Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

S U P P L E M E N T A R Y I N F O R M A T I O N

Theoretical analysis of electrochromism of Ni-deficient nickel oxide – From bulk to surfaces

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S1. Setting up computational parameters

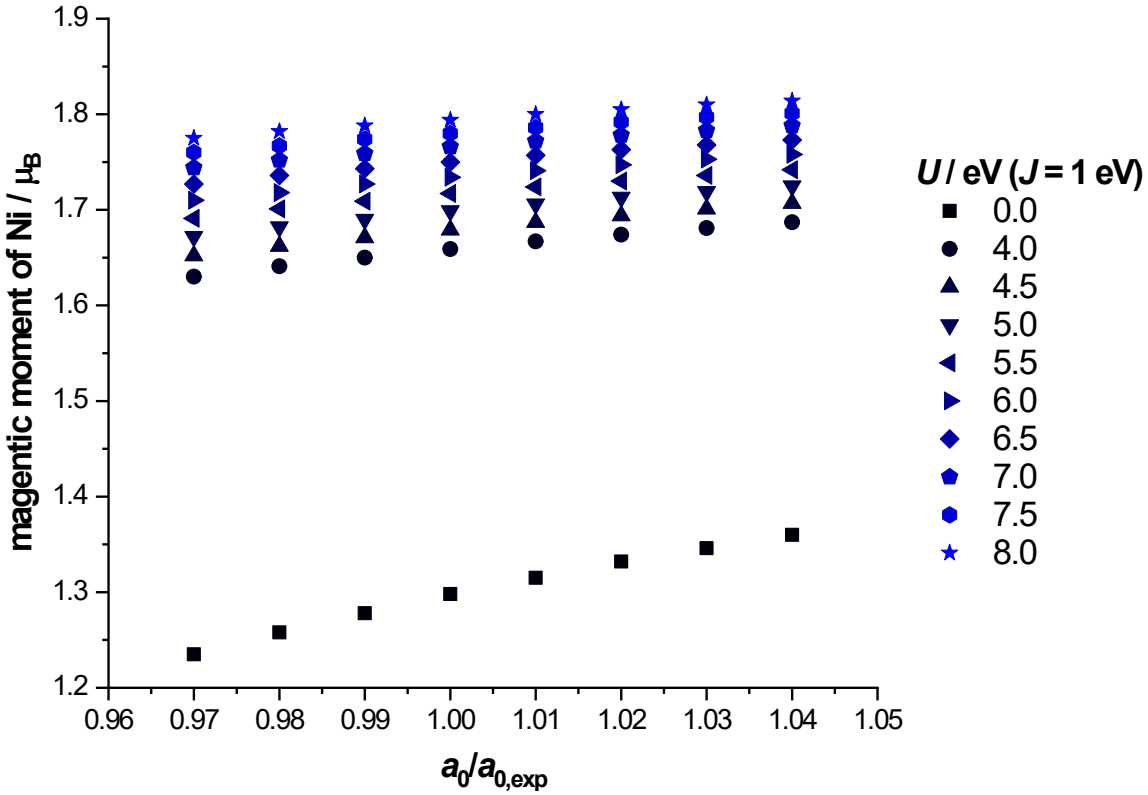

Figure S1. The dependence of Ni magnetic moment on the applied value of *U* and the lattice constant

