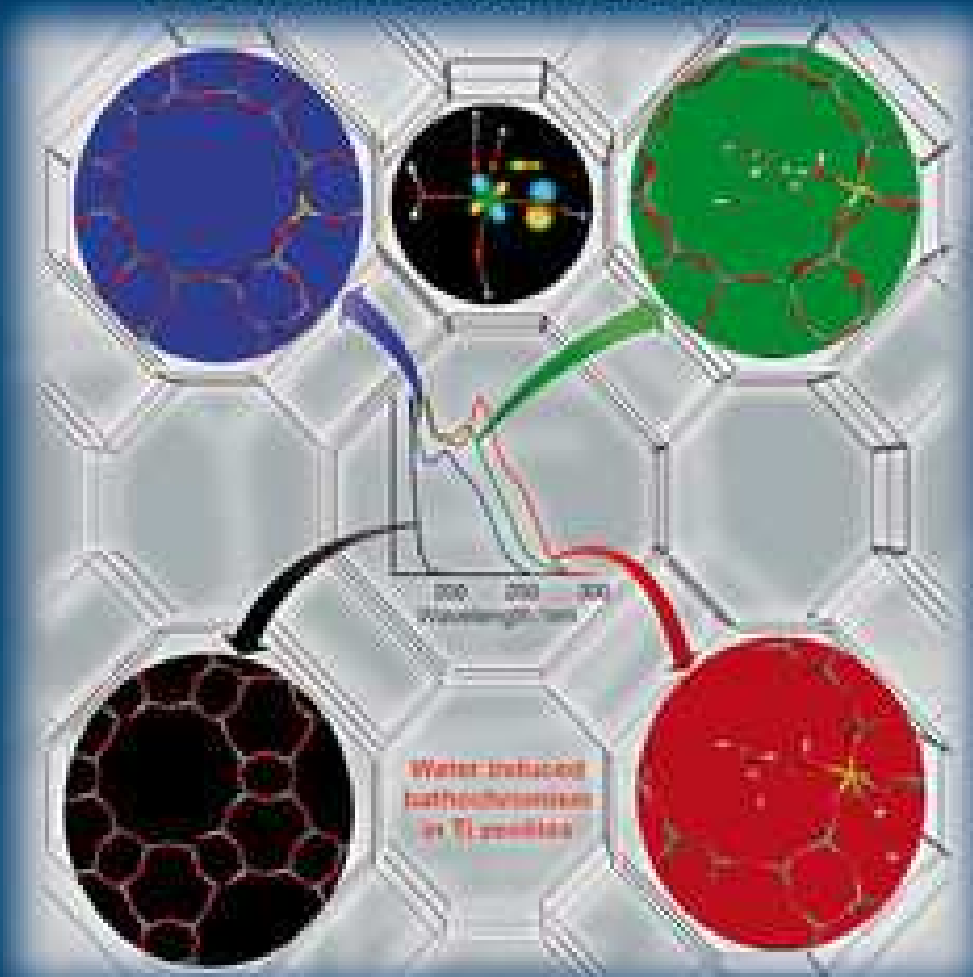


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Review: Aqueous Phase Frontier Between Chemistry and Physics

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Conference report: Unravelling Biological Processes

(J. Doores)

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Titanium acts as a Lewis acid relative to bases adsorbed in zeolites, attaining a coordination number of up to six. The red-shift of the LMCT electronic transitions detected by UV/Vis studies on titanium zeolites upon hydration is investigated using a DFT-based computational approach which takes into account the full periodicity of the crystalline phase.

Bathochromic Effects in Electronic Excitation Spectra of Hydrated Ti Zeolites: A Theoretical Characterization

Ettore Fois,* Aldo Gamba, and Gloria Tabacchi^[a]

Titanium-containing zeolites are a class of porous materials having widespread use in industry as catalysts for redox processes in mild conditions. At low titanium concentrations, titanium isomorphously replaces silicon in the tetrahedral sites of the zeolitic framework. Titanium may expand its coordination from four to six, acting as a Lewis acid with respect to bases adsorbed in the channel-and-cage systems typical of zeolites. Herein, we interpret the red-shift (bathochromic effect) of the ligand-to-metal-charge-transfer (LMCT) electronic transitions detected by UV/Vis studies on titanium zeolites upon hydration at the microscopic level by using a DFT-based computational approach which takes into account the full periodicity of the crystalline phase. The relationships among the structures of the zeolitic titanium sites, the adsorbed water molecules and the electronic excitation properties in models of titanium zeolites are discussed. The LMCT bands' profiles, edges and intensities are interlaced with both the location and the coordination of the water molecules at the titanium site.

