



# Adsorption of difluoromethane on titanium dioxide: Investigation of the FTIR spectra and quantum-mechanical studies of the adsorbate–substrate structures

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## ABSTRACT

The interaction of difluoromethane (CH<sub>2</sub>F<sub>2</sub>) with the TiO<sub>2</sub> surface (P25 Degussa) at room temperature has been studied by Fourier-transform infrared spectroscopy for the first time. From the comparison between the adsorption characteristics and the gas-phase spectra it can be deduced that the molecule adsorbs through an acid–base interaction between one F atom and the surface Lewis acid site (Ti<sup>4+</sup>) and an H-bond between the CH<sub>2</sub> group and the surface Lewis basic site (OH<sup>-</sup> or O<sup>2-</sup>). In order to obtain more information about the orientation geometry and the variation of the molecular structural parameters, a quantum-mechanical investigation at DFT/B3LYP level has been also performed, considering the anatase (1 0 1) surface and focusing on the O<sup>2-</sup> as Lewis basic site. The resulting adsorbate–substrate structures involve the formation of an acid–base interaction between one F atom and the Ti<sup>4+</sup> ion and differ for the number of the involved H-bonds. According to the scaled vibrational frequencies, the simulated adsorption model which better agrees with the experimental data corresponds to that in which the CH<sub>2</sub> group interacts with the surface by only one H-bond.

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## 1. Introduction

Difluoromethane (CH<sub>2</sub>F<sub>2</sub>), also known as HFC-32, is a relatively non-toxic gas which has been proposed for CFC and HCFC replacement in new refrigerant systems. Moreover, it is used as a source of fluorine CF free radicals for process etch during RF plasma processing [1]. However, although it has zero ozone depletion potential, it has a high global warming potential and for this reason its removal from the air should be desirable. An interesting approach to obtain this scope consists in its decomposition through heterogeneous photocatalysis on TiO<sub>2</sub> [2]. As consequence of the fact that the degradation starts after the adsorption of the molecule on the surface, a study on the adsorbate–substrate interaction should represent an important tool to achieve information to elucidate the reaction mechanisms and to develop successful applications. Among the possible techniques to adopt for this kind of investigation, infrared spectroscopy is one of the most important ones: in fact, it allows to obtain important information about the orientation geometry, which depends on several factors such as the surface and molecular sites involved in the adsorption, by considering the possible occurring differences between the spectrum of the adsorbed molecule and that of the free one in the gas-phase.

The aim of the current work is represented by the formulation of an adsorption model of CH<sub>2</sub>F<sub>2</sub> on TiO<sub>2</sub> at room temperature by analyzing the FTIR spectra of the adsorbed compound. The comparison between the adsorbed and isolated molecule has been done by considering the fundamentals above 1000 cm<sup>-1</sup> and in particular the bands related to the C–H and C–F stretching modes. The vibrations of the adsorbate have been assigned by taking into account those referred to the compound in gas-phase.

In order to achieve supplementary data useful for the formulation of the model as well as to obtain information on the variation of the molecular structural parameters, a quantum-mechanical investigation of all the possible adsorbate–substrate structures has been performed. The calculations have been carried out at DFT/B3LYP level by considering the most stable surface of anatase, i.e. the (1 0 1) one [3], which is reasonably present at the experimental level.

## 2. Experimental details

The sample of CH<sub>2</sub>F<sub>2</sub> has been obtained commercially (purity ~98%) from ABCR and has been employed without further purification.

TiO<sub>2</sub> powder (P25 Degussa, ~75% anatase and 25% rutile) has been pressed in the form of a self-supporting pellet (~20 mg cm<sup>-2</sup>) which has been placed in a Pyrex cell equipped with CaF<sub>2</sub> windows. Before carrying out the adsorption experiments, a pre-treatment of the surface has been performed in order to remove the impurities

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**Table 1**  
Fundamental frequencies ( $\text{cm}^{-1}$ ) of  $\text{CH}_2\text{F}_2$  free and adsorbed on  $\text{TiO}_2$  at room temperature.

