IR spectroscopy of CH₂BrF adsorbed on TiO₂ and quantum-mechanical studies

Jessica Scaranto, Paolo Stoppa, Andrea Pietropolli Charmet, Santi Giorgianni

► To cite this version:

Jessica Scaranto, Paolo Stoppa, Andrea Pietropolli Charmet, Santi Giorgianni. IR spectroscopy of CH₂BrF adsorbed on TiO₂ and quantum-mechanical studies. *Molecular Physics*, 2009, 107 (03), pp.237-244. 10.1080/00268970902773408 . hal-00513254

HAL Id: hal-00513254

<https://hal.science/hal-00513254>

Submitted on 1 Sep 2010

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

IR spectroscopy of CH₂BrF adsorbed on TiO₂ and quantum-mechanical studies

Journal:	<i>Molecular Physics</i>
Manuscript ID:	TMPH-2008-0310.R1
Manuscript Type:	Full Paper
Date Submitted by the Author:	22-Jan-2009
Complete List of Authors:	Scaranto, Jessica; University of Venice STOPPA, Paolo; University of Venice PIETROPOLLI CHARMET, Andrea; Universita' Ca' Foscari di Venezia, Dipartimento di Chimica Fisica GIORGIANI, Santi; University of Venice
Keywords:	1-Bromo-1-fluoroethene, Adsorption, TiO ₂ surface, Infrared spectra, Quantum-mechanical simulations

IR spectroscopy of CH₂CBrF adsorbed on TiO₂ and quantum-mechanical studies.

Jessica Scaranto, Paolo Stoppa, Andrea Pietropoli Charmet and Santi Giorgianni*

Dipartimento di Chimica Fisica, Università Ca' Foscari di Venezia, Dorsoduro 2137, I-30123 Venezia,
Italy

AUTHOR EMAIL ADDRESS: jeyscar@unive.it (J. Scaranto); stoppa@unive.it (P. Stoppa);
jacpnike@unive.it (A. Pietropoli Charmet); giorgian@unive.it (S. Giorgianni).

CORRESPONDING AUTHOR FOOTNOTE: J. Scaranto; Ca' Foscari di Venezia, Dorsoduro 2137,
I-30123 Venezia (Italy). Phone: +39 041 2348598; Fax: +39 041 2348594; E-mail: jeyscar@unive.it.

ABSTRACT

The adsorption at room temperature of 1-bromo-1-fluoroethene (CH_2CBrF) on TiO_2 has been investigated by Fourier-transform infrared spectroscopy after a preventive assignment of the fundamentals in the gas-phase, carried out for the first time. The spectrum resulting from the adsorption has been compared with the gas-phase one and the most important differences consist in a red-shift of the CH_2 stretching vibration and in the presence of two distinct absorptions for both the $\text{C}=\text{C}$ and $\text{C}-\text{F}$ stretching modes. Basing on the observed features it has been inferred that there is the formation of an H-bond between the CH_2 group and a surface Lewis basic site and that the adsorption can occur through the double $\text{C}=\text{C}$ bond or the F atom. Two proposed adsorbate-substrate structures have been investigated by periodic quantum-mechanical calculations at DFT/B3LYP level considering the rutile (110) surface. In the case of the adsorption by the F atom, also the formation of the H-bond has been considered. The interaction energy resulting from the adsorption through the double $\text{C}=\text{C}$ bond is smaller than that arising from the interaction by means the F atom and the H-bond. The shifts due to the adsorption of the calculated vibrational frequencies well reproduce the experimental data.

KEYWORDS

1-Bromo-1-fluoroethene; Adsorption; TiO_2 surface; Infrared spectra; Quantum-mechanical simulations.

