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CH_2ClF adsorbed on TiO_2: study of the adsorbate-substrate interaction by IR spectroscopy and DFT calculations

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Abstract. Fourier-transform infrared spectroscopy has been used for the first time to study the adsorption of chlorofluoromethane (CH_2ClF) on TiO_2 at room temperature. The obtained spectra allow to deduce that the adsorbate-substrate interaction occurs through both the Cl and F atoms of the molecule and the surface Lewis acid site (Ti^{4+}) and by means H-bonds involving the CH_2 group and the surface Lewis basic sites (O^{2-} or OH^-). In order to better comprehend these interactions, a periodic quantum-mechanical study at DFT/B3LYP level has been carried out by considering the anatase (101) surface and focusing the attention on the determination of the energetically possible adsorbate-substrate structures. According to the comparison between the experimental and calculated vibrational frequencies, it can be concluded that the molecule can adsorb on the surface both through the Cl atom and an H-bond and by means the F atom and two H-bonds.

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Key words: chloroflurometháne, adsorbate-substrate interaction, TiO_2 surface, infrared spectra, quantum-mechanical simulations.

1 Introduction

Chlorofluorocarbons, which are widely employed in the industrial field as refrigerants, give rise to serious problems at the atmospheric level because of their ozone depletion potential. For this reason, the presence of these compounds in the air should be limited.

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Among the possible techniques to remove a pollutant from the air, heterogeneous photocatalysis on TiO_2 represents a very interesting approach [1]. Since the adsorption of the compound on the surface corresponds to the starting point of its following decomposition, an investigation aimed to elucidate the interaction between the adsorbate and the substrate can provide useful information on the reaction mechanism and results in the development of successful applications. To this aim, the use of infrared spectroscopy allows to know details about the orientation geometry, e.g. the surface and molecular sites involved in the adsorption, by comparing the spectrum of the gas-phase molecule with that of the adsorbed one.

The adsorbate-substrate interaction between chlorofluoromethane (CH_2ClF) and TiO_2 at room temperature has been investigated through the analysis of the FTIR spectra above 1000 cm^{-1}, focusing mainly the attention on the bands referring to the C-H and C-F stretching modes. The assignments of the vibrations of the adsorbate have been done by considering those related to the isolated molecule.

Further information to better elucidate the adsorbate-substrate interaction have been obtained by performing periodic quantum-mechanical simulations at DFT/B3LYP level: the calculations have been carried out by focusing the attention on the anatase (101) which is reasonably present at the experimental level since it is one of the most stable surfaces of TiO_2 [2].

2 Experimental details

The sample of CH_2ClF has been obtained commercially (purity $\sim$ 99%) from SynQuest Labs and has been employed without further purification.

TiO_2 powder (P25 Degussa) has been pressed in the form of a self-supporting pellet ($\sim$ 20 $mg \cdot cm^{-2}$) which has been placed in a Pyrex cell equipped with CaF_2 windows. The TiO_2 has been preventively pre-treated at high temperature under vacuum before performing the adsorption experiments. The pre-treatment, which is necessary to remove the water and other possible adsorbed impurities, is described elsewhere [3]. The spectrum of the pre-treated TiO_2 shows some bands around 3000 cm^{-1} which are due to isolated OH^- groups [4]. These groups along with the surface under-coordinated oxygen ions (O^{2-}) correspond to the Lewis basic site of TiO_2.

The adsorption spectrum has been collected after the introduction of the gas into the cell at different values of pressure. The cut-off of TiO_2 allows the investigation of the spectral region from the lower limit of about 1000 cm^{-1}. All the spectra have been recorded with 20 scans at a resolution of 4 cm^{-1} employing the Bruker Vertex 70 FTIR spectrometer. The background is represented by the spectrum of TiO_2 obtained after the pre-treatment.

3 Computational details

The calculations have been carried out by using the periodic quantum-mechanical program CRYSTAL06 [5] at DFT/B3LYP level.

The basis set for the titanium and oxygen ions derives from a properly investigation on TiO_2 [6] and consists in an 86-51G* contraction (one s, three sp and one d shells) for O and an 8-411G contraction (one s and three sp shells) for Ti; the most diffuse sp exponents are $\alpha^{Ti} = 0.598$ and $\alpha^{O} = 0.184$ bohr^{-2}.