Since the first patent in 1985,^[1] titanium silicalite (TS-1) has been widely adopted in partial oxidations of hydrocarbons by using aqueous hydrogen peroxide as oxygen source.^[2] In as-prepared TS-1, titanium is pentacoordinated, via four framework oxygen atoms and one OH group.^[3] The OH group is released upon calcination, and, in evacuated (solvent free) zeolites, titanium is coordinated by the four framework oxygen atoms in a tetrahedral geometry. UV/Vis and EXAFS experiments show that water loading causes a reversible expansion of the coordination shell of titanium. Diffuse reflectance UV/Vis spectroscopy indicates a red-shift of a multiple band, in the 200–240 nm range in dry samples,^[4] and from ~ 200–250 nm in hydrated TS-1.^[5] EXAFS experiments confirm that such a red-shift occurs along with the formation of penta- and/or hexa-coordinated titanium centres.^[5, 6] Absorption in these ranges, which are characteristic of titanium sites in zeolites, are due to a LMCT mechanism.^[7]

While formation and reactivity of oxidizing intermediates in TS-1 have been the subject of many studies, the relationships between the extent of hydration, structure and electronic excitation spectra have received less attention. A description of the electronic excitation in titanium zeolites in non-oxidizing conditions at an atomistic level is, however, a topic of current interest, as it has been recently reported that titanium zeolites

might replace the semiconducting TiO₂ layer in photovoltaic cells.^[8]

Most of the reported data deals with experiments on TS-1, a zeolite with an MFI framework structure^[9] and a unit cell content of [Ti_xSi_{96-x}O₁₉₂], too large for extensive ab initio calculations. As a consequence, a number of theoretical studies have been performed on model clusters or by using embedded cluster approaches (see for example, ref. [10]). Smaller titanium zeolites have been studied by ab initio methods by taking into account periodicity.^[11, 12, 14–16] However, to the best of our knowledge, very few modelling studies devoted to electronic transition properties have been published so far.^[17–19] Recently a mixed approach was presented, where the titanium zeolite structure was optimized with a periodic DFT approach. The electronic excitation spectra were calculated via the time-de-pendent density functional theory^[20] approach (TD-DFT) on a titanium-centred cluster derived from the DFT-optimized crystal, thus obtaining absorption wavelengths in line with experiments.^[17] However, similar accuracy was also obtained by calculating the optical conductivity of periodic models of both titanium zeolites and mesoporous silicas with DFT.^[16, 21] Herein, the full periodic DFT approach is followed.

Results obtained from models of dry titanium zeolites characterized by different framework topologies are presented. The zeolites offretite (OFF), sodalite (SOD) and SSZ-35 (STF) were considered.^[9] Models of these titanium zeolites (referred to as Ti-OFF, Ti-SOD and Ti-STF respectively) were built by replacing one silicon atom with titanium in one of the framework's tetrahedral T sites. Titanium-silicon substitutions were performed in the crystallographically different T sites of each framework type, as detailed in the Theoretical Methods Section (see also Figure S1 in the Supporting Information). The analysis was extended to electronic spectra of titanium offretite (Ti-OFF) in wet conditions, that is, in the presence of water.

The excitation spectra calculated for the dry zeolite models are shown in Figure 1. All spectra show absorption peaks in the 200–240 nm region with tails of up to 260 nm, the typical range for UV/Vis spectra of dry titanium zeolites. As a control, the ss for the corresponding all-silica zeolites are calculated as well. In contrast to their titanium-containing counterparts, they do not present absorption beyond 180 nm, with the exception of the STF system, for which a very low intensity of absorption is calculated at about 200 nm (Figure 1a). Such a finding should not be surprising considering that the STF framework is characterized by five-membered rings (5-MRs) as building unit^[9, 22] and that moderate semiconductor behaviour was observed in a series of zeolites characterized by the presence of 5-MR.^[23]

Comparison of the calculated σ s indicates that the 200–240 nm absorption bands should be related to the presence of

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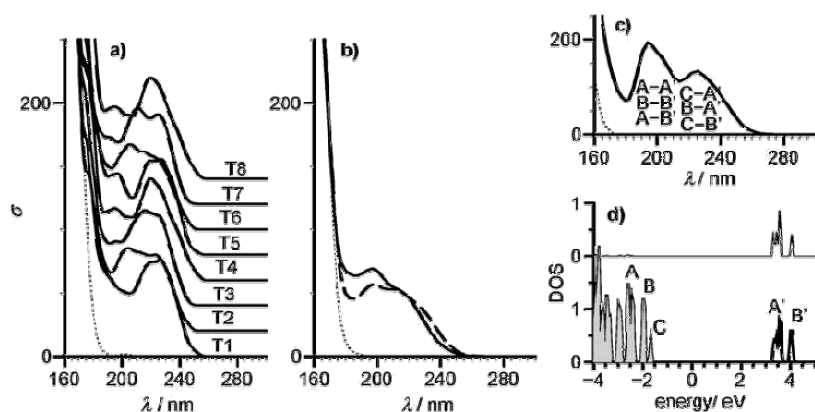