MANUSCRIPT TEXT

Introduction

Halogenated ethenes are widely employed in the industrial field. However, as consequence of their possible toxicity, the removal of these compounds from the air should be desirable. Among the possible approaches, heterogeneous photocatalysis on TiO_2 is one of the most interesting solutions [1]. Since the compound is decomposed after its adsorption on the surface, an investigation on the nature of the adsorbate-substrate interaction can bring useful information for a detailed comprehension of the reaction mechanisms and then, for the development of successful applications. The orientation geometry, depending on several factors such as the surface and the molecular interacting sites, represents one of the most important aspects which has to be considered for this study. Among the possible techniques, infrared spectroscopy is one of the most suitable for providing information on the orientation geometry since the spectrum of the adsorbed molecule is expected to be different from that concerning the gas-phase.

The study of adsorption of some vinyl halides (CH_2CHX with $\text{X} = \text{F}, \text{Cl}$) at room temperature by IR spectroscopy was the subject of a previous work [2]: the obtained results led to the conclusion that the molecules interact with the surface by means of an acid-base interaction between the halogen atom and the surface Lewis acid site (Ti^{4+}) and of an H-bond between the CH_2 group and a surface Lewis basic site (O^{2-} or OH^-). According to this adsorbate-substrate model, periodic quantum-mechanical calculations were performed on the vinyl fluoride [3-4].

The aim of the current investigation is to formulate the adsorption model of the 1-bromo-1-fluoroethene (CH_2CBrF) on TiO_2 at room temperature through the analysis of the FTIR spectra of the adsorbed compound. Since a vibrational analysis in the gas phase of this molecule is not available in the literature, a preventive assignment of the fundamentals of the free CH_2CBrF molecule needed. The comparison between the isolated and adsorbed molecule has been done focusing the attention on the fundamentals above 1000 cm^{-1} and in particular on the bands related to the C-H, C=C and C-F stretching

1 modes. The approximate description of the vibrations of the adsorbate has been performed by
2 considering the absorptions of the compound in the gas phase.
3

4
5 A quantum-mechanical study based on a formulated model has been carried out for obtaining
6 information about the variations of the molecular structural parameters. The calculations have been
7 performed at DFT/B3LYP level by using the most stable surface of TiO_2 , i.e. the rutile (110) one [5],
8 which is then reasonably present at the experimental level.
9
10
11
12
13

14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60

Experimental details

The sample of CH_2CBrF , with a natural bromine isotopic composition, has been obtained commercially (purity $\sim 97\%$) from ABCR and has been employed without further purification.

The gas-phase infrared spectra have been recorded at room temperature in the range $200 - 4500 \text{ cm}^{-1}$ using the Bruker Vertex 70 ($400 - 4500 \text{ cm}^{-1}$) and the Nicolet Magna 750 ($200 - 600 \text{ cm}^{-1}$) FTIR spectrometers, at the resolution of 0.2 and 1.0 cm^{-1} , respectively. In the Far-range, the spectrum has been obtained using a 16.0 cm path cell equipped with KRS-5 windows and a sample pressure of about 760 Torr. In the region $400 - 4500 \text{ cm}^{-1}$, a 13.4 and a 16.0 cm path cells both equipped with KBr windows, have been employed; sample pressures was up to 75 Torr. The given band centre value are believed to have, for well resolved absorption features, an accuracy of $\pm 0.5 \text{ cm}^{-1}$ and $\pm 0.1 \text{ cm}^{-1}$ in the Far- and Mir-range, respectively.

TiO_2 powder (P25 Degussa) has been pressed in the form of self-supporting pellet ($\sim 20 \text{ mg} \cdot \text{cm}^{-2}$) which has been placed in a Pyrex cell equipped with CaF_2 windows. Before performing the adsorption experiments, it has been necessary to pre-treat the TiO_2 pellet in order to remove the impurities arising from the contact with the air. The pre-treatment consisted in heating the cell up to 450°C for 5 h under dynamic vacuum (10^{-4} Torr); successively, a mixture of N_2/O_2 ($15\% \text{ O}_2$) at a pressure of 100 Torr has been introduced into the cell and removed before cooling the cell to room temperature.

