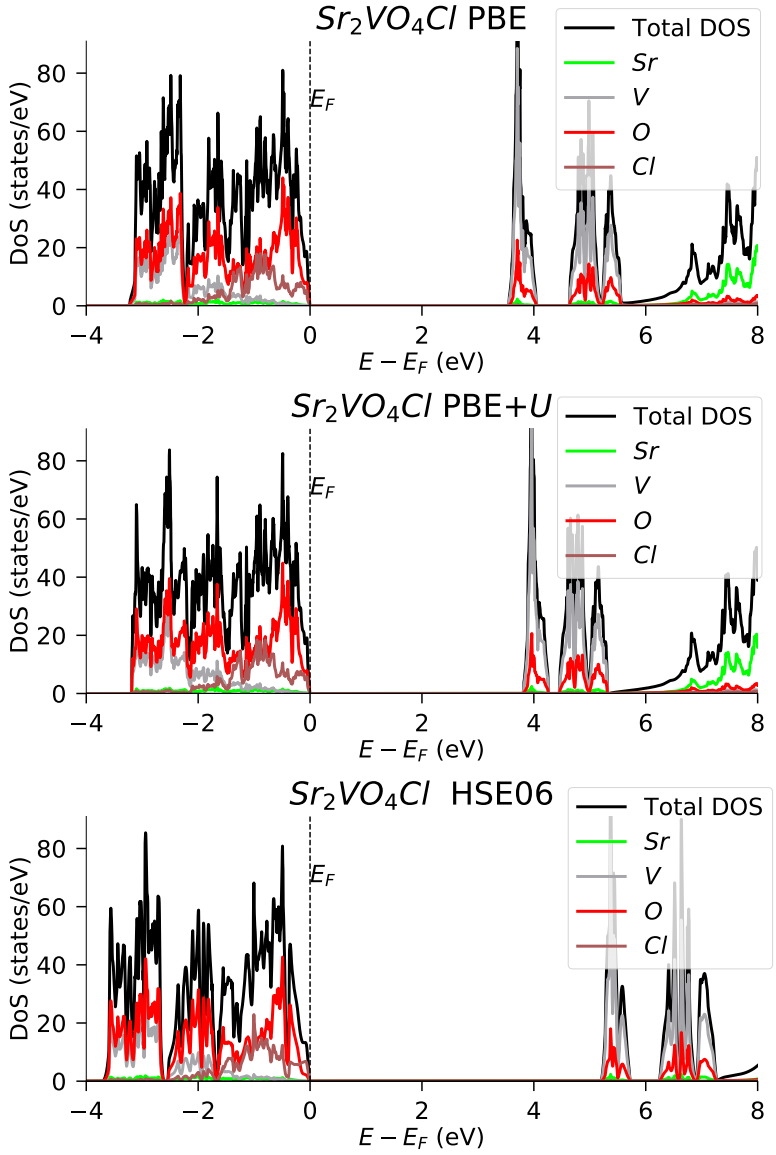


Fig-SI 22: DOS of Sr_2VO_4Cl calculated with PBE (top), PBE+U (middle) and HSE06 (bottom) functionals. The contribution of the strontium, vanadium, chlorine and oxygen atoms are represented in green, gray, brown and red, respectively.