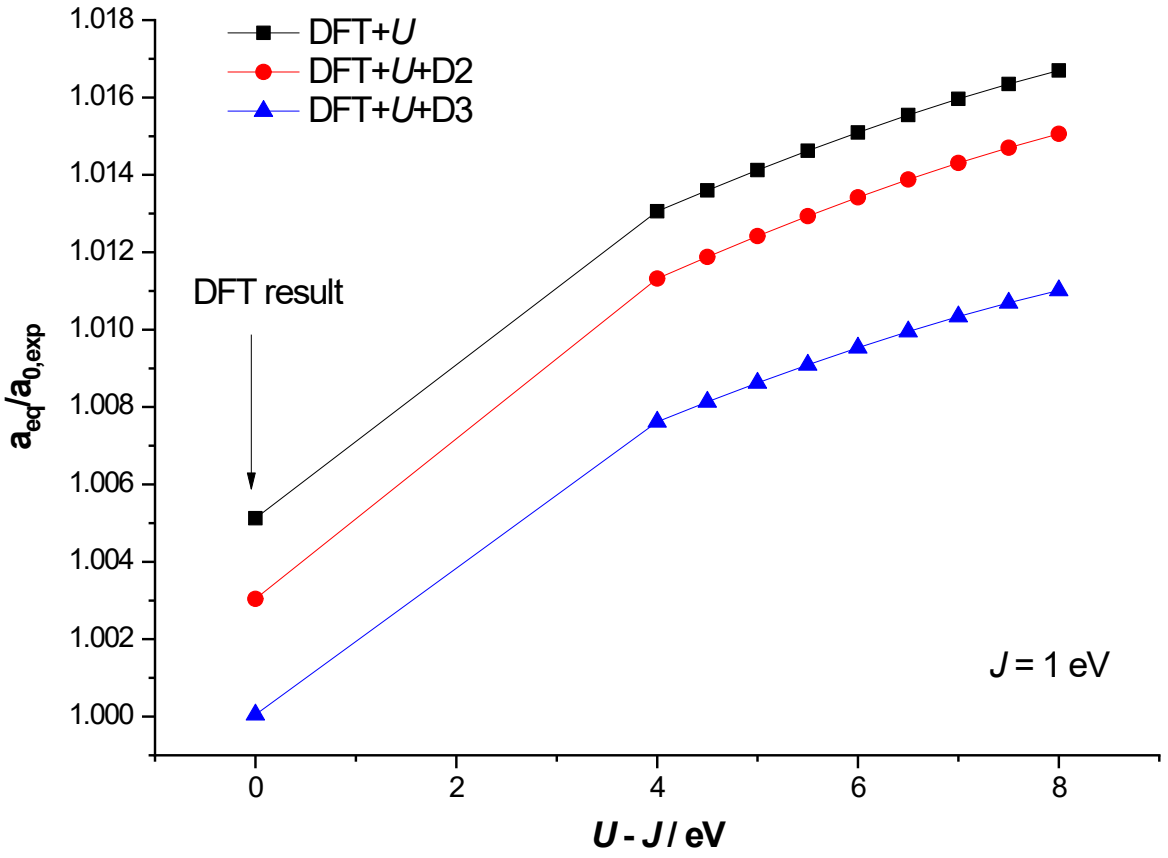

Figure S2. The dependence of calculated lattice constant of pristine bulk NiO on the applied $U - J$. For comparison, we also included the data with the dispersion correction (D2 and D3 of Grimme), which both improve lattice constant slightly, causing lattice compression. However, we not that dispersion correction was not further used in this work.