The infrared spectrum of TiO_2 obtained after the pre-treatment displays bands around 3000 cm^{-1} which are ascribed to residual surface OH groups [6-7]. According to a previous study, the pre-treated

TiO₂ surface contains two main Lewis acid sites involving two Ti⁴⁺ ions with different chemical surroundings and then, differing in the electrophilicity [2]. A possible difference between these two sites consists in the fact that the most electrophilic site is represented by a titanium ion which is tetra-coordinated, i.e. Ti(4f), while the less one is a penta-coordinated titanium ion, i.e. Ti(5f) [8].

The adsorption spectrum has been recorded after having introduced the gas into the cell. As consequence of the cut-off of TiO₂, the spectral region could be investigated down to the lower limit of $\sim 1000 \text{ cm}^{-1}$. All the spectra have been obtained with 20 scans at a resolution of 4 cm^{-1} employing the Bruker Vertex 70 FTIR spectrometer. The background was represented by the spectrum of TiO₂ obtained after the pre-treatment.

Computational details

The simulations have been carried out by using the periodic quantum-mechanical programs CRYSTAL03 and CRYSTAL06 [9-10]: the former has been used for the geometry optimisation while the latter for the vibrational frequencies determination. All the calculations have been performed at DFT level by adopting the hybrid B3LYP functional.

The titanium and oxygen atoms have been described by a basis set properly developed for the TiO₂ surface [11]: 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 CH₂CBrF molecule the standard 6-31G** contraction has been used [12-13].

The truncation thresholds for the Coulomb and exchange series have been set to 10^{-6} , 10^{-6} , 10^{-6} , 10^{-6} and 10^{-12} [9-10]; the Monkhorst-Pack shrinking factor has been placed equal to 4. A tolerance in the total energy of $1 \cdot 10^{-8}$ Hartree per unit cell has been adopted for the self consistent field procedure.

The geometry optimisation has been carried out by minimization of the total energy gradient calculated analytically with respect to the nuclear coordinates. The convergence has been determined from the root-mean-square (RMS) and the absolute value of the largest component of both nuclear displacements and gradients. The thresholds for the RMS and maximum atomic displacements have

been set to 0.00180 and 0.00120 a.u. while those for the forces to 0.00045 and 0.00030 a.u.. Geometry optimization has been terminated when all four conditions have been simultaneously satisfied [14-15].

The vibrational frequencies have been calculated from the dynamical matrix which has been obtained by numerical differentiation of the analytical gradient of the energy with respect to the atomic positions using a displacement of 0.001 Å in a two-point sampling [16-17].

Results and discussion

Gas-Phase spectrum

1-Bromo-1-fluoroethene is a planar molecule belonging to the C_s symmetry point group. The inertial a and b axes lie in the molecular plane and c axis is perpendicular to this plane. The molecule has 12 fundamental modes of which nine of A' symmetry (planar vibrations) and three of species A'' (out of plane modes). Thus, vibrations of A' species give rise to A-/B-hybrid bands, though one of the components might be predominant on the other, while A'' vibrations produce C-type band envelopes. A distinction between A-, B- and C-type bands is often possible on the basis of the rotational contour. A- and C-type bands exhibit a medium and strong Q-branch, respectively, while B-type bands present a depression at their centres. The fundamentals have been assigned considering the band contour characteristics, *ab initio* calculated anharmonic band centres and intensities. The quantum-mechanical calculations were carried out using the Gaussian 03 program suite [18] at the MP2/6-311++G(3d,2pd) level of theory and basis set. The wavenumbers of all the fundamentals resulting from the spectral analysis are listed in Table 1 together with their calculated values.