Figure 1. Optical conductivity S as a function of wavelength λ calculated for dry zeolites. a) STF systems. The dotted line refers to the all-silica form (SSZ-35). The labelled continuous lines refer to the eight optimized Ti-STF structures obtained by substituting one silicon atom with titanium in one of the T1 to T8 sites. b) Optical conductivity for the offretite systems. The dotted line refers to the all-silica offretite, the continuous line to Ti-OFF with one titanium atom in T1, thick dashed line to Ti-OFF with one titanium in T2. c) Conductivity of the SOD systems. The dotted line refers to the all-silica SOD, the continuous line to Ti-SOD. d) DOS calculated for the Ti-SOD system. The lower line refers to the total DOS, the higher (thin) line to the partial DOS projected on titanium d-states. The grey coloured part of the total DOS refers to occupied states.

zeolitic titanium. The calculated band profiles confirm those already reported in ref. [17] on the basis of TD-DFT results, namely that a single titanium centre shows absorption bands characterized by a multippeak structure. Moreover, different titanium sites present different profiles, even when they belong to the same framework type (see Figures 1 a and b). The multi-peak profile of a single titanium site is due to the splitting of the empty titanium d-states caused by the zeolitic environment and the different energies of the occupied states localized on the titanium-bonded framework oxygen atoms. Such features are clearly distinguishable by inspecting the electronic density of states (DOS) calculated for the Ti-SOD system (Figure 1 d). The titanium d-states are split into two groups (labeled A' and B') in the 3.5–4.2 eV range, while the lone pairs of the titanium-bonded O states form three groups (labeled A, B and C) in the 2.4 to 1.5 eV range. The two main peaks centred at 194 nm and 225 nm in the Ti-SOD excitation spectrum arise from transitions from the A, B and C set of occupied states to the empty A' and B' set as detailed in Figures 1c and d. This titanium centre in Ti-SOD, characterized by four equal Ti O bond lengths (1.785 Å), four equal Ti O Si bond angles (149.98) and two groups of O Ti O bond angles (4 0 105.38 and 2 0 118.38),^[17] is the most symmetric among those studied here. The other model titanium zeolites, characterized by lower symmetry at the titanium centres, show electronic excitation spectra in the same UV region. However, different geometries and state energies lead to variations in the position, number and intensity of the peaks. For example, in the most stable among the eight Ti-STF structures, obtained when titanium replaces silicon in the T8 position,^[22] two peaks at 194 nm and 219 nm, and a shoulder at 227 nm are clearly identified (see Figure 1 a). In the Ti-OFF case, the most stable structure is the one where titanium replaces silicon in T1, and shows an excitation peak at 195 nm and a broader band at 214 nm. In the other dry Ti-OFF model (Ti in site T2) the spectral profile presents a peak at 197 nm and two broad features at 214 nm and 231 nm (Figure 1 b).

The first excited electronic singlet state for dry titanium zeolite crystals was calculated with the restricted open shell Kohn–Sham (ROKS) formalism^[24]. For selected structures, Figure 2 shows the maximally localized Wannier orbitals corresponding to the states that become singly occupied upon excitation. In each of the investigated titanium zeolites, the calculated lowest excitation is localized on the titanium centre and involves atomic-like d-orbitals. Such a finding provides clear evidence of the

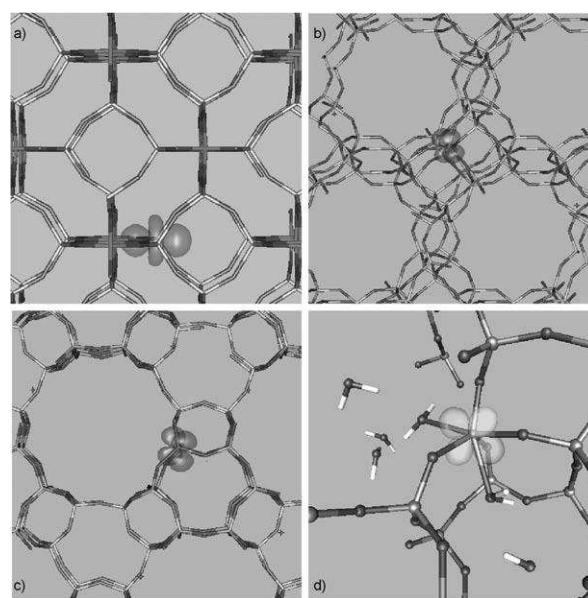


Figure 2. Ball-and-stick representations of the titanium zeolite models. a) Ti-SOD. b) Ti-STF (Ti in T1 site). c) Dry Ti-OFF (Ti in T1 site). d) Hexa-coordinated titanium centre in 6W₂. Silicon and titanium atoms are in pale grey, oxygen atoms in dark grey, hydrogen atoms in white. Titanium atoms can be identified by the electron density contours, which represent the maximally localized Wannier functions corresponding to the first excitation calculated with the ROKS approach.