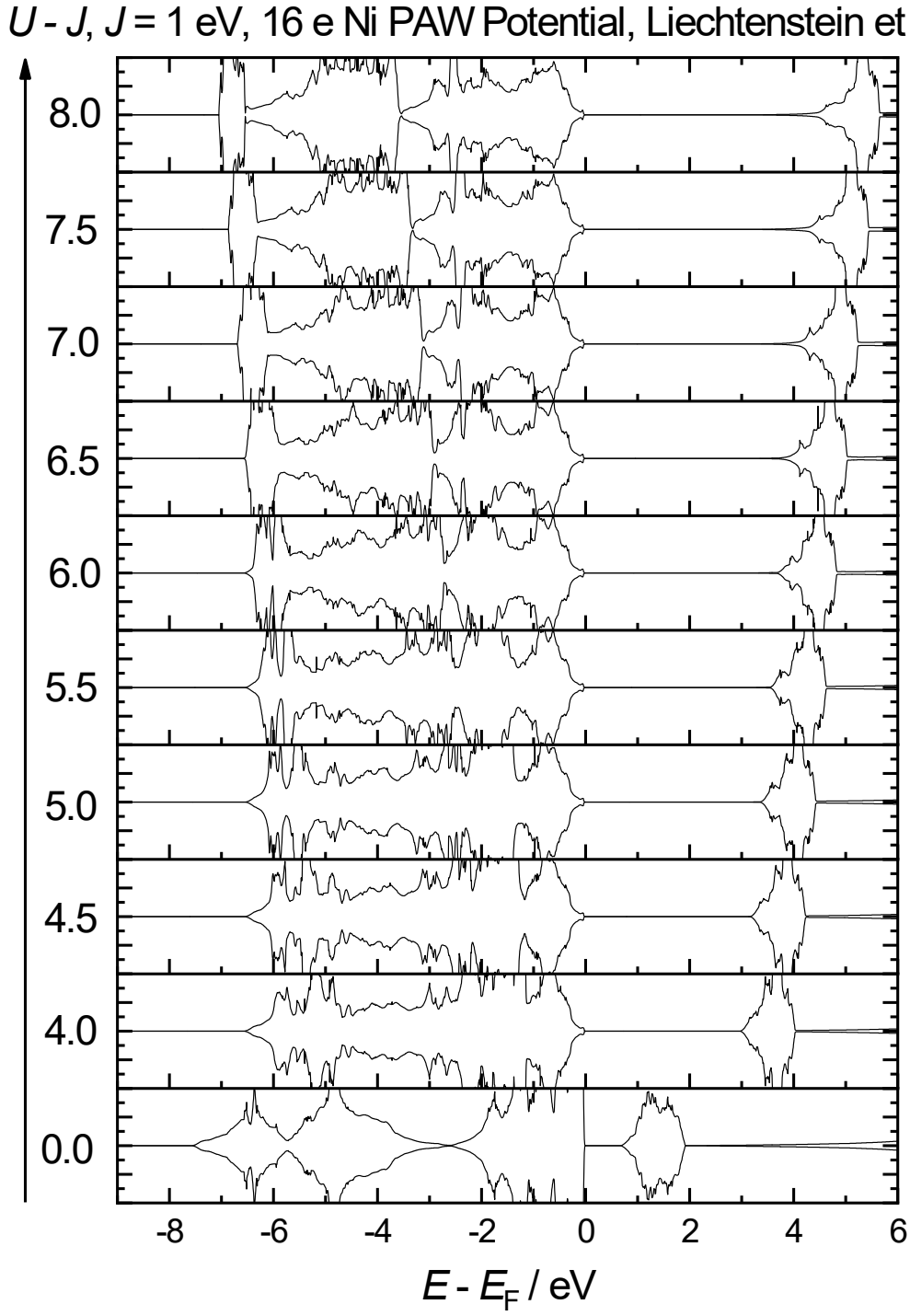

Figure S3. Calculated densities of states of pristine bulk NiO for different applied values of $U - J$.