The CH_2ClF molecule is described by using the standard 6-31G** contraction [7,8].

The geometry optimization and the calculation of the vibrational frequencies have been performed by adopting the computational parameters reported elsewhere [9]. The calculated vibrational frequencies have been corrected for the anharmonicity by using the scaling factor suggested by the NIST and equal to 0.961.

4 Results and discussion

4.1 Adsorption spectra

Chlorofluoromethane is a molecule belonging to the C_s symmetry point group with 9 fundamental modes of which 6 of A′ symmetry and 3 of A″ symmetry.

The infrared spectra of CH_2ClF adsorbed on TiO_2 surface at increasing pressures along with that in gas-phase are reported in Fig. 1. The gas phase contributions have been subtracted out from the adsorption spectra. Basing on the assignments of the isolated molecule, which are given in Table 1, seven fundamentals occur above 1000 cm^{-1}: they correspond to the stretching and deformation modes of the CH_2 group and to the C-F stretching vibration. As it can be seen from the spectrum (Fig. 1(a)), the CH_2 scissoring (1468 cm^{-1}) and rocking (1002 cm^{-1}) vibrations are too weak to be detectable. Focusing on the adsorption spectra (Figs. 1(b)-(d)), the IR region typical of the H-bond (3800-3400 cm^{-1}) shows some negative bands, which result from a decrease of the isolated OH groups of the surface, and a broad band. As reported in Table 1, the adsorption spectra also show peaks at about 3067, 2994, 1461, 1353, 1237, 1070, 1020 and 948 cm^{-1}. The five absorptions above 1200 cm^{-1} have been attributed to the CH_2 asymmetric and symmetric stretching, scissoring, wagging and twisting vibrations, respectively. The band at 1020 cm^{-1} has been connected with the CH_2 rocking mode while the two peaks at 1070 and 948 cm^{-1} have been assigned to two different C-F stretching vibrations.

Basing on the features of the adsorption spectra, it is possible to deduce that the molecule can adsorb on the surface interacting with the surface Lewis acid site (Ti^{4+}) by means of the Cl or the F atom and by H-bonds involving the CH_2 group and a surface Lewis basic site (OH^- or O^{2-}).

The acid-base interaction between the Ti^{4+} ion and one of the two halogen atoms explains the presence of the two different C-F stretching vibrations: in fact, the absorption at highest frequency (1070 cm^{-1}), very close to the C-F stretching frequency in the free

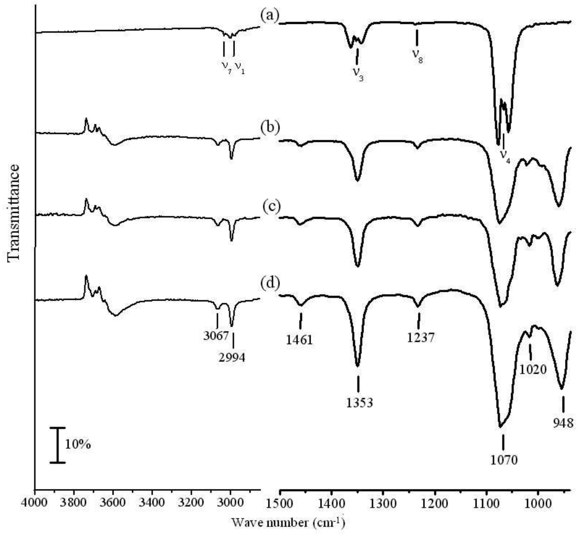

Figure 1: Low-resolution IR spectra of CH_2ClF in gas-phase (a) and adsorbed on TiO_2 (b)-(d). (a) Room temperature, $P \sim 1.0$ Torr, 16 cm cell. Infrared spectrum of TiO_2 taken after being in contact with ~ 1 (b), ~ 1.7 (c) and ~ 2.4 (d) Torr of CH_2ClF at room temperature.

Table 1: Fundamental frequencies (cm^{-1}) of CH_2ClF free and adsorbed on TiO_2 at room temperature.