LMCT character of the UV/Vis spectra in dry titanium zeolites. However, as the titanium environment affects the splitting of d-states (Figure 1 d and Figure 5 g), the lowest excitation involves different d-orbitals (e.g. d_{z^2} or d_{xy}).

Geometry optimizations were performed on different monohydrated structures of Ti-OFF, with stoichiometry $[\text{TiSi}_{17}\text{O}_{36}]\cdot\text{H}_2\text{O}$ and titanium in the T1 site. Three model structures were considered, with the water molecule located: (1) at the centre of the 12-MR channel (1W₀), (2) inside the 12-MR channel, bonded as a ligand to titanium (1W₁) and (3) in the

gmelinite cage, bonded to titanium ($1W_2$). Three more structures characterized by a hydrolyzed titanium centre were simulated. Indeed, since the early work on titanium zeolites it is argued that water might hydrolyze a Ti-O-Si bridge, with formation of a titanol Ti-OH and a silanol Si-OH.^[25] Moreover, it has been reported recently that a TS-1 model with a hydrolyzed Ti-O-Si bridge is energetically disfavoured with respect to a non-hydrolyzed Ti-O-Si bridge plus a gas phase water molecule.^[26] However, stabilization of the hydrolyzed site may occur via the so-called hydrolysis-and-inversion mechanism,^[26] whereby hydrolysis of a Ti-O-Si bridge is followed by a rotation of the titanium-centred tetrahedron (see ref. [26]). Besides a structure characterized by simple hydrolysis of a Ti O Si bridge ($1W_H$), hydrolyzed systems characterized by both a single inversion ($1W_{Hinv}$) and a double inversion ($1W_{Hinv2}$) were optimized. As already reported in ref. [26], a single inversion actually stabilizes the hydrolyzed structure. However the hydrolysis-and-inversion systems are less stable than the system in which water is bonded at the titanium site as a ligand.^[11, 16] Relative energies and significant geometric parameters of the six optimized $[TiSi_{17}O_{36}] \cdot H_2O$ systems are reported in Table 1, while graphical representations can be found in the Supporting Information (Figure S2).

Calculated σ s for the monohydrated Ti-OFF systems are shown in Figure 3. It emerges that the presence of an unligated water molecule in a titanium zeolite pore leads to an increase of the intensity in the 180–230 nm region with respect

	ΔE	Ti-W	Ti-Of
$1W_0$	6.7	5.157	1.808
$1W_1$	0.0	2.259	1.829
$1W_2$	9.6	2.315	1.824
$1W_H$	21.2	-	1.815
$1W_{Hinv}$	16.1	-	1.821
$1W_{Hinv2}$	26.6	-	1.821

to the dry system, accompanied by a modest blue-shift of the peak at 195 nm and a minor red-shift of the absorption edge (Figure 3 a). With respect to anhydrous Ti-OFF, the two systems characterized by hydrolysis-and-inversion show an intensity increase and a blue-shift of the main peaks, together with a modest blue-shift of the absorption threshold, more pronounced in the doubly inverted hydrolyzed Ti-OFF. Only the

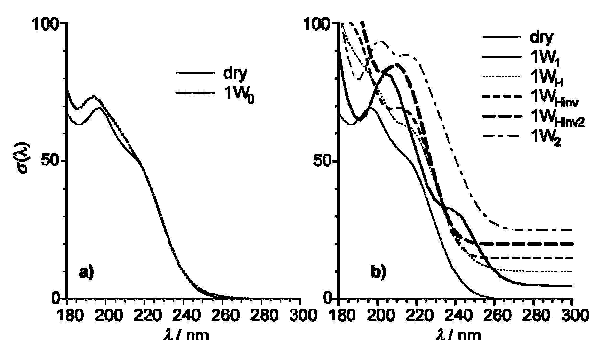


Figure 3. Optical conductivity σ calculated for dry Ti-OFF and mono-hydrated Ti-OFF models as a function of wavelength λ . a) Dry Ti-OFF compared with the $1W_0$ system. b) Comparison of the σ s of dry Ti-OFF with Ti-OFF pentacoordinated at titanium ($1W_1$ and $1W_2$) and with the hydrolyzed systems ($1W_H$, $1W_{Hinv}$ and $1W_{Hinv2}$).

simply hydrolyzed system $1W_H$ shows a modest threshold red-shift. On the other hand, the penta-coordinated $[TiSi_{17}O_{36}] \cdot H_2O$ systems (with water as a ligand) show a significant (~ 20 nm) edge red-shift (bathochromic effect) and are characterized by a new feature centred at about 245 nm. Such a red-shift is more pronounced in the more stable $1W_1$ system, namely when the water ligand is at 2.259 Å from titanium in the 12-MR, with respect to the $1W_2$ case, where the water ligand is positioned in the gmelinite cage at 2.315 Å from titanium.

