Origin of Optical Excitations in Fluorine-doped Titania from Response Function Theory: Relevance to Photocatalysis

(Supporting Information)

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The effect of the U parameter on the DFT+U simulated optical spectra of undoped anatase, brookite and rutile and the corresponding structures for F-O substitutions (F-Anatase, F-Brookite and F-Rutile) has been investigated by test calculations with U = 2, 4 and 6 eV. In all cases, the U parameter with identical numerical value was applied to Ti(3d) and O(2p) levels. Apart from the variation in U, all calculations were run with the same computational setup described in the main text. Thus, the calculations with different U value concern: i) relaxation of lattice and internal coordinates of undoped structures ii) calculation of the optical response function of anatase, brookite and rutile iii) relaxation of the internal coordinates of the doped structures iv) calculation of the optical response function of F-anatase, F-brookite and F-rutile.

Lattice parameters and electronic band gap of undoped anatase, brookite and rutile, calculated with different U values, are reported in Table 1. Clearly, increasing the numerical value of U leads to an ~7-8 % overestimation (compared to the the experimental data) of the cell volume of anatase, brookite and rutile. On the contrary, the predicted energy gap between valence and conduction bands becomes more and more accurate and match the experiment when U=6 eV. The choice of U=6 eV seems then natutal if one aims at adopting a computational scheme properly describing the main features of the electronic structure of titania in spite of a minor accuracy in the calculation of the cell volume. The main hypothesis here is that a proper description of the undoped systems will also properly describe the effect of Fluorine doping on the optical spectra

2

Table 1. Lattice parameters (Å) and band gap (eV) of anatase, brookite and rutile as a function of the Hubbard's parameter, U (eV).

	a	b	c	Band Gap
Anatase				
U=2	3.833	3.833	9.726	2.36
U=4	3.856	3.856	9.740	2.66
U=6	3.878	3.878	9.770	3.01
Exp	**3.796**	**3.796**	**9.444**	**3.2**
Brookite				
U=2	9.298	5.518	5.227	2.37
U=4	9.328	5.539	5.264	2.61
U=6	9.366	5.561	5.296	2.94
Exp	**9.18**	**5.43**	**5.16**	**3.1**
Rutile				
U=2	4.6563	4.6563	2.9969	2.02
U=4	4.6639	4.6639	3.0212	2.30
U=6	4.6712	4.6712	3.0465	2.65
Exp	**4.6021**	**4.6021**	**2.9563**	**3.0**

Figure 1, 2 and 3 report the density of states of undoped and F-doped anatase, brookite and rutile respectively and show that increasing U leads to larger band gap values for both undoped and doped phases. However, it is important to point out that U has also an influence on the location of the gap states in F-anatase and F-brookite. With U=2 eV, the exceeding electron is directly injected in the conduction band for both F-anatase and F-brookite while with U=6 eV there is a well defined populated gap state 1 eV above the valence band,. Setting U=4 eV leads to an intermediate situation, with a gap state in F-anatase and a quasi-metallic system for F-brookite. In the case of F-rutile, the populated state due to the doping always remains very close to the valence band and its energy rises up by augmenting the value of U.

Figure 1. Density of states of undoped (left) and doped (right) anatase at different value of U. The top of the valence band is set as E=0.