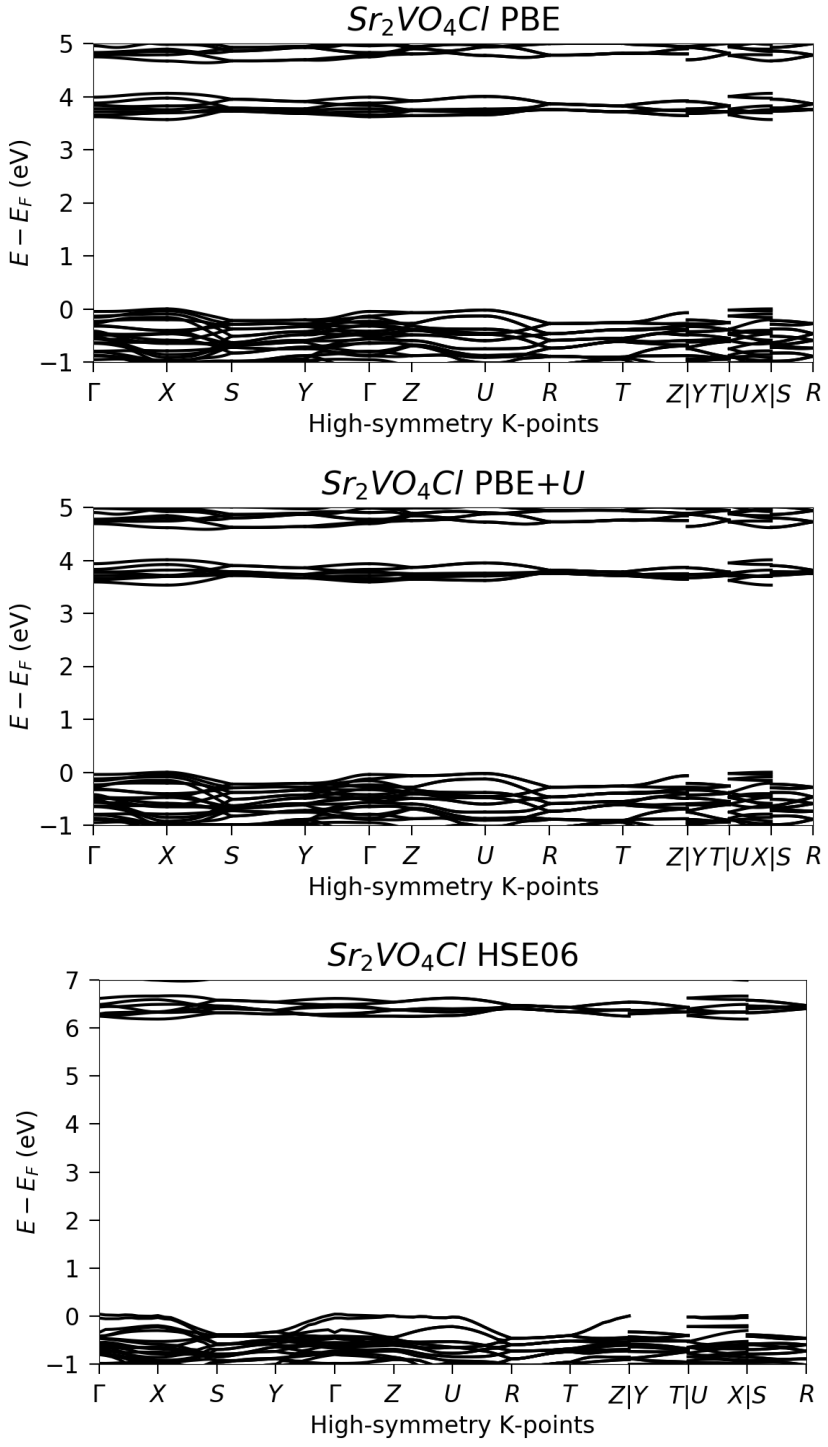


Fig-SI 23: Band structure of Sr_2VO_4Cl calculated with PBE (top), PBE+U (middle) and HSE06 (bottom) functionals. The considered path and high symmetry K-points are defined in [2].

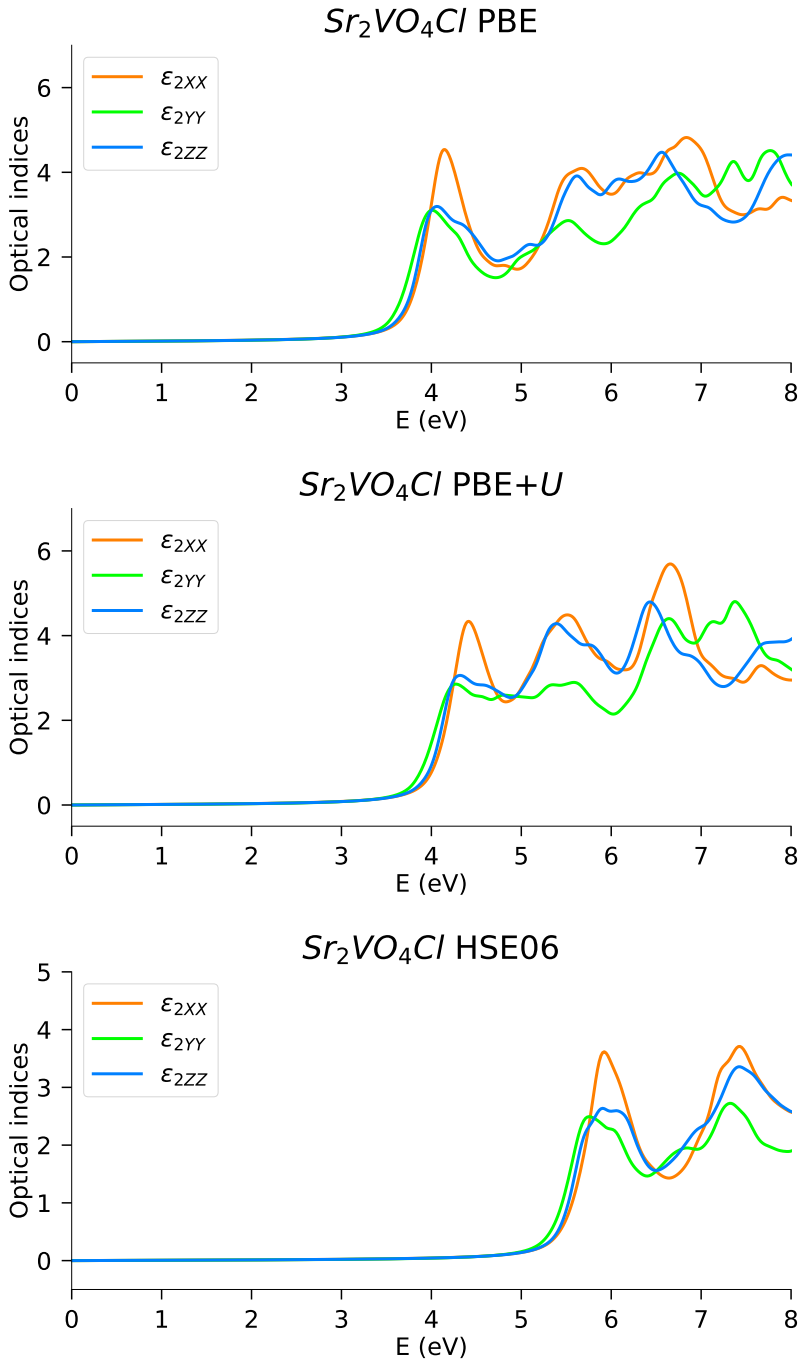


Fig-SI 24: Imaginary part of the dielectric tensor ϵ_2 of Sr_2VO_4Cl calculated with PBE (top), PBE+U (middle) and HSE06 (bottom) functionals. The components ϵ_{2xx}, ϵ_{2yy} and ϵ_{2zz} are in orange, green and blue, respectively.