Adsorption spectra

The infrared spectra of CH_2CBrF adsorbed on TiO_2 surface at increasing pressures are shown in Fig. 1; the gas phase contributions have been subtracted out. For comparison, the low resolution IR spectrum of the compound in the gas phase is included in the same figure. According to the assignments

of the isolated molecule (Table 1), five fundamentals, corresponding to the CH_2 asymmetric stretching, the CH_2 symmetric stretching, the $\text{C}=\text{C}$ stretching, the CH_2 bending and the $\text{C}-\text{F}$ stretching modes, lie above 1000 cm^{-1} . Focusing on the adsorption spectra, five absorptions occurring at 3135, 3036, 1643, 1632 and 1348 cm^{-1} are observed in the IR region above 1200 cm^{-1} ; the spectrum below 1200 cm^{-1} shows two bands, each being splitted by about 10 cm^{-1} and thus resulting in four peaks at 1166, 1156, 1122 and 1112 cm^{-1} . The observed fundamental frequencies of CH_2CBrF adsorbed on TiO_2 are reported in Table 2. The two absorptions at around 3000 cm^{-1} and the weak one at about 1350 have been assigned to the two CH_2 stretchings and the CH_2 asymmetric in-plane wag vibrations, respectively; the two bands at around 1600 cm^{-1} have been attributed to the $\text{C}=\text{C}$ stretching mode while the four peaks below 1200 cm^{-1} have been assigned to the $\text{C}-\text{F}$ stretching vibration. The variation of the surface coverage results in a slight shift of the absorptions and then, it can be reasonably concluded that the reported adsorption spectra refer to a situation of low coverage. For completeness, the shift with respect to the frequencies of gaseous CH_2CBrF are reported in the same table.

Basing on the observed features it can be inferred that, concerning the CH_2 group, the behaviour of the present compound is to some extent similar to that of the vinyl fluoride [2]: in fact, the red-shift observed for the two CH_2 stretching modes lead to suppose the formation of an H-bond between the CH_2 group and a surface Lewis acid site. However, the spectrum of CH_2CBrF noticeable differs from that of CH_2CHF for the presence of two bands associated with the $\text{C}=\text{C}$ stretching and four peaks concerning the $\text{C}-\text{F}$ stretching absorption. Focusing on the spectral behaviour of the ν_3 and ν_5 vibrations (see Table 2), it can be proposed that the CH_2CBrF molecule adsorbs on the TiO_2 surface according to two different adsorbate-substrate structures which are depicted in Fig. 2: the surface Lewis acid site can interact by the double $\text{C}=\text{C}$ bond (**I**) or by the F atom (**II**). The former structure (**I**) should be associated to the absorptions of the $\text{C}=\text{C}$ stretching (ν_3) at 1632 cm^{-1} and of the $\text{C}-\text{F}$ stretching (ν_5) at 1166 and 1156 cm^{-1} while the latter one (**II**) should produce the absorptions at 1643 cm^{-1} ($\text{C}=\text{C}$ stretching) and 1122, 1112 cm^{-1} ($\text{C}-\text{F}$ stretching). The splitting of the two bands associated with the $\text{C}-\text{F}$ stretching vibration can be explained by considering the presence of the two distinct surface Lewis acid sites. It can

be noticed that, as for the CH_2CHF molecule, it is possible to consider the existence of two different Lewis acid sites only for the absorption associated to the C-F stretching: the splitting for the other vibrations could not be detected and this is probably due to the small frequency separation between the two involved absorptions. Again, a possible explanation for which only one absorption for the modes involving the CH_2 group is detected can be due to a very low intensity of the bands associated to one of the two adsorbate-substrate structures: however, a further increase of the pressure does not lead to additional absorptions.

It is important to notice that the two adsorbate-substrate structures can involve the same kind of surface Lewis acid site: this means that the two possible adsorption modes can occur either on the most electrophilic site or on the less electrophilic one.