$\text{CH}_2\text{F}_2^{\text{a}}$ (gas)				$\text{CH}_2\text{F}_2/\text{TiO}_2$
Vibration	Symmetry species	Approx. description	Wavenumber	Wavenumber
$\nu_1$	$A_1$	$\text{CH}_2$ sym stretching	2948	2955
$\nu_2$	$A_1$	$\text{CH}_2$ scissoring	1508	1496
$\nu_3$	$A_1$	$\text{CF}_2$ sym stretching	1113	1125 <sup>c</sup>
$\nu_4$	$A_1$	$\text{CF}_2$ scissoring	529	n.o. <sup>b</sup>
$\nu_5$	$A_2$	$\text{CH}_2$ twisting	1262	n.o. <sup>b</sup>
$\nu_6$	$B_1$	$\text{CH}_2$ asym stretching	3014	3020
$\nu_7$	$B_1$	$\text{CH}_2$ rocking	1178	1161
$\nu_8$	$B_2$	$\text{CH}_2$ wagging	1435	1423
$\nu_9$	$B_2$	$\text{CF}_2$ asym stretching	1090	972 <sup>c</sup>

<sup>a</sup> From Ref. [10].

<sup>b</sup> Means not observable.

<sup>c</sup> The vibrational frequency refers to a C–F stretching (see text).

arising from the contact with the air. In particular, the cell has been heated up to  $450^\circ\text{C}$  for 3 h under dynamic vacuum ( $10^{-4}$  Torr); then a mixture of  $\text{N}_2/\text{O}_2$  (15%  $\text{O}_2$ ) at a pressure of 100 Torr has been introduced into the cell and kept there for 1 h. Successively, the cell has been degassed for 1 h and finally, it has been cooled to room temperature.

The pre-treated  $\text{TiO}_2$  contains isolated OH groups which give rise to bands around  $3000\text{ cm}^{-1}$ , as it has been described in the literature [4]. The  $\text{OH}^-$  represents one possible surface Lewis basic site along with the oxygen ion ( $\text{O}^{2-}$ ) constituting the surface itself.

The adsorption spectrum has been recorded after the introduction of the gas into the cell at different values of pressure. As consequence of the cut-off of  $\text{TiO}_2$ , the spectral region could not be investigated down to the lower limit of  $\sim 1000\text{ cm}^{-1}$ . All the spectra have been collected with 20 scans at a resolution of  $4\text{ cm}^{-1}$  employing the Bruker Vertex 70 FTIR spectrometer. The spectrum of  $\text{TiO}_2$  obtained after the pre-treatment has been used as background.

### 3. Computational details

The simulations have been performed by employing the periodic quantum-mechanical program CRYSTAL06 [5] at DFT/B3LYP level.

The titanium and oxygen atoms have been described by a basis set properly developed for the  $\text{TiO}_2$  surface [6]: it 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  $\alpha^{\text{Ti}} = 0.598$  and  $\alpha^{\text{O}} = 0.184\text{ bohr}^{-2}$ . For the  $\text{CH}_2\text{F}_2$  molecule the cc-pVTZ contraction has been used [7].

The computational parameters controlling the geometry optimization and the procedure to calculate the vibrational frequencies are reported elsewhere [8]. In order to take into account the anharmonicity, the present calculated frequencies have been scaled by using a scaling factor equal to 0.965 which has been obtained by the NIST [9] for the method and basis set adopted for the  $\text{CH}_2\text{F}_2$  molecule.