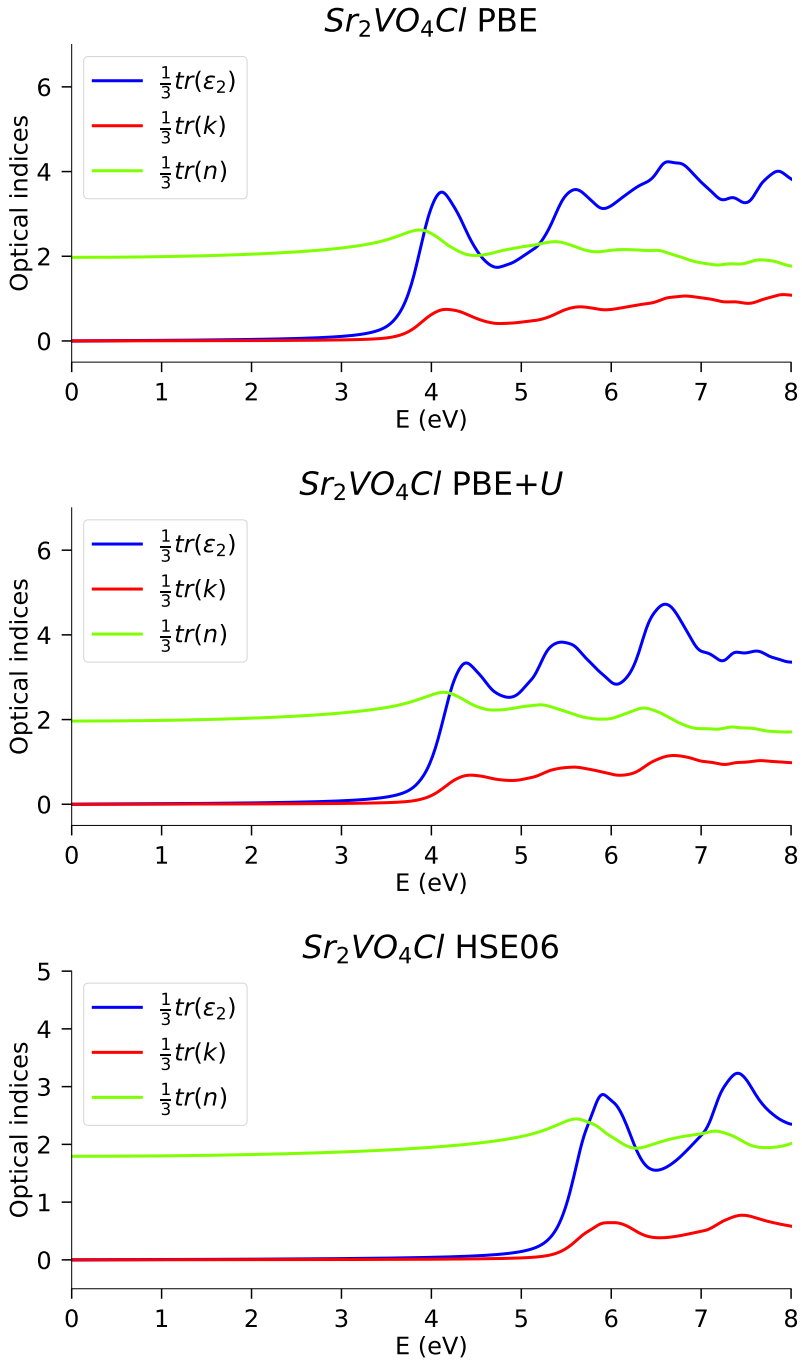
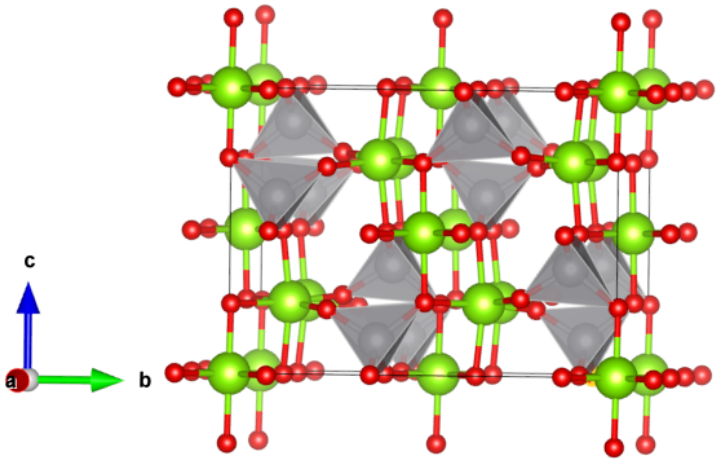


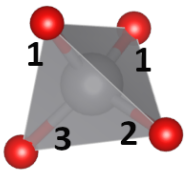
Fig-SI 25: Trace of the imaginary part of the dielectric tensor ϵ_2 (blue), of the refractive index n (green), and of extinction coefficient k (red) of Sr_2VO_4Cl, calculated with PBE (top), PBE+U (middle) and HSE06 (bottom) functionals.

5 $Mg_3V_2O_8$



$Mg_3V_2O_8$	a	b	c	α	β	γ
Expt	6.053	11.442	8.330	90.00	90.00	90.00

Fig-SI 26: Conventional cell of $Mg_3V_2O_8$ taken from [6]. This cell contains 52 atoms. The Mg atoms are in green, the O atoms are in red, and the vanadium are represented by the gray polyhedron. The experimentally measured cell parameters and angles of the conventional cell are also given.



$Mg_3V_2O_8$	Expt	PBE	PBE+U	HSE06
1	1.695	1.716	1.722	1.692
2	1.809	1.810	1.823	1.786
3	1.716	1.732	1.737	1.706
Average	1.729	1.743	1.751	1.719

Fig-SI 27: Experimental and theoretical (calculated with PBE, PBE+U and HSE06) inter-atomic V-O distances in Å of the VO_4 cluster contain in $Mg_3V_2O_8$. The reported distances are labeled by numbers and the corresponding positions are indicated by the pictures. Experimental data taken from [6].