S2. Density of States of Ni-deficient NiO

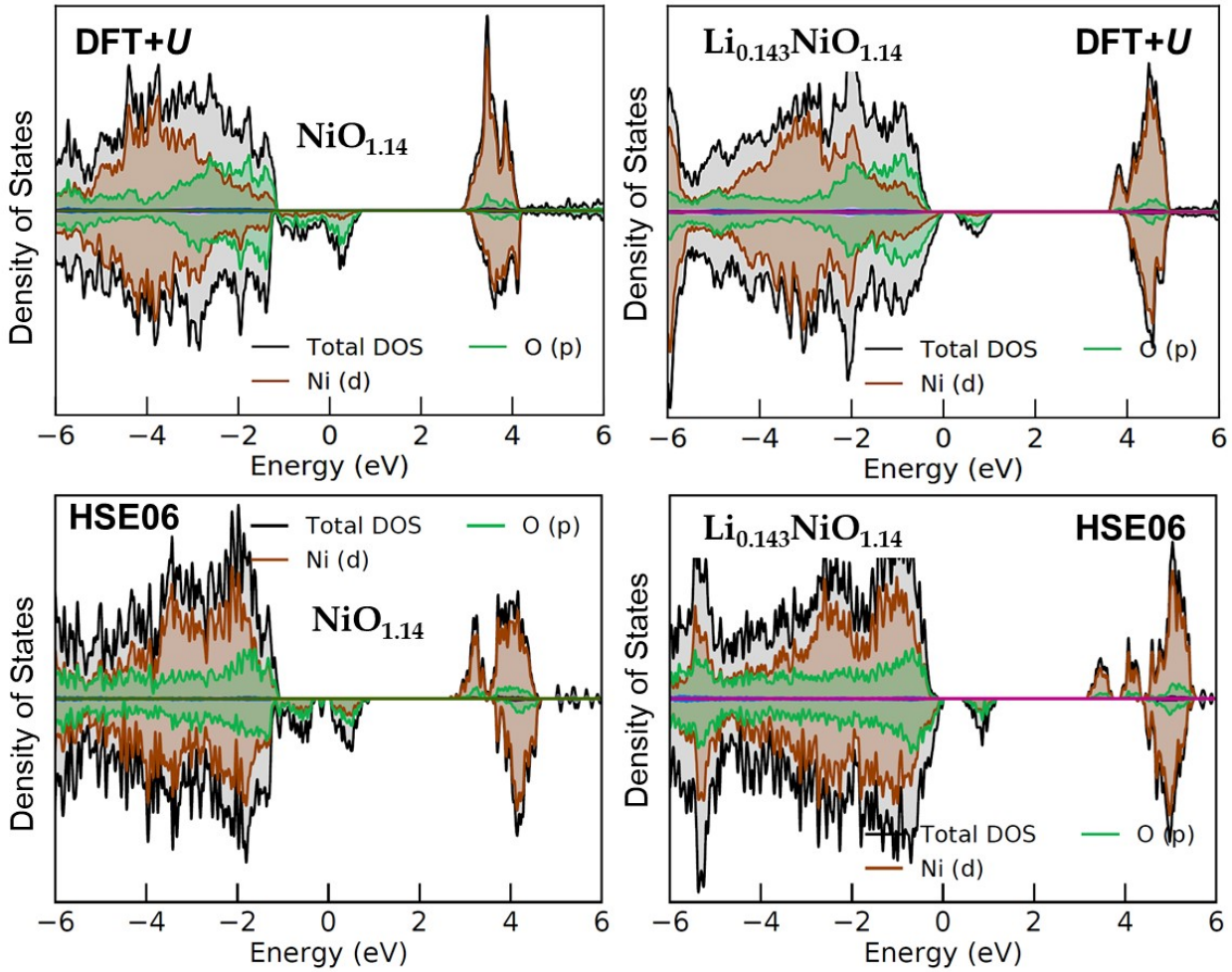

Figure S4. Comparison of DOS plots of Ni-deficient NiO ($NiO_{1.14}$) and $Li_{0.143}NiO_{1.14}$ obtained by DFT+*U* and HSE06 hybrid calculations. For hybrid calculations k-poin mesh was sparcer to reduce computational costs.