$CH_2ClF_{(gas)}$				CH_2ClF_2/TiO_2
Vibration	Symmetry species	Approx. description	Wave number	Wave number
ν_7	A″	CH_2 asym stretching	3035	3067
ν_1	A′	CH_2 sym stretching	2992	2994
ν_2	A′	CH_2 scissoring	1468	1461
ν_3	A′	CH_2 wagging	1353	1353
ν_8	A″	CH_2 twisting	1237	1237
ν_4	A′	CF stretching	1068	1070; 948[a]
ν_9	A″	CH_2 rocking	1002	1020

[a] The two frequencies refer to two different CF stretchings.

molecule, indicates that the adsorption occurs through the Cl atom while the other one (948 cm^{-1}) should derive from the interaction by means of the F atom. In fact, it can be expected a negligible shift of the ν_4 in the former case and a large red-shift in the latter one.

The presence of H-bonds between the molecule and the surface explains the presence of negative bands and the broad band around 3000 cm^{-1}. The H-bonds can involve one or both the two H atoms of CH_2ClF and one or both the two surface Lewis basic sites, i.e. the isolated OH group or an O atom of TiO_2 itself.

4.2 Quantum-mechanical calculations

The simulation of the adsorbate-substrate system has been carried out by considering the O^{2-} ion as the surface Lewis basic site interacting with the molecule. The anatase (101) surface has been cut from the bulk whose parameters have been previously optimized [10]. As it is depicted in Fig. 2 (a), the surface is formed by sixfold and fivefold coordinated titanium ions, labelled Ti(6f) and Ti(5f) and threefold and twofold coordinated oxygen ions, labelled as O(3f) and O(2f). The Ti(5f) and O(2f) ions correspond to the surface Lewis acid and basic sites, respectively. The surface has been modelled by a 12-atomic layers slab having a (2 × 2) periodicity which corresponds to a surface coverage equal to 0.25 (see Fig. 2 (b)): this periodicity should allow to limit the presence of the lateral effects arising from the interaction between the neighbouring adsorbed molecules.

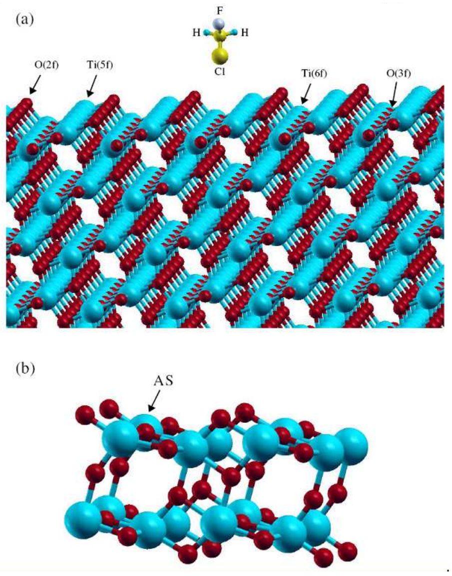

Figure 2: (a) Model of the anatase (101) surface and the CH_2ClF molecule: Ti(5f) and Ti(6f) represent fivefold and sixfold coordinated titanium ions while O(2f) and O(3f) correspond to twofold and threefold coordinated oxygen ions. (b) Model of surface unit cell used for the simulation: the surface Lewis acid site (AS) involved in the interaction with the molecule is indicated. (a) and (b) have been obtained by using the XCRYSDEN program [13].

The full relaxation of the adsorbate-substrate system has been performed after having optimized the isolated CH_2ClF molecule which has been positioned on the relaxed surface by taking into account the adsorption through one or both the two halogen atoms. The final structures are represented in Figs. 3(a)-(f) and can be described as follows:

- Structure (**Cl1**): acid-base interaction through the Cl atom and one Ti^{4+} ion and H-bond between one H atom and one O^{2-} ion (Fig. 3 (a));
- Structure (**Cl2**): acid-base interaction through the Cl atom and one Ti^{4+} ion (Fig. 3 (b));
- Structure (**Cl3**): acid-base interaction through the Cl atom and one Ti^{4+} ion and two H-bonds between two H atoms and two O^{2-} ions (Fig. 3 (c));
- Structure (**F1**): acid-base interaction through the F atom and one Ti^{4+} ion and H-bond between one H atom and one O^{2-} ion (Fig. 3 (d));
- Structure (**F2**): acid-base interaction through the F atom and one Ti^{4+} ion and two H-bonds between two H atoms and one O^{2-} ion (Fig. 3 (e));
- Structure (**F3**): acid-base interaction through the F atom and one Ti^{4+} ion and two H-bonds between two H atoms and two O^{2-} ions (Fig. 3 (f)).