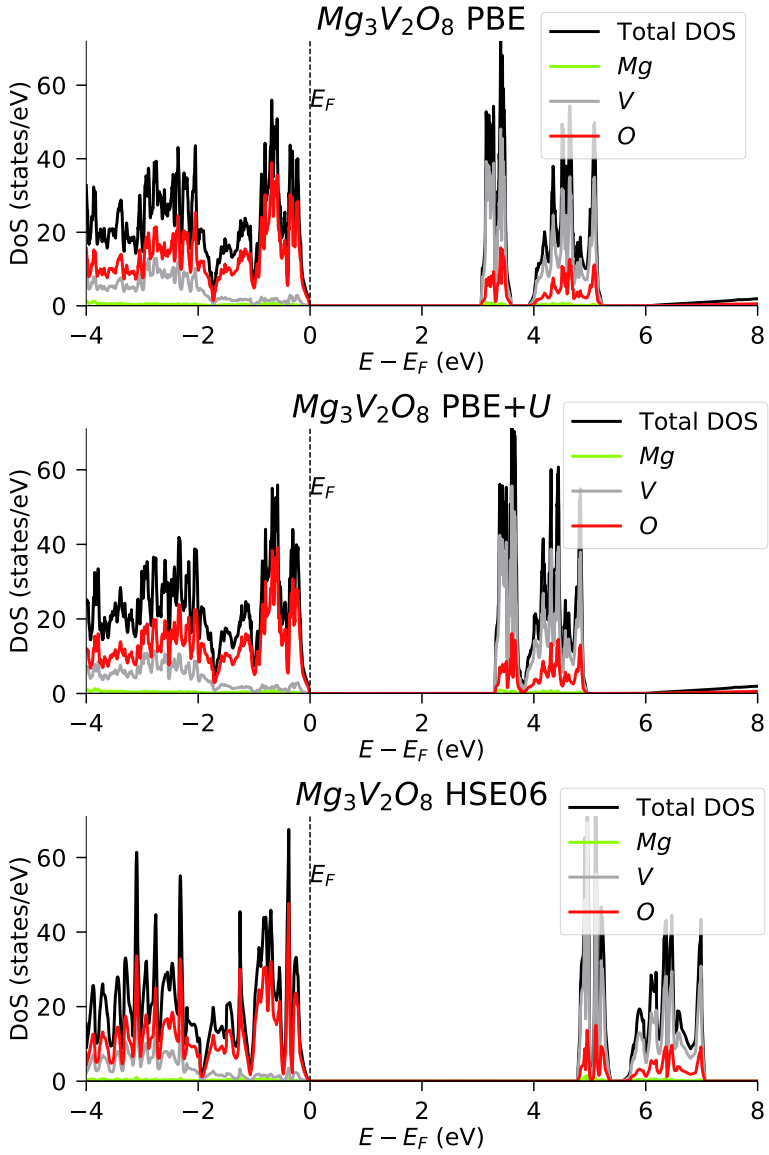


Fig-SI 28: DOS of $Mg_3V_2O_8$ calculated with PBE (top), PBE+U (middle) and HSE06 (bottom) functionals. The contribution of the magnesium, vanadium, and oxygen atoms are represented in green, gray and red, respectively.

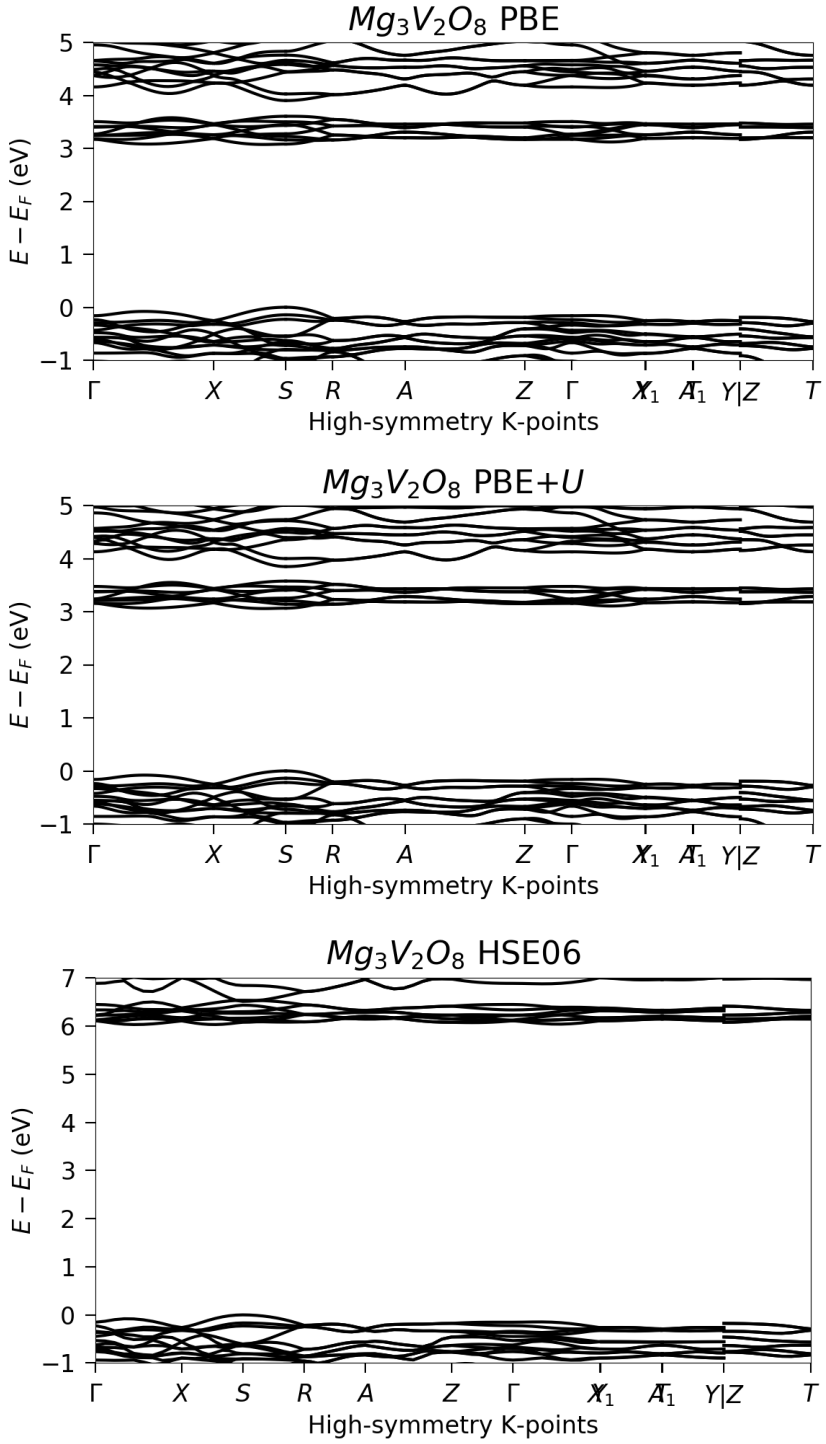


Fig-SI 29: Band structure of $Mg_3V_2O_8$ calculated with PBE (top), PBE+U (middle) and HSE06 (bottom) functionals. The considered path and high symmetry K-points are defined in [2]. In the reciprocal space, the points Y and X_1, as well as the points A_1 and T, are very close but does not coincide.