Model Ti-OFF systems characterized by higher water loading are considered as well. Geometry optimizations were performed on $[TiSi_{17}O_{36}] \cdot (H_2O)_2$, $[TiSi_{17}O_{36}] \cdot (H_2O)_5$ and $[TiSi_{17}O_{36}] \cdot (H_2O)_6$. In these systems, none of the four Ti O Si bridges is hydrolyzed and titanium is in T1 (see Table 2 and Figure S3 in the Supporting Information). The lowest excitation involves a d-orbital localized on the titanium atom, thus confirming the LMCT character of the electronic transitions. The corresponding maximally localized Wannier function for the $6W_2$ system is represented in Figure 2.

Quite interestingly, the only hexa-coordinated titanium-centre was detected in the $6W_2$ model, characterized by four water molecules in the 12-MR and two in the gmelinite cage (Figure 2). The hexa-coordination at the titanium centre is due to four chemically bonded framework oxygen atoms, one water ligand from the 12-MR channel and a second water ligand in the gmelinite cage. The two ligands are therefore

	R	G	n	Ti-W	Ti-Of	OTiO	TiOSi
$2W_1$	2	0	1(R)	2.214	1.834 (0.017)	107.6 (13.0)	142.1 (16.3)
$2W_2$	0	2	1(G)	2.180	1.834 (0.016)	108.8 (10.1)	134.4 (8.5)
$2W_3$	1	1	1(R)	2.240	1.834 (0.016)	108.0 (14.3)	140.2 (11.1)
$5W$	5	0	1(R)	2.204	1.836 (0.020)	107.3 (12.7)	139.2 (12.6)
$6W_1$	5	1	1(R)	2.190	1.837 (0.021)	107.2 (13.0)	138.9 (10.7)
$6W_2$	4	2	2(R,G)	2.246(R); 2.237(G)	1.866 (0.030)	108.1 (15.7)	133.4 (7.6)

bonded to titanium from different pores and from opposite sides. However, such a 4–2 arrangement (four H₂O in a 12-MR, two in gmelinite) with hexa-coordinated titanium is energetically disfavoured by 45.4 kcal/mol with respect to the 5–1 arrangement in the 6W₁ system (five H₂O in a 12-MR, one in gmelinite) with penta-coordinated titanium. Also, the water–oxygen–titanium distances in 6W₂ are longer than the water–oxygen–titanium distances found in the penta-coordinated titanium sites (see Table 2). It seems that, when titanium is already penta-coordinated from the 12-MR side, another water ligand from a different cage can approach titanium at coordination distance only if it is solvated by at least one other water molecule, indicating that solvent co-operative effects play a relevant role in titanium-shell expansion.^[11, 14]

For titanium to

become hexa-coordinated, a sixth ligand should be activated, by hydrogen bonding or solvation, for example, since the Lewis acidity of titanium is lowered when it is penta-coordinated.^[11, 14] Even though the details of such behaviour may seem to be peculiar to the offretite channel's system, the lowering of the Lewis acid character of zeolitic titanium with increasing coordination appears to be more general. Indeed, hexa-coordinated titanium centres were detected in highly hydrophilic samples of titanium-beta zeolite,^[6] while in hydrophobic samples only penta-coordinated titanium-sites were found, indicating that water accessibility affects titanium coordination.

Hydration degree and titanium coordination influence the calculated ss. Indeed, an increase in both factors implies bathochromic effects, as clearly shown in Figure 4. The presence of penta-coordinated titanium is related to the appearance of a band at 245 nm (Figure 4a). This band's intensity and edge depend on both the degree of hydration and the degree of filling, defined here as the simultaneous presence of water in different pores of the zeolitic system. The largest red-shift is detected for the 6W₂ system (Figure 4b), where titanium is hexa-coordinated. The intense absorption centred at about 250 nm (with a tail of up to 275 nm) should be attributed to the simultaneous presence of two water molecules ligated to titanium (system 6W₂). It may be therefore concluded that the bathochromic effect observed for hydrated titanium zeolites is mainly due to the increase in the titanium coordination number induced by water.