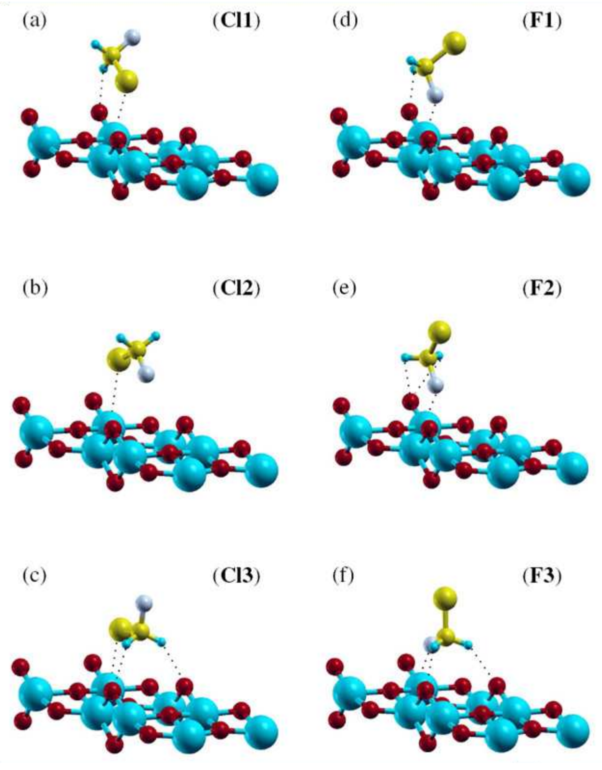

Figure 3: (a)-(f) Models of the CH_2ClF/TiO_2 system (see text). In (a)-(f) only the outermost surface ions are depicted; the dashed lines represent the bonds between CH_2ClF and TiO_2. (a)-(f) have been obtained by employing the XCRYSDEN program [13].

The geometry resulting by an initial configuration having the two halogen atoms above two different Ti^{4+} ions leads to a Structure very close to the (**F1**) one. It is important to notice that the adsorption following the Structures (**Cl1**) and (**F1**) results in a decrease of the molecular symmetry from the C_s point group to the C_1 one and then, in a possible different behaviour of the two C-H bonds.

Table 2 summarizes the main structural parameters of the obtained adsorbate-substrate systems along with those concerning the optimized isolated molecule which have been found to be in good agreement with the available experimental values [11]. The variations in the molecular structural parameters due to the adsorption can be summarized as follows:

- the C-Cl bond length increases when the adsorption occurs through the Cl atom and decreases when the molecule interacts by means the F atom;
- the C-F bond length increases when the molecule adsorbs through the F atom and decreases when the acid-base interaction involves the Cl atom.
- the two C-H bond lengths and the Cl-C-F bond angle decrease in all the cases, except for the Structure (**Cl2**);
- the two Cl-C-H bond angles decrease when the adsorption involve the Cl atom and increase when the molecule interacts with the F atom;
- the H1-C-H2 bond angle increases in all the cases.

The energetics associated to the adsorption have been investigated by considering not only the binding energy (BE) but also the real strength of the final adsorbate-substrate interaction (i.e. the interaction energy E_{int}) and the variations of the geometry due to the electronic redistribution occurring inside the molecule and the surface as a consequence of the adsorption (i.e. the total distortion energy E_{dis} which results from the sum of the monolayer E_{dis}^{mon} and surface E_{dis}^{sur} distortion energies). The three energies are linked by the following relationship

$$BE = E_{int} + E_{dis}, \tag{1}$$

where BE, E_{int} and E_{dis} have been calculated according to the following formulas

$$\begin{aligned} BE &= E_{sys} - (E_{mon} + E_{sur}), & (2)\\ E_{int} &= E_{sys} - (E_{mon@sys} + E_{sur@sys}), & (3)\\ E_{dis} &= E_{dis}^{mon} + E_{dis}^{sur} \\ &= (E_{mon@sys} - E_{mon}) + (E_{sur@sys} - E_{sur}), & (4) \end{aligned}$$

where E_{sys}, E_{mon} and E_{sur} represent the optimized energy of the adsorbate-substrate system, the monolayer and the surface, respectively, while $E_{mon@sys}$ and $E_{sur@sys}$ correspond to the energies of the monolayer and the surface calculated at the geometry of the final system. Basing on the used formulas, a negative (positive) value of BE and E_{int} means that the adsorption is a favourable (unfavourable) process and that there is an attraction (repulsion) between the adsorbate and the substrate. All the obtained energies are reported in Table 3: the Counterpoise (CP) method [12] has been adopted to correct the BE and E_{int} for the basis set superposition error (BSSE). As it can be seen, the Structure (**Cl2**) is not possible and then, confirms that the molecule interacts with the surface also