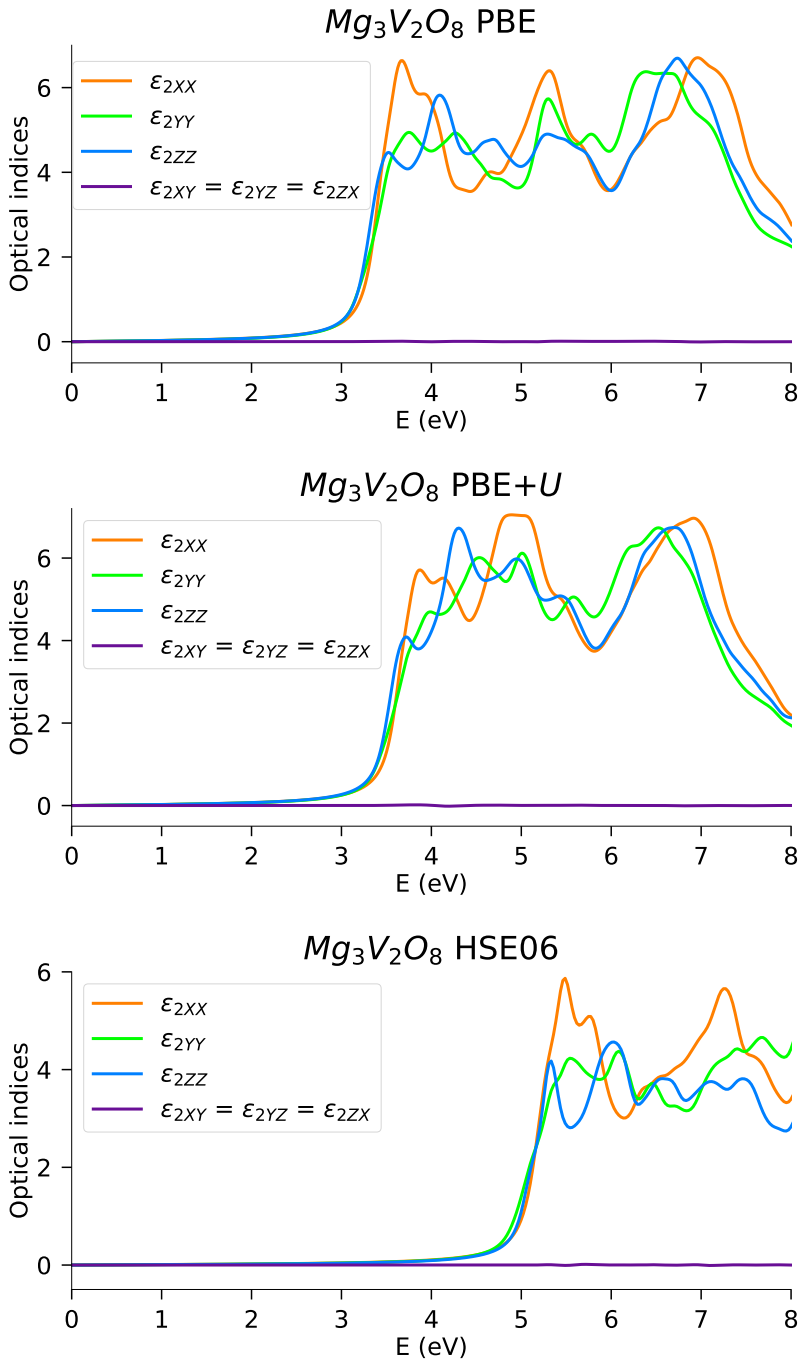


Fig-SI 30: Imaginary part of the dielectric tensor ϵ_2 of $Mg_3V_2O_8$ calculated with PBE (top), PBE+U (middle) and HSE06 (bottom) functionals. The components ϵ_{2xx}, ϵ_{2yy} and ϵ_{2zz} are in orange, green and blue, respectively.

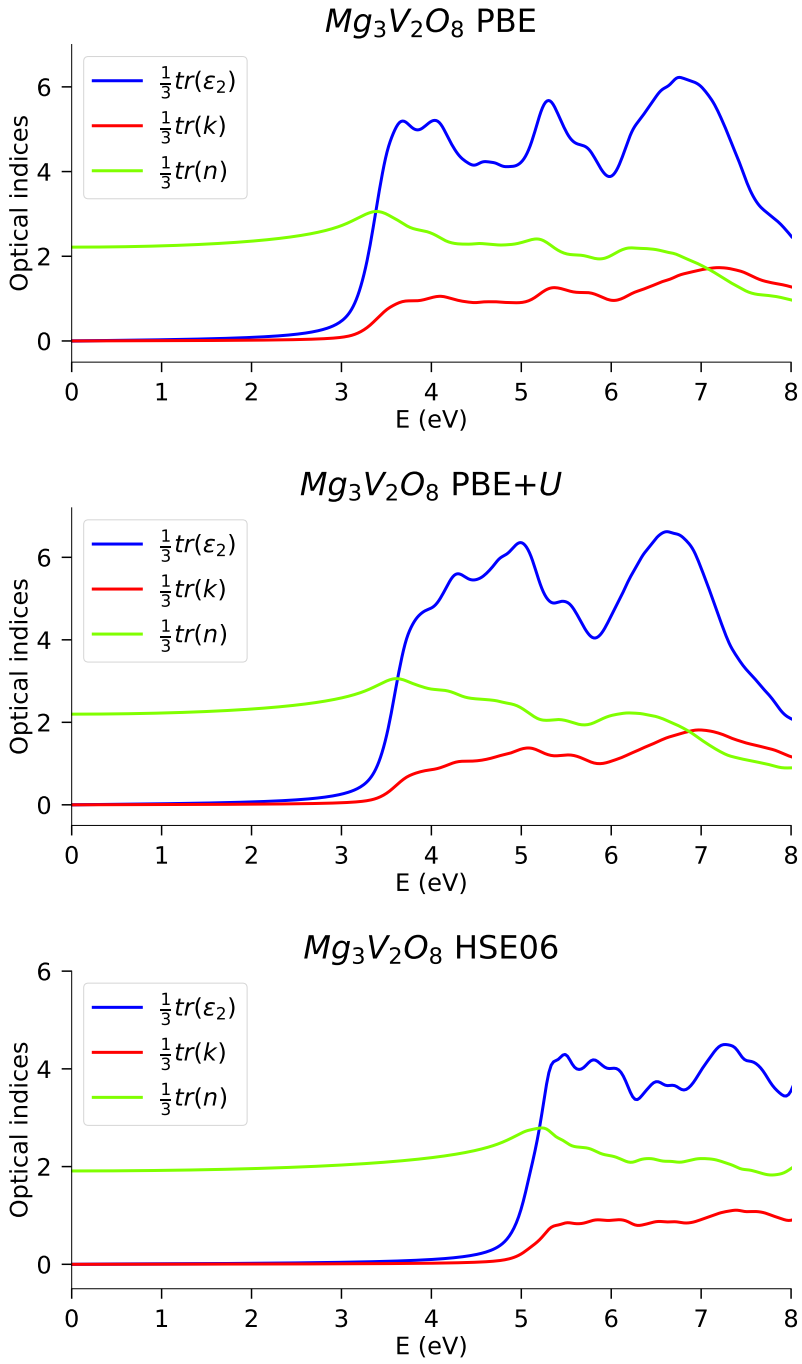
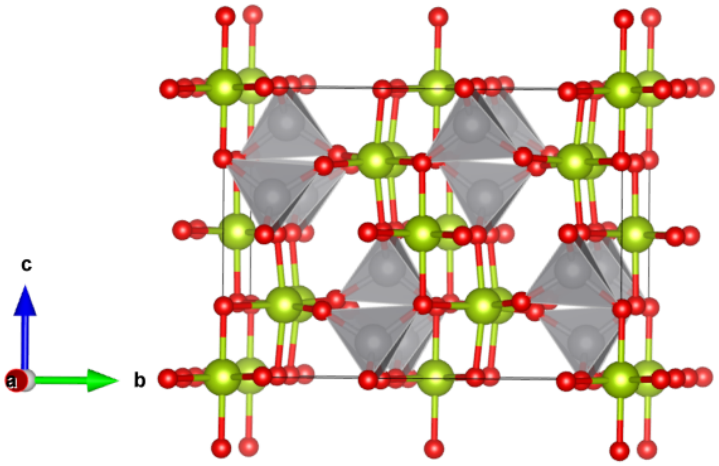