S3. Optical properties

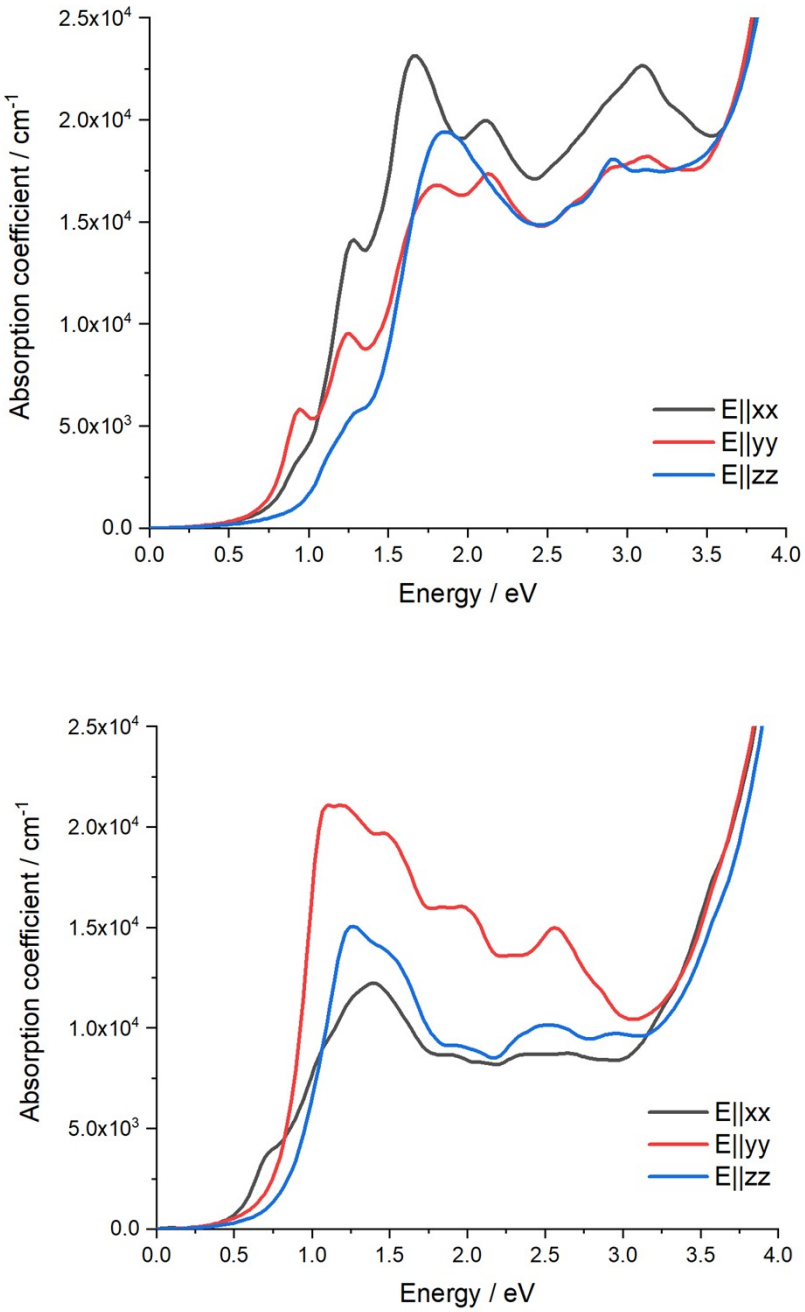

Figure S5. Diagonal components of the absorption coefficients of $NiO_{1.019}$ (top) and Li-intercalated in $NiO_{1.019}$ (bottom) with respect to photon energies, as calculated by DFT+*U*.

S4. Bader analysis

The following results are obtained for the smaller rhombohedral cell, but identical results are obtained in the larger hexagonal cell. Namely, when the Ni vacancy is formed, Ni atoms bear rather uniform partial charges between +1.28 and +1.29 e. This means that the Ni partial charge is almost the same as in pristine NiO (+1.27 e). Upon insertion of Li into the Ni vacancy, 0.89 e is transferred to the NiO lattice. This charge does not cause a significant change in Ni atoms' partial charges like upon Li insertion, partial charges of Ni range between +1.26 and +1.27 e. In total, only 0.12 e (out of 0.89) is transferred to Ni atoms.