Table 2: Optimized structural parameters for the free and adsorbed CH_2ClF^a.

	Free		Adsorbed^b											
		$\%_{exp}{}^c$	**Cl1**	%	**Cl2**	%	**Cl3**	%	**F1**	%	**F2**	%	**F3**	%
C-Cl	1.803	2.3	1.828	1.4	1.815	0.7	1.841	2.1	1.772	-1.7	1.769	-1.9	1.767	-2.0
C-F	1.359	-0.8	1.358	-0.1	1.350	-0.7	1.352	-0.5	1.413	4.0	1.415	4.1	1.425	4.9
C-H1	1.092	0.2	1.091	-0.1	1.092	0.0	1.090	-0.2	1.088	-0.4	1.087	-0.5	1.088	-0.4
C-H2	1.092	0.2	1.091	-0.1	1.092	0.0	1.090	-0.2	1.088	-0.4	1.087	-0.5	1.088	-0.4
Cl-C-F	110.4	0.3	109.3	-1.0	110.8	0.4	108.3	-1.9	108.9	-1.4	108.1	-2.1	108.0	-2.2
Cl-C-H1	107.2	-2.0	105.3	-1.8	106.3	-0.8	106.1	-1.0	110.3	2.9	110.3	2.9	110.6	3.2
Cl-C-H2	107.2	-2.0	105.7	-1.4	106.3	-0.8	106.1	-1.0	109.3	2.0	110.3	2.9	110.6	3.2
H1-C-H2	112.1	1.5	114.2	1.9	112.5	0.4	112.6	0.5	114.8	2.4	112.8	0.6	112.3	0.2
Cl-Ti(s)			3.046		3.337		3.040							
F-Ti(s)									2.254		2.242		2.232	
H1-O(s)			2.120				2.274		2.167		2.638		2.295	
H2-O(s)							2.274				2.638		2.295	
C-Cl-Ti(s)			100.9		126.5		117.1							
C-F1-Ti(s)									125.5		122.6		137.8	
C-H1-O(s)			140.5				144.8		122.3		86.7		143.8	
C-H2-O(s)							144.8				86.7		143.8	

[a] Lengths and angles are reported in Å and degrees, respectively.

[b] The six structures refer to the adsorption modes described in the text.

% corresponds to the percentage deviation with respect to the isolated optimized molecule.

[c] $\%_{exp}$ is the percentage deviation with respect to the experimental values [12].

through the formation of one or two H-bonds. In general, the adsorption by means the F atom is associated to an absolute value of E_{int} bigger than that arising from the interaction through the Cl atom. However, it can be seen that all the five possible Structures have a similar value of BE.

Table 4 reports the scaled vibrational frequencies of the free and adsorbed CH_2ClF along with an approximate description of the corresponding eigenvectors. According to the percentage deviation with respect to the experimental values, which are also reported in Table 4, and to the shift between the isolated and adsorbed molecule, it can be deduced that the Structure (**Cl1**) corresponds to the best representation for the adsorption of CH_2ClF through the Cl atom. Basing on the behaviour of the C-F stretching vibration,

Table 3: Interaction, distortion and binding energies ($kJ \cdot mol^{-1}$) for the adsorbed CH_2ClF^a.