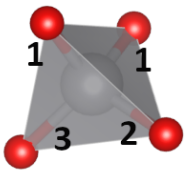
Fig-SI 31: Trace of the imaginary part of the dielectric tensor ϵ_2 (blue), of the refractive index n (green), and of extinction coefficient k (red) of $Mg_3V_2O_8$, calculated with PBE (top), PBE+U (middle) and HSE06 (bottom) functionals.

6 $Zn_3V_2O_8$



$Zn_3V_2O_8$	a	b	c	α	β	γ
Expt	6.088	11.489	8.280	90.00	90.00	90.00

Fig-SI 32: Conventional cell of $Zn_3V_2O_8$ taken from [7]. This cell contains 52 atoms. The Zn atoms are in green, the O atoms are in red, and the vanadium are represented by the gray polyhedron. The experimentally measured cell parameters and angles of the conventional cell are also given.



$Zn_3V_2O_8$	Expt	PBE	PBE+U	HSE06
1	1.715	1.718	1.722	1.694
2	1.797	1.810	1.824	1.779
3	1.736	1.743	1.748	1.713
Average	1.741	1.747	1.754	1.720

Fig-SI 33: Experimental and theoretical (calculated with PBE, PBE+U and HSE06) inter-atomic V-O distances in Å of the VO_4 cluster contain in $Zn_3V_2O_8$[7]. The reported distances are labeled by numbers and the corresponding positions are indicated by the pictures.

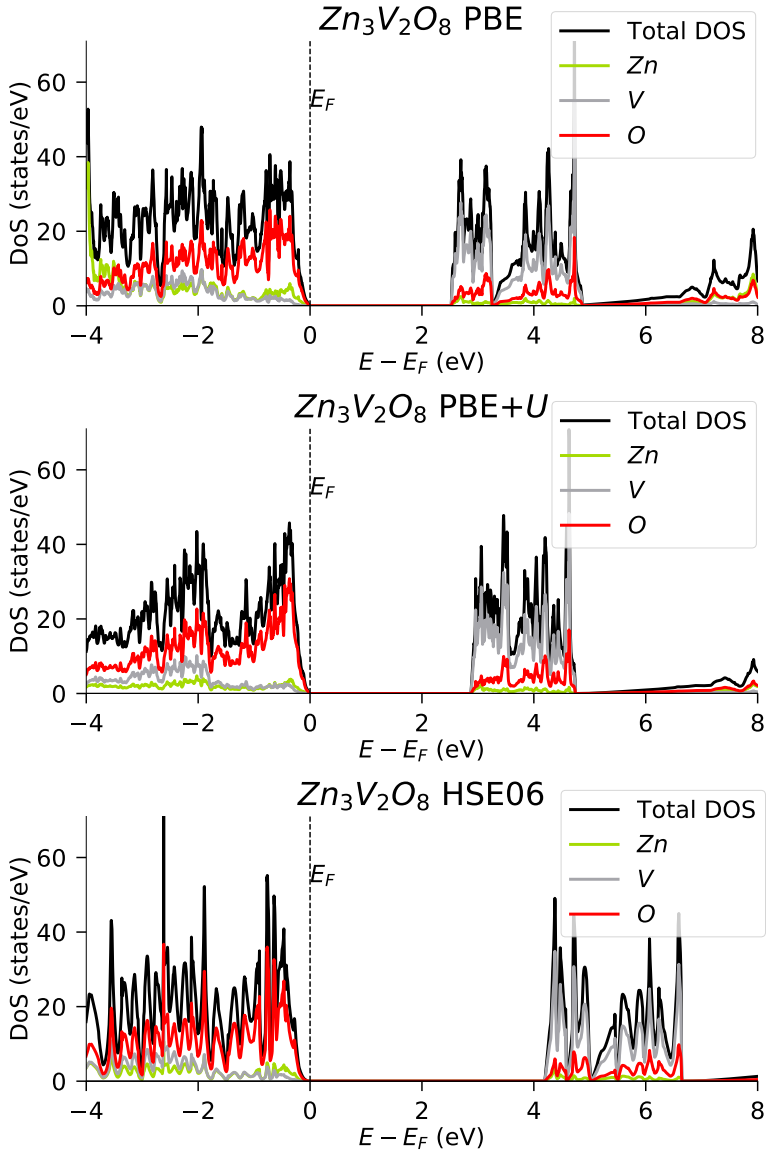


Fig-SI 34: DOS of $Zn_3V_2O_8$ calculated with PBE (top), PBE+U (middle) and HSE06 (bottom) functionals. The contribution of the zinc, vanadium, and oxygen atoms are represented in green, gray and red, respectively.