S5. NiO surfaces

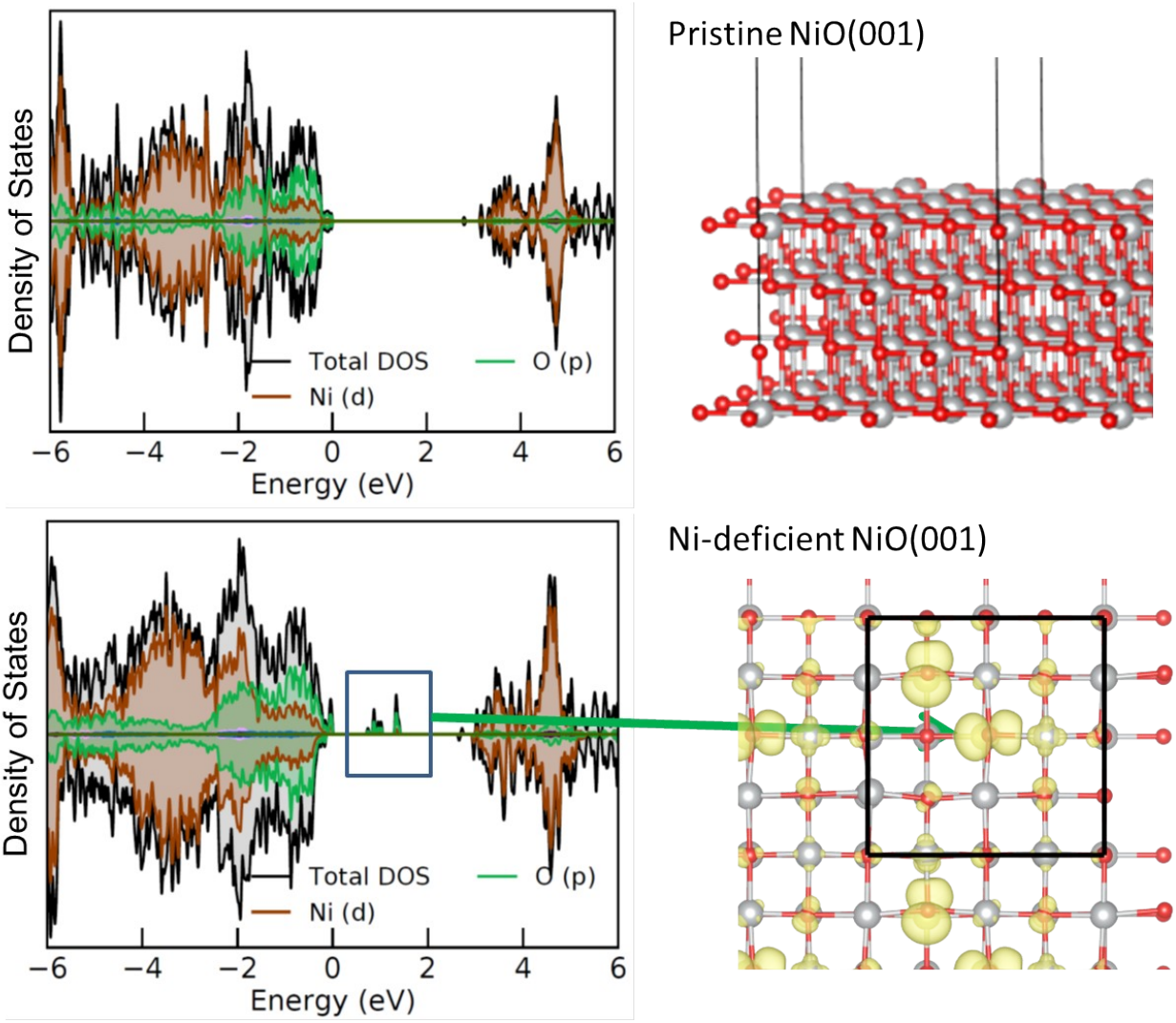

Figure S6. Top row – DOS plot and the model of pristine NiO(001) surface. Bottom row – DOS plot of NiO(001) with Ni surface vacancy, including the isosurface of the integrated density of states of the hole bipolaron formed around the Ni-vacancy.