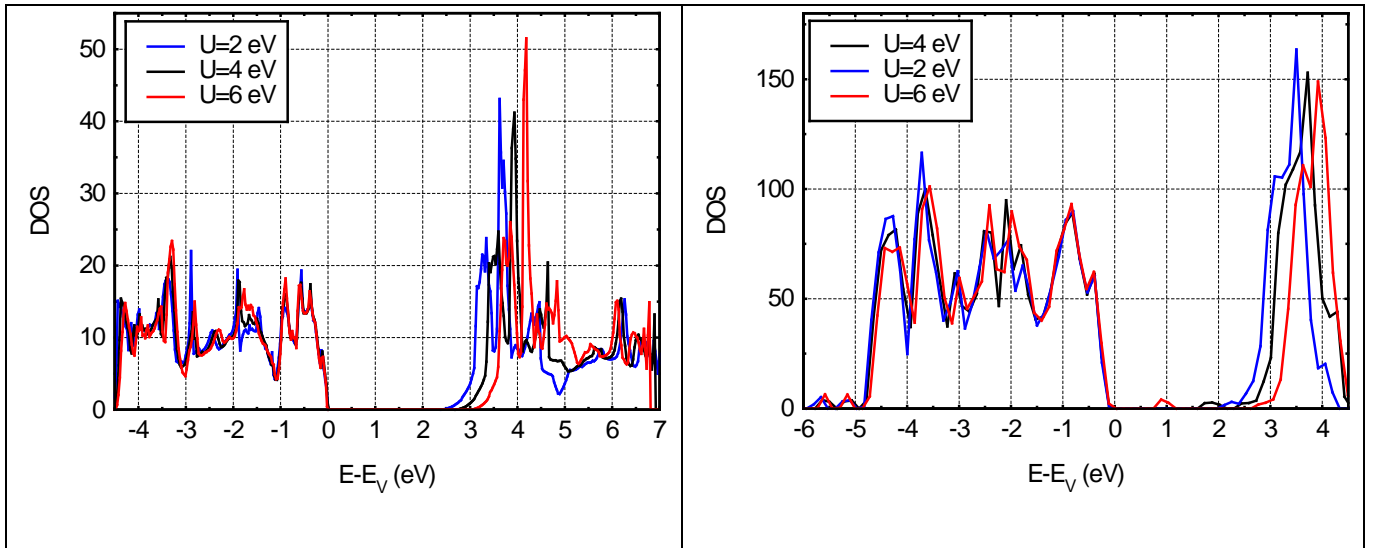
Figure 2. Density of states of undoped (left) and doped (right) brookite at different value of U. The top of the valence band is set as E=0.
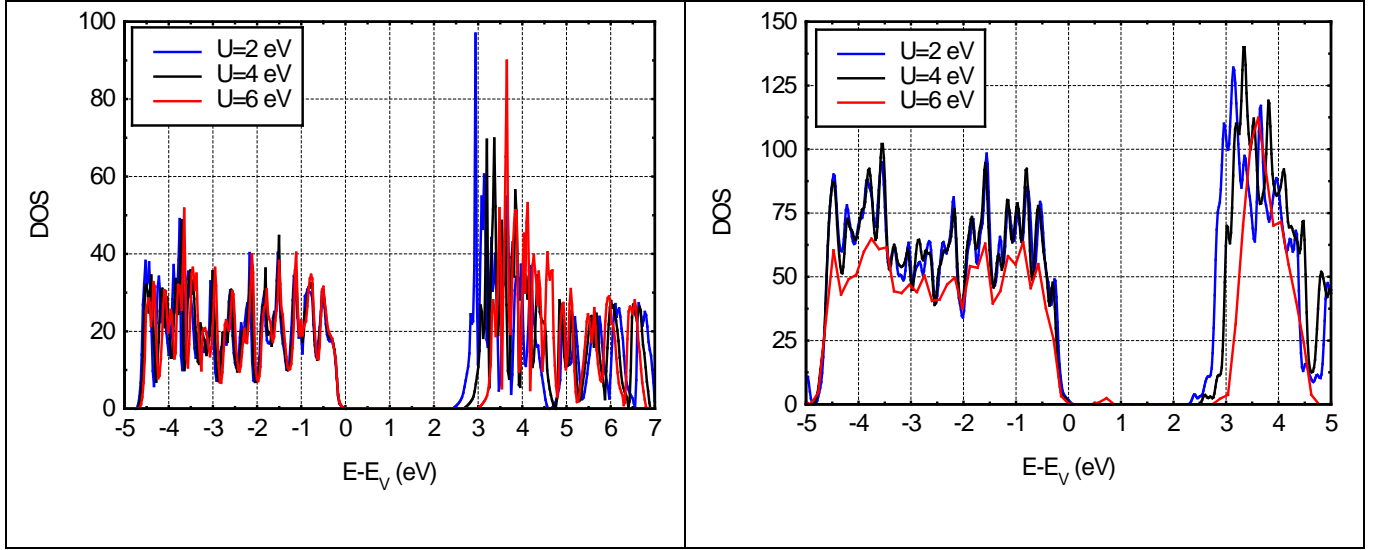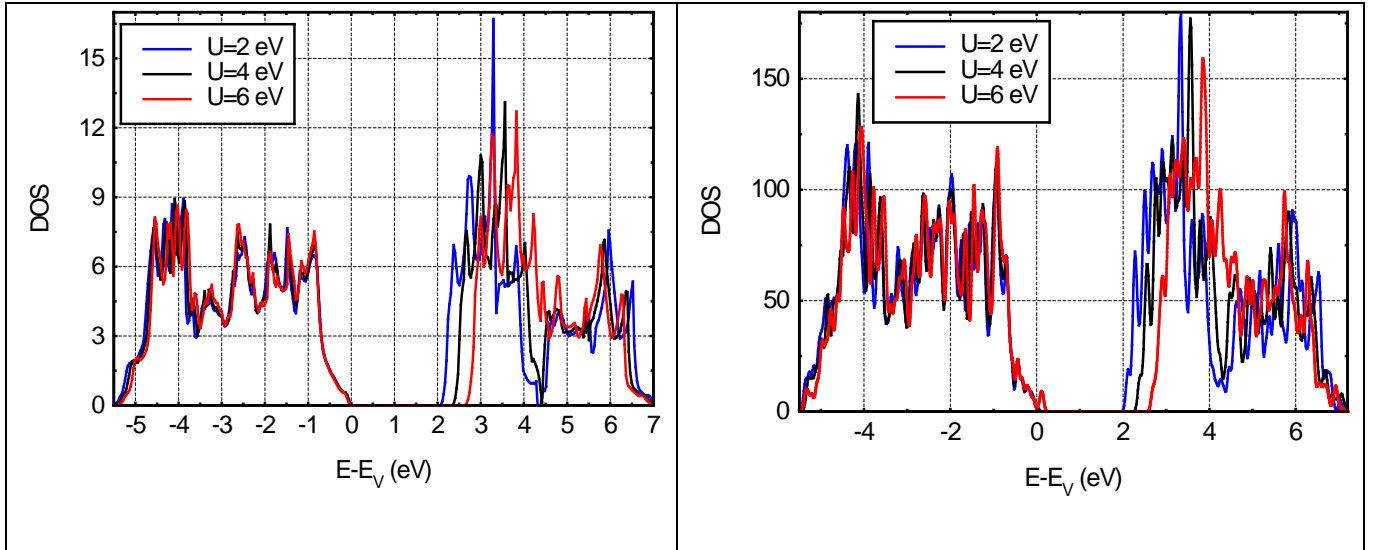

Figure 3. Density of states of undoped (left) and doped (right) rutile at different value of U. The top of the valence band is set as E=0.

Figures 4, 5 and 6 report the optical response function for undoped anatase, brookite and rutile at U=2, 4, 6 eV. For all the components of the response function in each polymorph it is possible to firmly state that the main features of the spectra are almost unaltered by going from U=2 to U=6 eV. With U=6 eV, moreover, the position of the peaks is in agreement with the Polarized Resonance measurements on anatase[1] and rutile.[2] However, reducing the U, the absorption edge is shifted at lower energies, coherently with what suggested by the analysis of the density of states. Next, we analyze the effect of U for the F-doped systems. Figure 7 allows for a comparison between the optical spectra of anatase and F-anatase for U=2, 4, 6 eV. In all three cases, doping induces a red-shift close to 50 nm and the appearance of a new band. However, for U=2 the latter is located above 450 nm, while for U=4 and U=6 it is encountered at 400-450 nm and 350-400 nm respectively. Thus, the qualitative shape of the spectra does not depend on the value of U, as in the case of undoped titania. However, the energy of the lowest energy optical transition follows the trend of the density of states and is therefore red-shifted by reducing the value of U. For brookite, doping does not have an effect on the absorption spectra although increasing U results in a blue-shift of the absorption edge (Figure 8). The optical spectra of rutile and F-rutile at U=4 eV and U=6 eV look similar and show a small red-shift due to the doping. Once again, reducing U from 6 to 4 eV leads to a red-shift of 50 nm in the absorption edge of both undoped and doped rutile. With U=2, surprisingly, undoped rutile looks even red-shifted compared to F-rutile. However, it can be concluded that U=2 eV is simply a too small value to provide any physically meaningful result on fluorine-doped titania

Figure 4. Orthogonal (above) and parallel (below) components of the optical response function of anatase as a function of U.