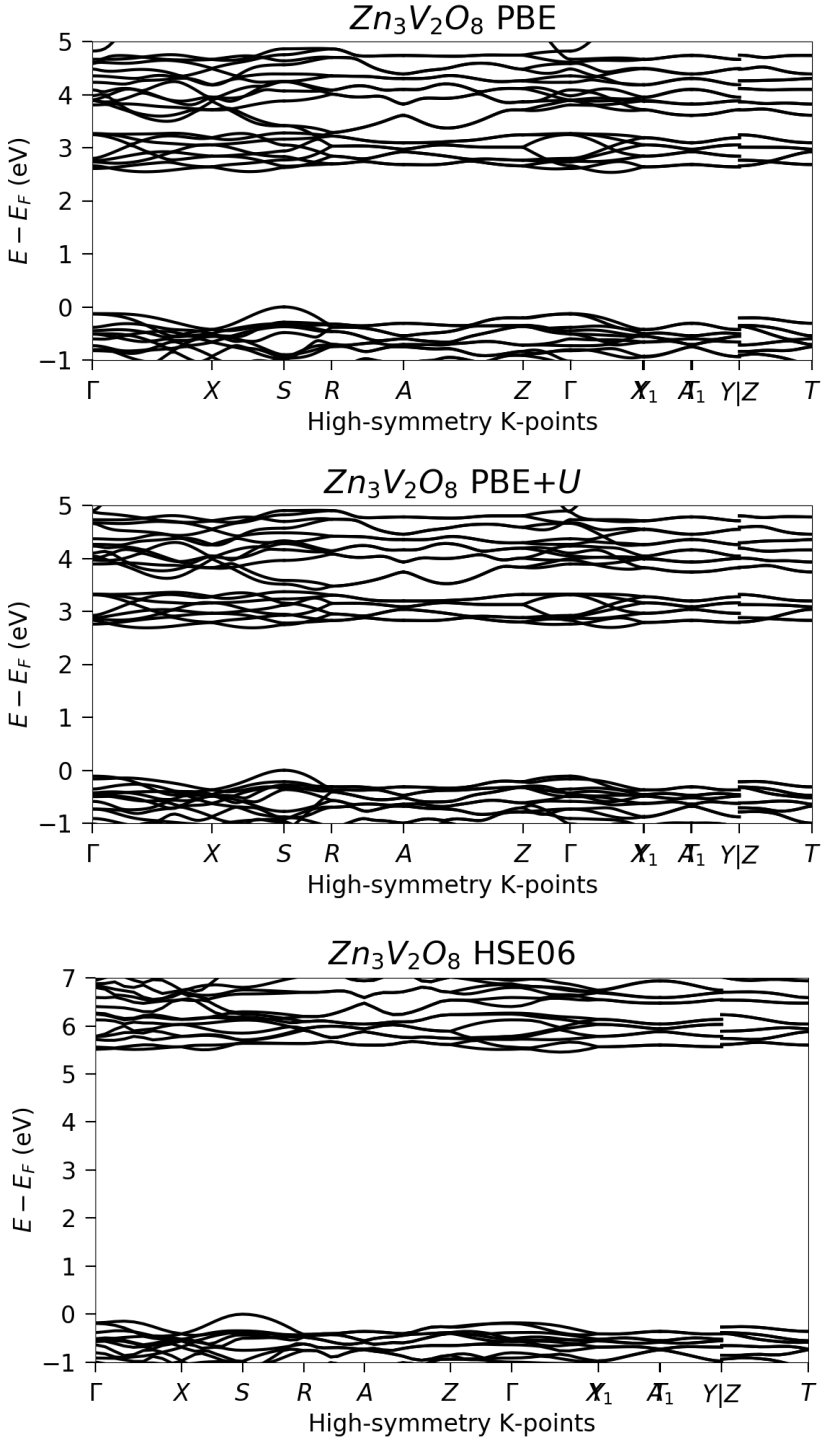


Fig-SI 35: Band structure of $Zn_3V_2O_8$ calculated with PBE (top), PBE+U (middle) and HSE06 (bottom) functionals. The considered path and high symmetry K-points are defined in [2].