Higher water loading in the same pore (e.g. the 12-MR channel) leads to an intensity increase of the absorption band and

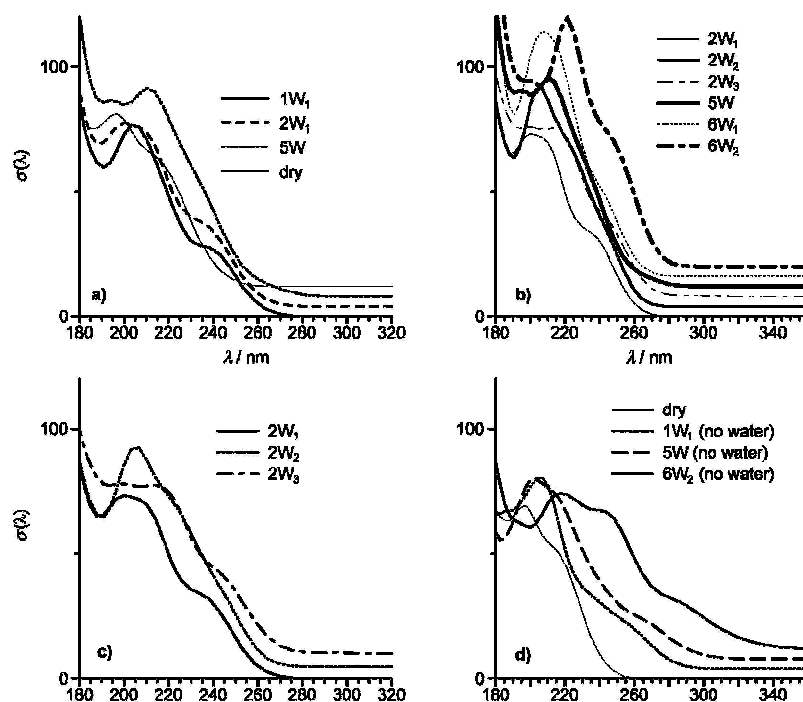


Figure 4. Optical conductivity σ calculated for hydrated Ti-OFF models as a function of wavelength λ . a) Comparison of σ s for Ti-OFF systems characterized by progressive filling of the 12-MR channel. b) Optical conductivity profiles for 2W₁, 2W₂, 2W₃, 5W, 6W₁ and 6W₂. c) Comparison of calculated σ s for bi-hydrated Ti-OFF systems. d) Optical conductivity σ calculated for anhydrous systems: the optimized (dry) Ti-OFF, and the evacuated framework structures corresponding to 1W₁, 5W and 6W₂ systems

a very small bathochromic effect, as deduced by comparing the σ s of the 1W₁, 2W₁ and 5W systems where titanium is always penta-coordinated and the additional water molecules are solvating the water molecule ligated to titanium (see Figure 4a and Figure S3 of the Supporting Information). In this sequence, the increase of the absorption intensity is parallel to the increase in hydration.

The effects of the degree of filling on the absorption edge can be dissected by comparing the ss of the three bi-hydrated systems characterized by penta-coordinated titanium (Fig. 4c and Figure S3 of the Supporting Information). With respect to 2W₁ and 2W₂, when both ligand and solvent water molecules are located in the same pore, a modest threshold red-shift is detected for 2W₃, where the ligand is in the 12-MR channel and the solvent in the gmelinite cage. Therefore, water molecules approaching the titanium centre from different pores also cause a bathochromic effect on the LMCT absorption edge.

A deeper insight in the effect of water may be obtained by removing water molecules from the hydrated models while keeping the distorted framework structure, and analyzing the electronic excitations of the evacuated systems. In Figure 4d, the σ s calculated for the evacuated framework structures corresponding to the 1W₁, 5W and 6W₂ systems (i.e. without the water molecules) are compared to the optimized dry Ti-OFF system one. Remarkably, threshold red-shifts even greater than those calculated in the presence of water are found, indicating that deformations at the titanium site are responsible for a large bathochromic effect. Such an effect is related to the