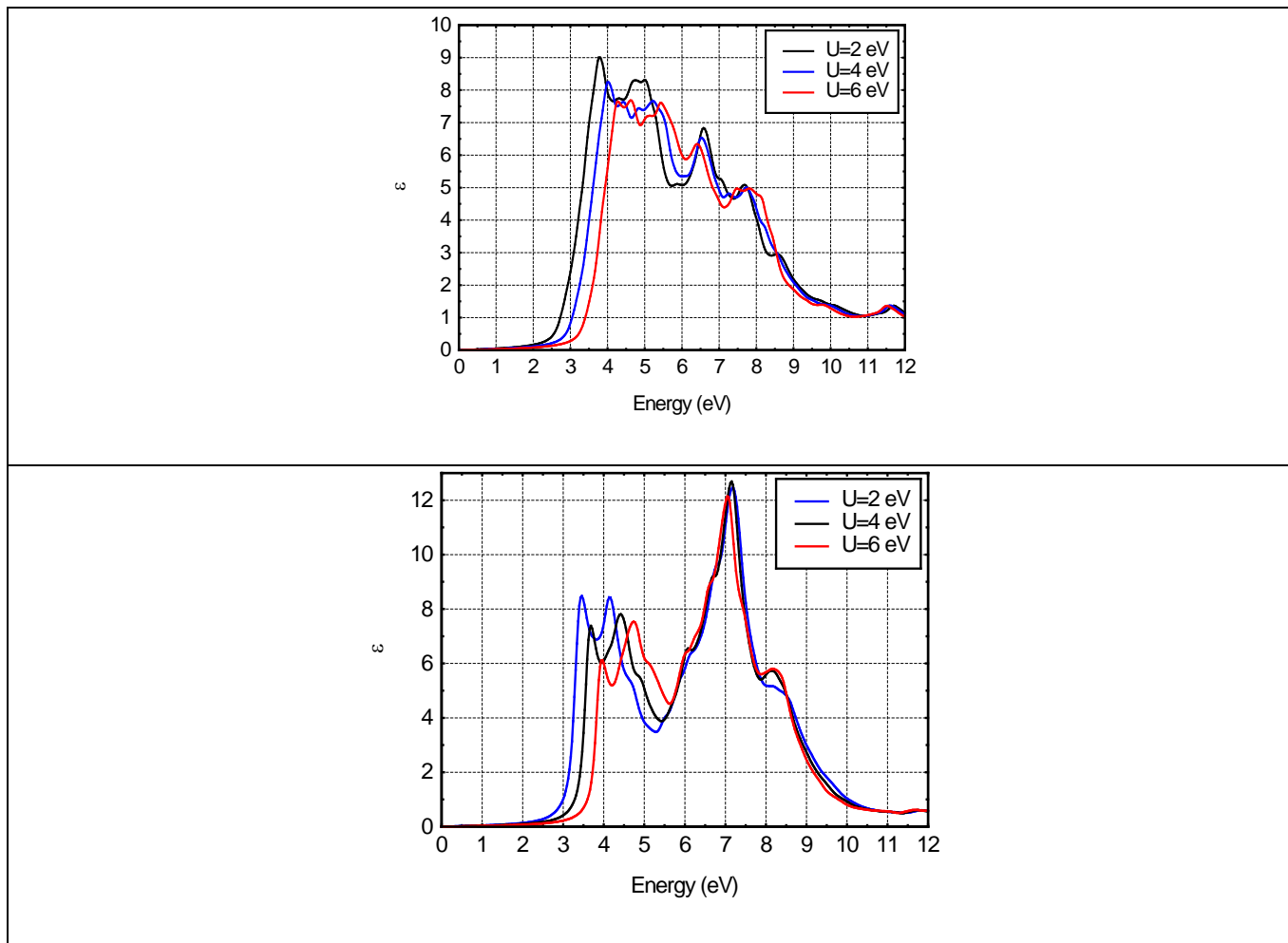
Figure 5. X (above), Y (middle) and Z (below) components of the optical response function of brookite as a function of U.