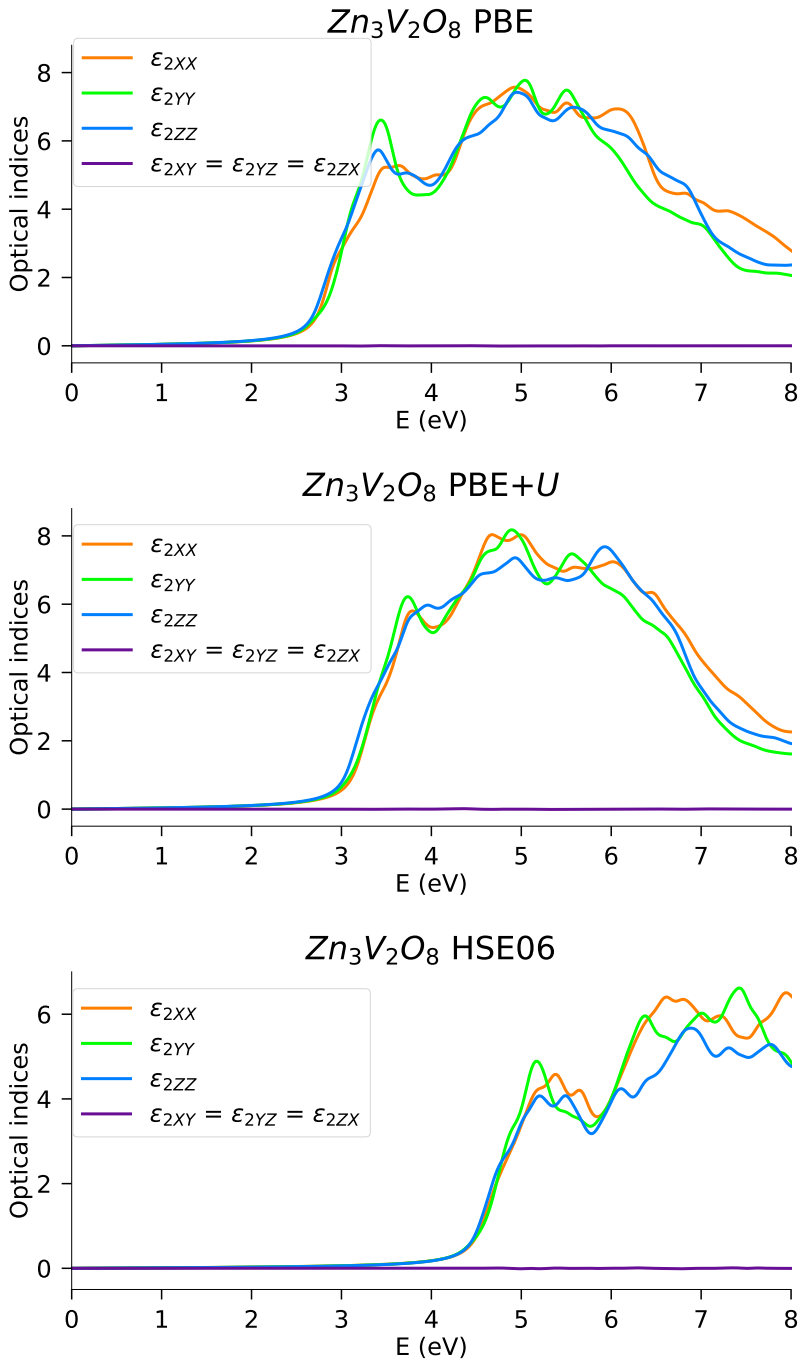


Fig-SI 36: Imaginary part of the dielectric tensor ϵ_2 of $Zn_3V_2O_8$ calculated with PBE (top), PBE+U (middle) and HSE06 (bottom) functionals. The components ϵ_{2xx}, ϵ_{2yy} and ϵ_{2zz} are in orange, green and blue, respectively.

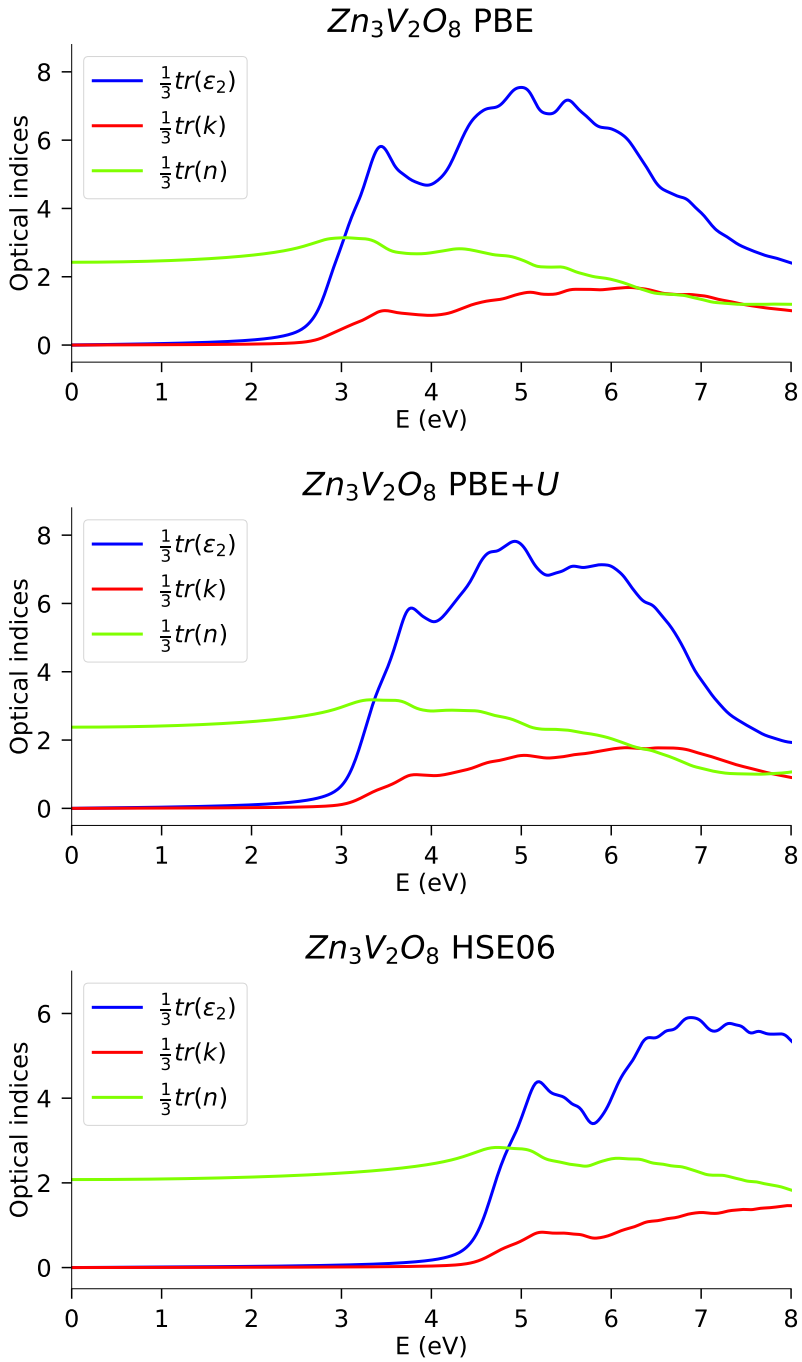


Fig-SI 37: Trace of the imaginary part of the dielectric tensor ϵ_2 (blue), of the refractive index n (green), and of extinction coefficient k (red) of $Zn_3V_2O_8$, calculated with PBE (top), PBE+U (middle) and HSE06 (bottom) functionals.

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