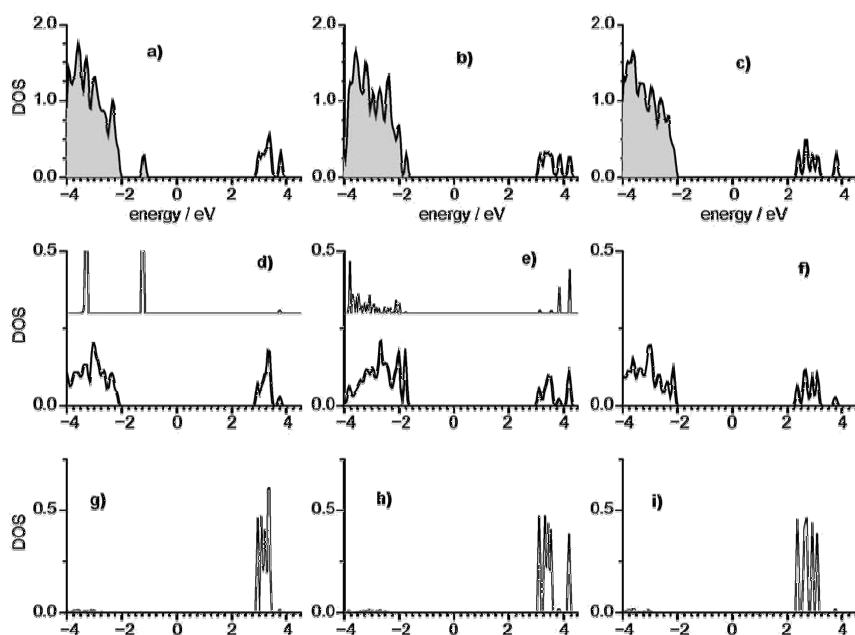


Figure 5. Calculated DOS for $1W_0$, $1W_1$ and evacuated $1W_1$. a) Total DOS in $1W_0$. b) Total DOS in $1W_1$. c) Total DOS in evacuated $1W_1$. d) $1W_0$ projected DOS on the titanium-bonded framework oxygen atoms (lower part), and projected DOS on the water molecule's oxygen atom (upper part, thin line). e) $1W_1$ projected DOS on the Ti-bonded framework oxygen atoms (lower part), and projected DOS on the water molecule's oxygen atom (upper part, thin line). f) Evacuated $1W_1$ projected DOS on the Ti-bonded framework oxygen atoms. g) $1W_0$ projected DOS on the d-states of titanium. h) $1W_1$ projected DOS on the d-states of titanium. i) Evacuated $1W_1$ projected DOS on the d-states of titanium. In the total DOSs, the grey areas correspond to the occupied states.

lengthening of Ti-O bonds and distortion of the TiO_4 tetrahedron upon water coordination (Table 2). However, water seems to quench such an effect by acting as a Lewis base, namely by donating charge to titanium and thus lowering its electron-acceptor character. This is indeed the case, as can be seen from the total and partial electronic density of states (DOS) calculated for the $1W_0$, $1W_1$ systems and for the evacuated $1W_1$ framework. When water is at the centre of the channel, at 5.157 Å from titanium (in $1W_0$), the edges of the highest occupied states of the titanium-bonded framework oxygen atoms and of the lowest empty titanium d-states are at 2.1 and 3.1 eV respectively (Figures 5 a, d, g). These states are responsible for the electronic absorption threshold (~ 240 nm). Even though the highest occupied state (HOMO) is at 1.2 eV (Figures 5 a, d), no LMCT arises from this state because it is localized on the water molecule's oxygen atom, far apart from titanium (5.157 Å, Table 1). In system $1W_1$ (Figures 5 b, e, h) in which a water molecule is ligated at 2.259 Å from titanium, the water lone pairs are stabilized by interaction with the Lewis acid centre (Ti), as indicated by the mixing with the titanium-d empty states in the water-oxygen partial DOS (Figure 5 e). While the lower energy edge of the d-states increases by ~ 0.1 eV with respect to $1W_0$, the upper energy edges of the occupied states localized on the titanium-bonded oxygens rise by ~ 0.4 eV, corresponding to a net decrease of their energy difference of about 0.3 eV and to an electronic absorption edge of ~ 250 nm. The origin of the bathochromic effect is therefore to be ascribed to the destabilization of the electronic states localized on the titanium-coordinated framework oxygens (p-type lone pairs) due to the structural distortions at the titanium centre. Inspection

of the DOS calculated for the evacuated $1W_1$ framework supports such a finding: Removal of the water molecule induces a significant lowering of the empty titanium d-states' energy edge. Such a lowering is caused by the decrease of electronic density on titanium due to the missing Lewis base. Therefore, this makes titanium a more effective electron attractor in the distorted structure.

In summary, a series of calculations is presented that unravels the relationships among water loading, coordination at titanium and electronic excitation spectra. The increase of the titanium coordination number (from four to five and six) produces a bathochromic effect in the excitation spectra. Independently of the loading and coordination, all excitations are localized LMCT transitions. Such a finding raises the challenging question on how an

LMCT excitation mechanism alone could account for the semi-conducting properties of titanium zeolites exploited in the photovoltaic devices based on titanium zeolites recently described.^[8] The LMCT transitions are determined by the relative energies of the titanium-bonded framework oxygen states and titanium d-levels. At the microscopic level, the bathochromic effect on such LMCT spectra is induced by water coordination. A twofold role of the water has been highlighted: it enhances the donor properties of the framework oxygen atoms by distorting the titanium centre's structure and modulates the acceptor properties of the metal centre via a Lewis acid-base interaction with the titanium centre.