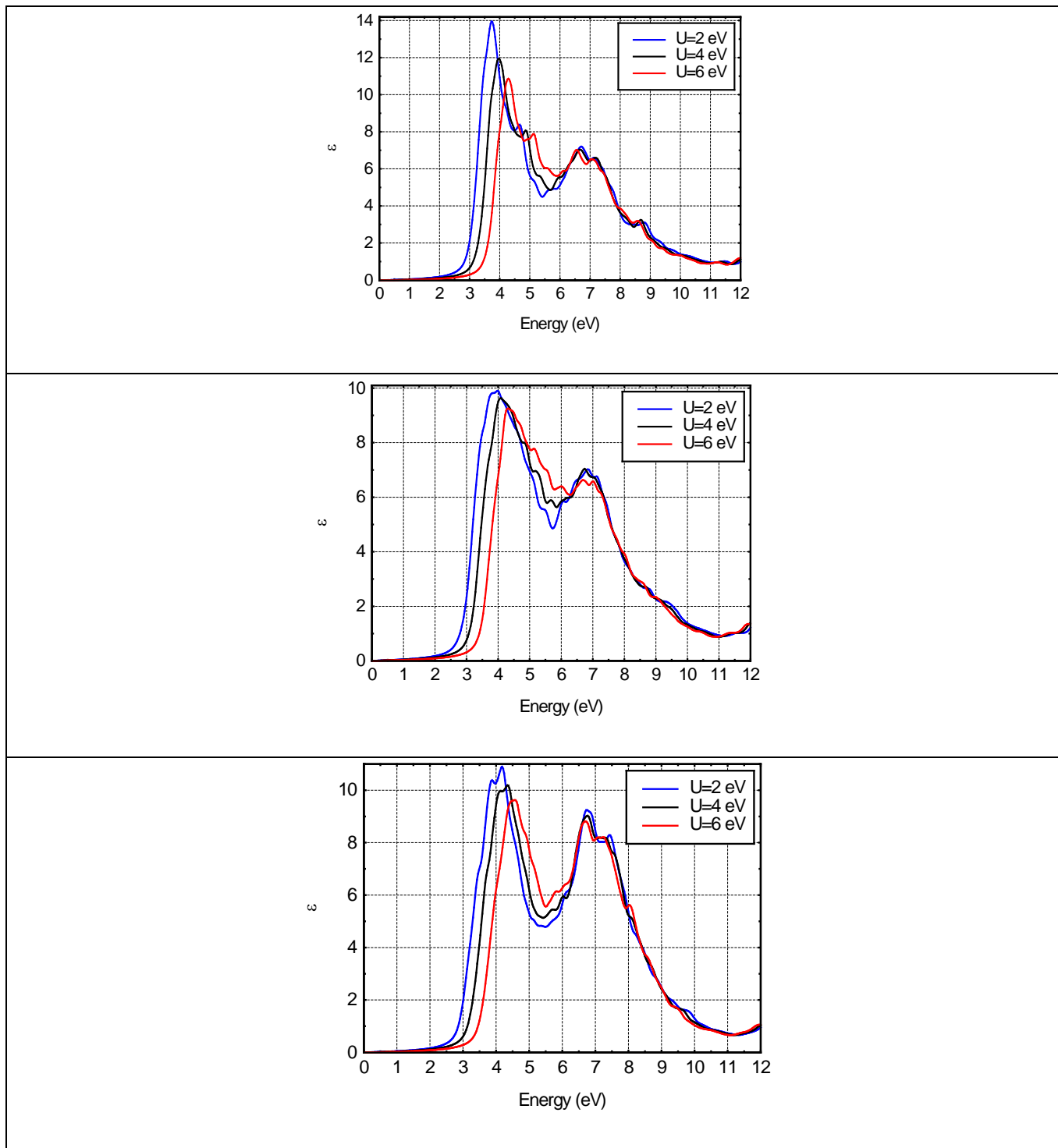
Figure 6. Orthogonal (above) and parallel (below) components of the optical response function of rutile as a function of U.
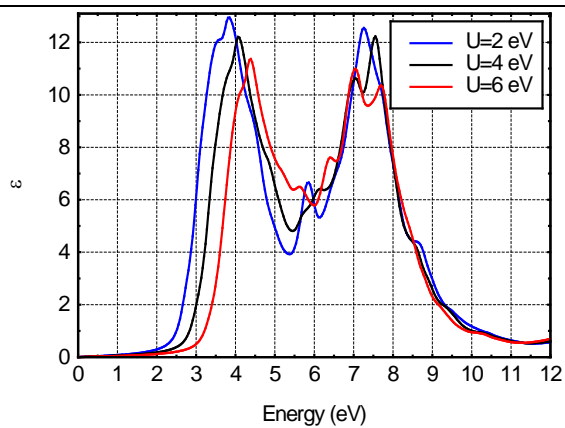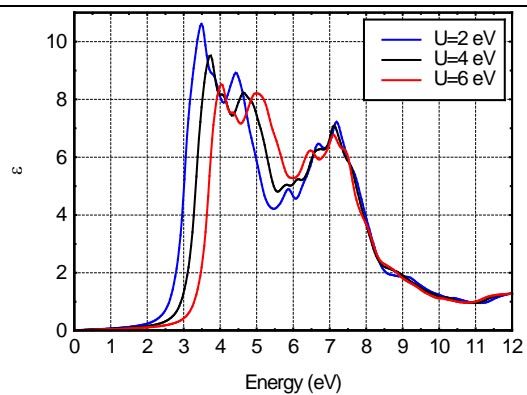
Figure 7. Frequency-dependent averaged optical response function for F-doped stoichiometric anatase and undoped anatase at U=2 eV (top), U=4 eV (middle) and U=6 eV (bottom)
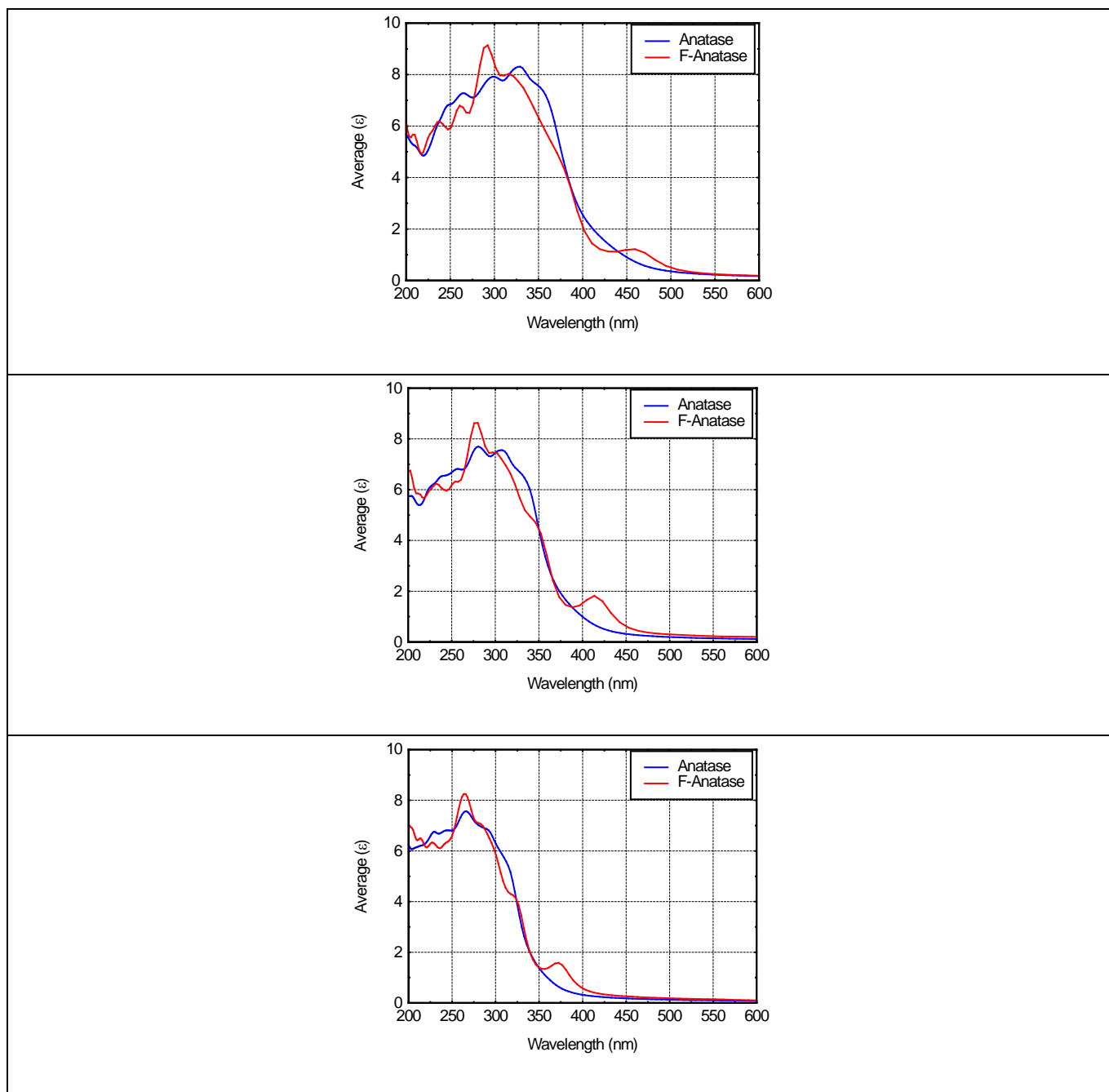