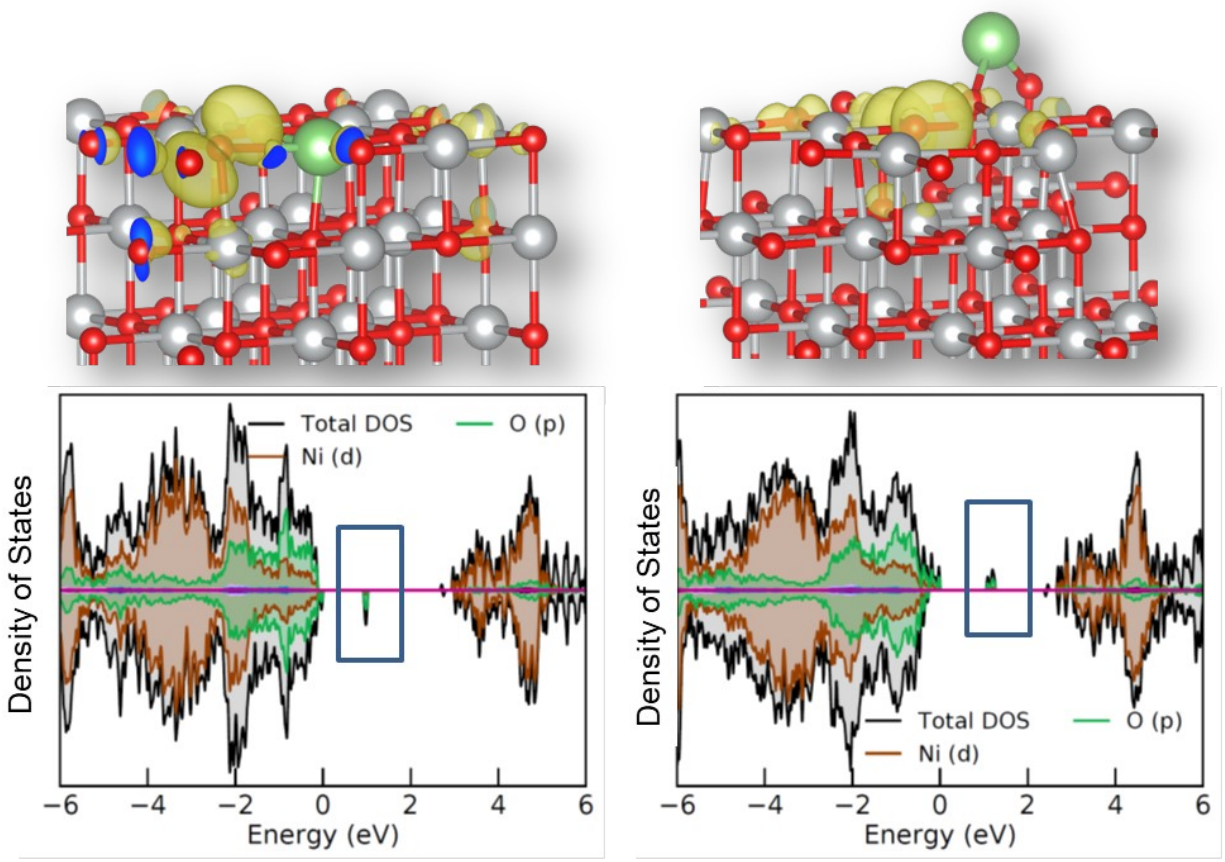

Figure S7. The top row shows the optimized structure of Li embedded in the Ni surface vacancy (left) and adsorbed near the vacancy, with the isosurface of ILDOS of the hole states indicated in the corresponding DOS plots (bottom row).

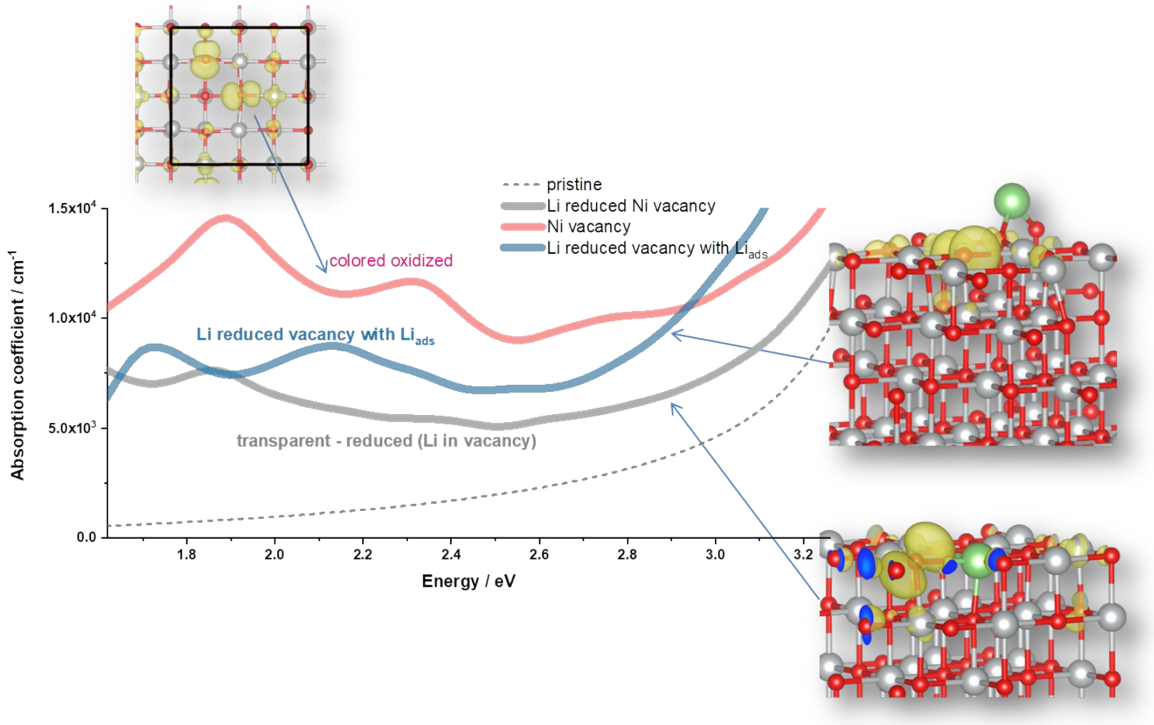

Figure S8. Optical spectra of Li embedded in the Ni surface vacancy and adsorbed near the vacancy, compared to the optical spectra of the pristine NiO(001) surface and the clean NiO(001) with the surface vacancy.