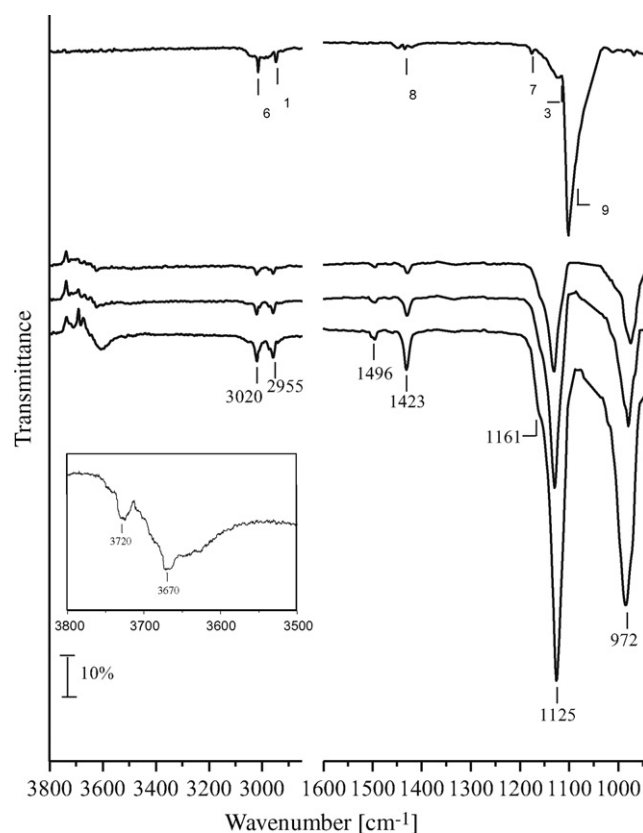
### 4. Results and discussion

#### 4.1. Adsorption spectra

Difluoromethane is a molecule which belongs to the  $\text{C}_{2v}$  symmetry point group and has 9 fundamental vibrations of which 4 of  $A_1$  symmetry, 1 of species  $A_2$ , 2 of  $B_1$  and 2 of  $B_2$  symmetry.

The infrared spectra of  $\text{CH}_2\text{F}_2$  in gas-phase and adsorbed on  $\text{TiO}_2$  surface at increasing pressures are shown in Fig. 1; the gas-phase contributions have been subtracted out from the adsorption spectra. According to the assignments of the isolated molecule [10], reported in Table 1, eight fundamentals occur above  $1000\text{ cm}^{-1}$  corresponding to the stretching and deformation modes of the  $\text{CH}_2$

group and to the stretching vibrations of the  $\text{CF}_2$  one; as it can be seen from the spectrum (Fig. 1a), the  $\text{CH}_2$  scissoring vibration is too weak to be detectable while the  $\text{CH}_2$  twisting is inactive. Focusing on the adsorption spectra (Fig. 1b–d), it can be seen that in the IR region around  $3700\text{ cm}^{-1}$  there are some negative bands indicating a decrease of the isolated OH group of the surface. Moreover a broad band appears in the region typical of the H-bond, i.e. that is included in the  $3500\text{--}3700\text{ cm}^{-1}$  range. In the IR region above  $1400\text{ cm}^{-1}$  four absorptions occurring at about 3020, 2955, 1496,  $1423\text{ cm}^{-1}$  are detected while in that below  $1200\text{ cm}^{-1}$  two strong bands at about 1125 and  $972\text{ cm}^{-1}$  and a shoulder at  $1161\text{ cm}^{-1}$  are observed. The frequency values for the adsorbate–substrate system are also reported in Table 1. In particular, the two absorptions



**Fig. 1.** Low-resolution IR spectra of  $\text{CH}_2\text{F}_2$  in gas-phase (a) and adsorbed on  $\text{TiO}_2$  (b–d). (a) Room temperature,  $P \sim 1.0$  Torr, 16 cm cell. Infrared spectrum of  $\text{TiO}_2$  taken after being in contact with  $\sim 1$  Torr (b),  $\sim 2$  Torr (c) and  $\sim 3$  Torr (d) of  $\text{CH}_2\text{F}_2$  at room temperature. Inset: IR spectra of the blank  $\text{TiO}_2$  sample in the OH stretching region ( $3500\text{--}3800\text{ cm}^{-1}$ ).

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