Figure 8. Frequency-dependent averaged optical response function for F-doped stoichiometric brookite and undoped brookite at U=2 eV (top), U=4 eV (middle) and U=6 eV (bottom)
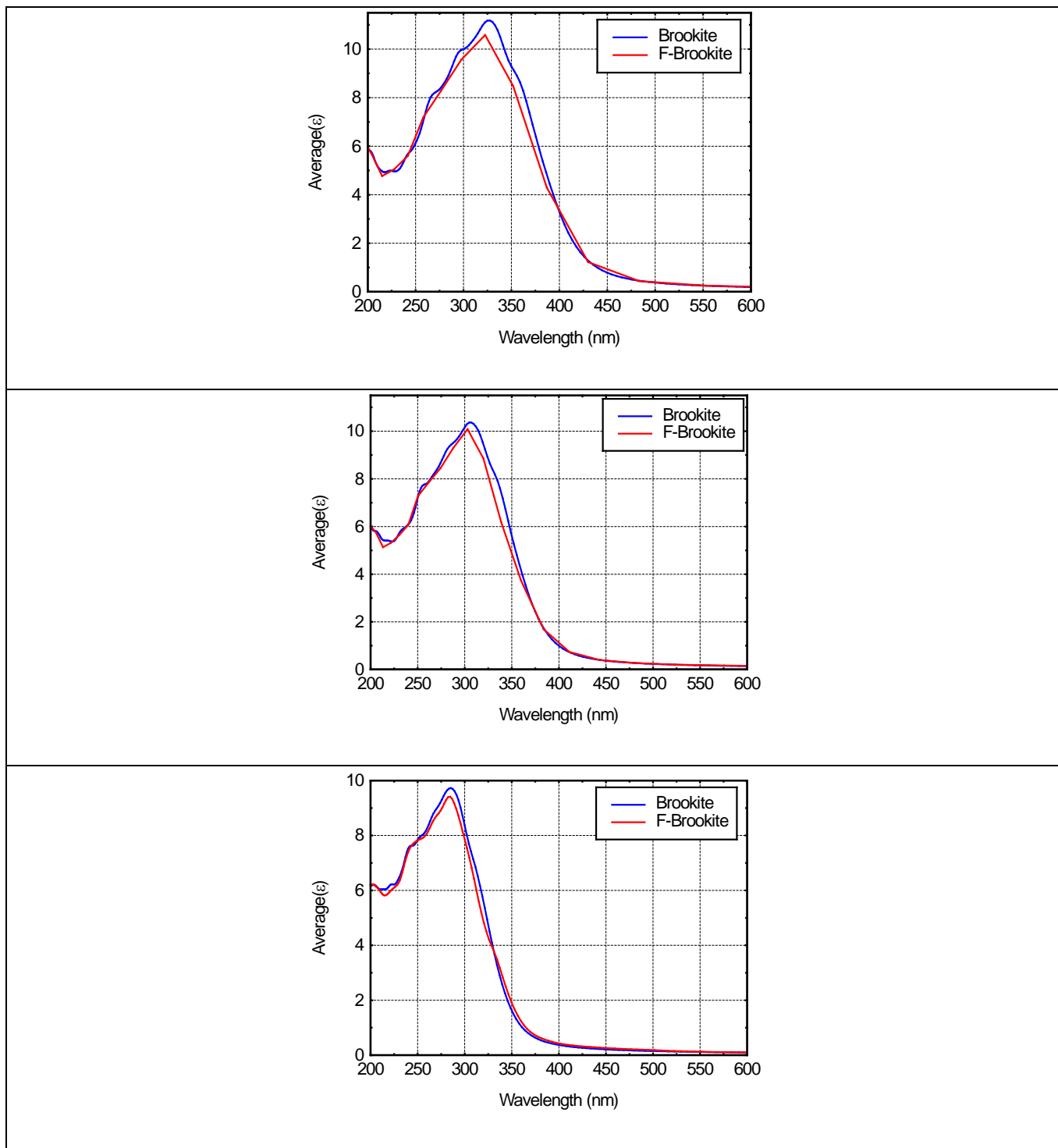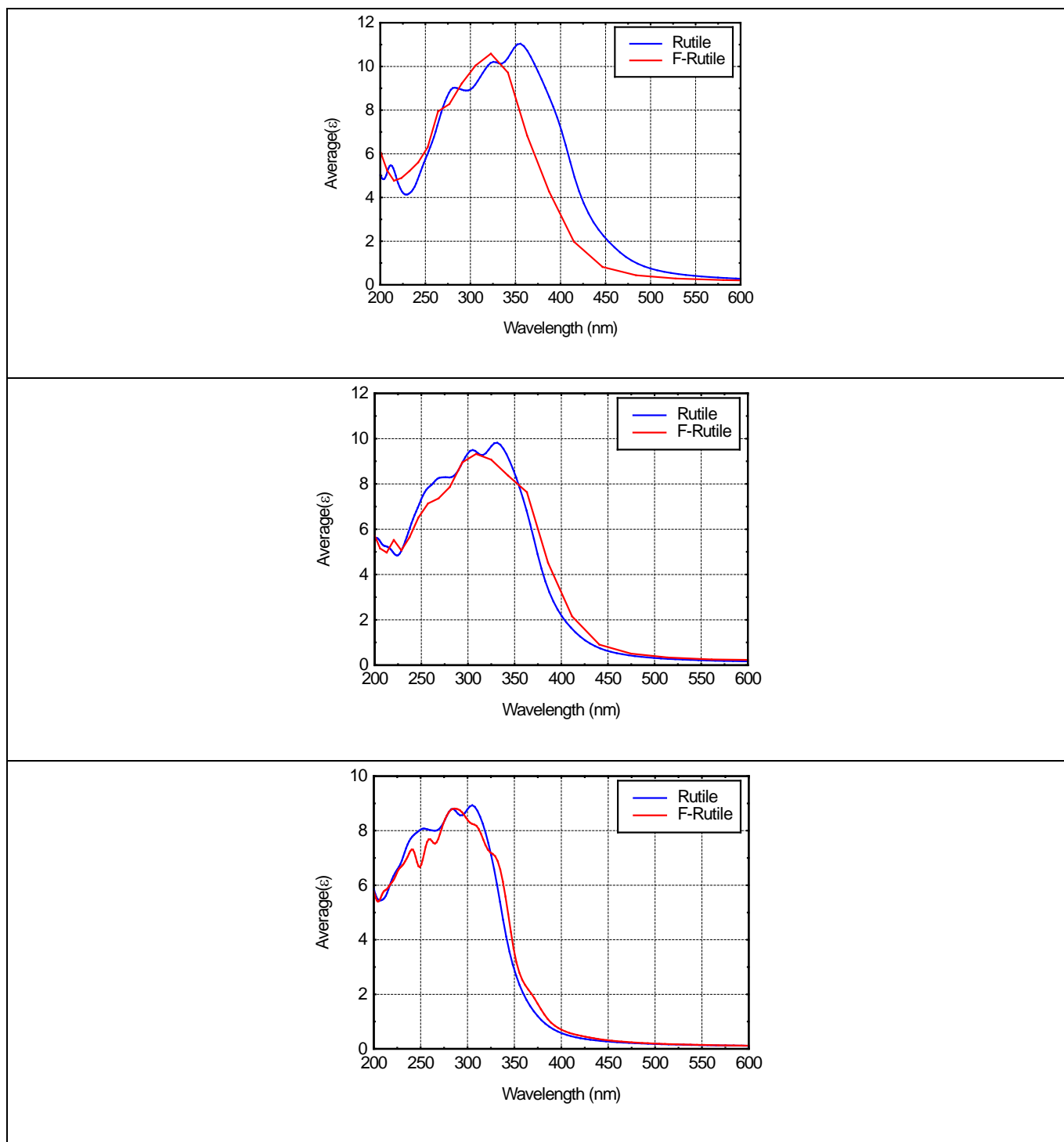
Figure 9. Frequency-dependent averaged optical response function for F-doped stoichiometric rutile and undoped rutile at U=2 eV (top), U=4 eV (middle) and U=6 eV (bottom)

To summarize, U determines the gap and also the position of the defect level. For the undoped material the larger the U, the larger the predicted gap is, matching experiment for U = 6 eV. However, comparing the simulated spectra of the undoped and doped materials reveals that the effect of U in both materials is almost identical. Thus, increasing U induces a blue-shift of the overall spectra of the undoped and doped material but does not introduce new features in the spectra. For U=6 eV the predicted band gap of anatase matches the experimental value but, at the same, time shifts the impurity level which appears too deep in the gap in contrast with EELS experiments on reduced titania.[3]Nevertheless, the results for the spectra simulated from the optical response function show that the appearance of a well defined peak for F-anatase is not artifact of U even if the prediction of the precise location of the peak requires more accurate methods not presently available.

(1) Hosaka, N.; Sekiya, T.; Satoko, C.; Kurita S. Optical Properties of Single Crystal Anatase TiO$_2$. *J. Phys. Soc. Japan* **1997**, *66*, 877-880.

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