	Cl1	**Cl2**	**Cl3**	**F1**	**F2**	**F3**
E_{int}	-17.3	1.2	-21.6	-30.8	-29.8o	-37.7
E_{dis}^{mon}	1.6	1.7	2.0	6.5	6.0	8.1
E_{dis}^{sur}	4.2	0.7	5.7	8.1	7.8	13.4
BE	-11.5	3.6	-13.9	-16.2	-16.0	-16.2

[a] E_{int}, E_{dis}^{mon}, E_{dis}^{sur}, BE mean interaction, distortion of monolayer, distortion of surface and binding energies,respectively. The six structures refer to the adsorption models described in the text.

it can also be deduced that both the Structures (**F2**) and (**F3**) can well describe the interaction of the molecule by means the F atom. The percentage deviation (10 - 14%) of the CH_2 rocking (ν_9) for the (**F1 - F3**) structures appears anomalous. It cannot be excluded that for the adsorption of CH_2ClF through the F atom the ν_9 shifts from 1020 to around 950 cm^{-1} and the related very weak absorption is overlapped by the stronger one of the C-F stretching. Such a behaviour could be due to a mixing between the ν_4 and ν_9 vibrations since a decrease of the molecular symmetry for the adsorbate - substrate structures now occurs.

Table 4: Scaled vibrational frequencies (cm^{-1}) of the free and adsorbed CH_2ClF.

Band	Approx. description		$\%_{exp}$[b]	**Cl1**	%	**Cl2**	%	**Cl3**	%	**F1**	%	**F2**	%	**F3**	%
ν_7	CH_2 asym stretching	3048	0.4	3069	0.1	3050	-0.6	3085	0.6	3100	1.1	3122	1.8	3106	1.3
ν_1	CH_2 sym stretching	2946	-0.5	2978	-0.5	2977	-0.6	2995	0.0	3007	0.4	3036	1.4	3018	0.8
ν_2	CH_2 scissoring	1460	-0.6	1470	0.6	1461	0.0	1473	0.8	1437	-1.6	1438	-1.6	1450	-0.8
ν_3	CH_2 wagging	1331	-1.6	1324	-2.1	1327	-1.9	1347	-0.4	1335	-1.3	1319	-2.5	1351	-0.1
ν_8	CH_2 twisting	1209	-2.3	1216	-1.7	1209	-2.3	1204	-2.7	1201	-2.9	1193	-3.6	1213	-1.9
ν_4	CF stretching[c]	1078	1.0	1092	2.1 15.2	1100	2.8 16.0	1100	2.8 16.0	978	-8.6 3.2	955	-10.7 0.7	937	-12.4 -1.2
ν_9	CH_2 rocking	975	-2.7	995	-2.5	975	-4.4	980	-3.9	919	-9.9	914	-10.4	875	-14.3

[a] The six structures refer to the adsorption modes described in the text.

% corresponds to the percentage deviation with respect to the experimental values of the adsorbed molecule.

[b] $\%_{exp}$ is to the percentage deviation with respect to the experimental values of the molecule in gas-phase [10].

[c] The two deviations refer to the two different CF stretching frequencies (1070, 948 cm^{-1}).

5 Conclusions

The current work reports the first infrared study of chlorofluoromethane (CH_2ClF) adsorbed on TiO_2 at room temperature. According to the results, it can be concluded that the molecule adsorbs on the surface Lewis acid site (Ti^{4+}) through the Cl and the F atoms and by means the formation of H-bonds between the CH_2 group and a surface Lewis basic site (O^{2-} or OH^-). In order to better understand the obtained results, a periodic quantum-mechanical study at DFT/B3LYP level has been carried out by focusing the attention on one of the two most stable surfaces of TiO_2, i.e. the anatase (101) one. The calculations which have been performed by considering the O^{2-} ion as surface Lewis basic site result in five energetically possible adsorbate-substrate structures which differ for the kind of acid-base interaction (i.e. through the Cl or the F atom) and for the number of H-bonds. In general, it has been found that the C-X bond (where X = Cl, F) increases when the X atom is involved in the interaction, otherwise it decreases; in all the cases, the two C-H bonds decrease as consequence of the adsorption.

The comparison between the observed frequencies and the computed scaled ones leads to conclude that the molecule can interact through the Cl or the F atom with the surface Lewis acid site (Ti^{4+}). Moreover, the formation of H-bonds between the CH_2 group and the basic Lewis site (O^{2-} or OH^-) involves one H or both two H atoms when the interaction occurs through the Cl or the F atom, respectively.

Spectroscopic techniques combined with quantum-mechanical calculations allow to obtain important information to understand the adsorbate-substrate interaction involved in the adsorption of pollutants on photocatalysts.

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