Theory and Methodology

Ti-offretite ($Ti-OFF$)^[13] has been the subject of several ab initio molecular dynamics studies in both dry and wet conditions.^[14–16] Offretite is characterized by having maximally 12-membered (12-MR) pore openings and two crystallographic tetrahedral T sites, namely T1 (12 sites per unit cell) and T2 (6 sites per cell).^[9] The hexagonal cell parameters for $Ti-OFF$ [$TiSi_{17}O_{36}$] are $a = 13.229$ Å and $c = 7.338$ Å, as in ref. [14, 16]. Two model $Ti-OFF$ structures were considered, one with one titanium atom replacing silicon in a T1 site, and the other with the replacement in a T2 site. So far, titanium sodalite and titanium SSZ-35 have no experimental counterparts and will be considered as simple models. Sodalite (its all-silica form has the unit cell formula $[Si_{12}O_{24}]$) is characterized by a maximum pore opening formed by 6-MRs and one crystallographic T site.^[9] The model titanium-sodalite ($Ti-SOD$) has the chemical formula $[TiSi_{11}O_{24}]$, and its cubic cell parameter ($a = 8.9751$ Å) is taken from a low Zn-content sodalite^[27]. The chemical formula per unit cell of triclinic SSZ-35^[9, 22] is $(Si_{16}O_{32})$.

Like silicalite, SSZ-35 is characterized by 10-MR channels as maximum pore opening and by 5-MRs as building units. Eight crystallographically different T sites are present (T1-T8).^[22] The cell parameters of titanium SSZ-35 (Ti-STF, [TiSi₁₅O₃₂]) are obtained by isotropically expanding the all-silica SSZ-35 cell parameters^[22] in order to achieve a unit cell volume increase of ~ 8%. They are $a = 11.506 \text{ \AA}$, $b = 11.622 \text{ \AA}$, $c = 7.438 \text{ \AA}$, $\alpha = 94.66^\circ$, $\beta = 96.21^\circ$ and $\gamma = 104.89^\circ$. Such a volume increase is the same as adopted in building up a model of a low-content titanium chabasite as reported in ref. [12]. Eight model Ti-STF structures were built, each characterized by a titanium-silicon substitution in one of the different T sites.

Calculations were performed by using a gradient-corrected approximation to DFT, that is, the Becke^[28] and Perdew^[29] corrections to the local density approximation. Periodic boundary conditions were used and the electronic states were expanded in plane waves up to a kinetic energy cutoff of 60 Ry (240 Ry for the density) at the G point. Norm-conserving^[30] semilocal^[31] pseudopotentials were used for the valence electron interactions of the ionic cores. Non-locality up to $l = 2$ was adopted for each atom type with the exception of H, for which a local pseudopotential was used. All pseudopotentials, in numerical form, were obtained via the Troulliers and Martins scheme.^[32] Tests on this computational scheme can be found elsewhere.^[16] Moreover such a scheme was already used in many studies concerning zeolites and other framework materials (see e.g. refs. [33, 34]). Geometry optimizations were performed with a convergence criterium of 1.00×10^{-4} a.u. for the maximum gradient on the nuclear positions. Besides optimization of the dry titanium zeolites, Ti-SOD, Ti-STF and Ti-OFF, we have performed a series of geometry optimizations for titanium-OFF at different water content. Since the anhydrous Ti-OFF model with titanium in the T1 site was found to be more stable than the T2 one (by 4.6 kcal/mol), calculations on the hydration effects were performed with titanium always in T1.

The Frank-Condon optical conductivity σ is calculated for the optimized structures by using the following equation:^[35, 36]

$$\sigma(\omega) = \frac{2\pi}{3\omega V} \sum_{i,j=1}^N (f_i - f_j) P_{ij}^2 \delta[(\epsilon_i - \epsilon_j - \hbar\omega)]$$

with $P_{ij} = \langle i | p | j \rangle$, ω the frequency, ϵ_i the eigenvalue of state i with occupation number f_i , V the cell volume and p the electronic momentum operator. The sum is extended from occupied i -states ($f_i = 2$) to empty j -states ($f_j = 0$). The summation was extended to include up to 60 empty states.

While geometry optimizations were performed with a 60 Ry cut-off, the Kohn-Sham^[37] states and eigenvalues needed for obtaining s were calculated by adopting a cut-off of 90 Ry. Besides vertical electronic excitations (eigenvalues and eigenstates of the Kohn-Sham equations), the first excited singlet states have been obtained by using the ROKS formalism for the calculation of low spin excitation states,^[24] from which the maximally localized Wannier functions were obtained via the procedure of ref [38]. The partial electronic DOS was obtained by projecting the 90 Ry Kohn-Sham states used in the s -calculations onto the s , p and d atomic pseudowavefunctions obtained in the pseudopotentials generation.^[32] Calculations were performed by using the CPMD computer code.^[39]

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