Quantum-mechanical calculations

The calculations have been performed according to the two models depicted in Fig. 2. The rutile (110) surface has been cut from the bulk whose parameters have been previously optimized [19]. As it is illustrated in Fig. 3a, the surface is constituted by sixfold and fivefold coordinated titanium ions, labelled Ti(6f) and Ti(5f) and by threefold and twofold coordinated oxygen ions, labelled as O(3f) and O(2f). The Ti(5f) and O(2f) ions represent the surface Lewis acid and basic site, respectively. According to the coordination number, the Ti(5f) ion should represent the less electrophilic site of the TiO_2 surface adopted at the experimental level. A 6-atomic layers slab has been used for simulating the surface; the lateral effect arising from the interaction between the neighbouring adsorbed molecule have been limited choosing a (2 x 1) periodicity, corresponding to a surface coverage equal to 0.5.

Before obtaining the adsorbate-substrate system, the isolated CH_2CBrF molecule has been optimized and then, positioned on the relaxed surface with the double C=C bond or the F atom above one of the Ti(5f) represented in Fig. 3a: as it can be seen, also an H-bond between the CH_2 group and the O(2f) has been taken into account in the case of the adsorption by means the F atom. The full optimization of the system has been carried out by relaxing all the atoms of the system.

Table 3 reports the main structural parameters of the $\text{CH}_2\text{CBrF}/\text{TiO}_2$ system. The interaction of the molecule by means of the double $\text{C}=\text{C}$ bonds (Fig. 3b) results in the following molecular structural variations:

- the $\text{C}_1=\text{C}_2$, $\text{C}_2\text{-H}_1$, $\text{C}_2\text{-H}_2$ bond lengths and the $\text{Br-C}_1\text{-C}_2$ bond angle increase;
- the $\text{C}_1\text{-Br}$, $\text{C}_1\text{-F}$ bond lengths and the $\text{F-C}_1\text{-C}_2$, $\text{H}_1\text{-C}_2\text{-C}_1$, $\text{H}_2\text{-C}_2\text{-C}_1$ bond angles decrease.

As consequence of the adsorption through the F atom (Fig. 3c) the molecular structural parameters change as it follows:

- the $\text{C}_1\text{-F}$, $\text{C}_2\text{-H}_2$ bond lengths and the $\text{Br-C}_1\text{-C}_2$, $\text{H}_2\text{-C}_2\text{-C}_1$ bond angle increase;
- the $\text{C}_1=\text{C}_2$, $\text{C}_1\text{-Br}$ bond length and the $\text{F-C}_1\text{-C}_2$, $\text{H}_1\text{-C}_2\text{-C}_1$ bond angles decrease;
- the $\text{C}_2\text{-H}_1$ bond length does not change;

Focusing on the structure resulting from the interaction by means the double $\text{C}=\text{C}$ bond (**I**), it is interesting to notice that the $\text{C}_1\text{-Ti}$ distance is longer than the $\text{C}_2\text{-Ti}$ one; this can be easily explained by considering that the C_1 atom has a partially negative charge smaller than that of the C_2 atom and then, it interacts with the $\text{Ti}(5f)$ ion in a weaker manner.

Concerning the interaction energy (E_{int}), the value associated with the adsorption through the double $\text{C}=\text{C}$ bond is smaller than that associated to the interaction by means the F atom and the H-bond.

The calculated vibrational frequencies of the free and adsorbed CH_2CBrF along with an approximate description of the corresponding eigenvectors are reported in Table 4. The values have been scaled by using a scaling factor equal to 0.961 [20]. The frequencies of the adsorbed molecule have been placed in correspondence of those of the isolated molecule on the basis of the eigenvectors of the normal modes.

Considering the vibrations occurring below 1000 cm^{-1} , it can be seen that the adsorption through the double $\text{C}=\text{C}$ bond (structure **I**) gives rise to a blue-shift of the CFBr out-of-plane wag mode, while no significant differences are observed for the other vibrations. For the interaction by means the F atom (structure **II**) the largest variations consist in a large red-shift of the CH_2 planar rock, the CFBr out-of-plane wag vibrations and in a consistent blue-shift of all the other modes. However, the attention is focused mainly on the vibrations lying above 1000 cm^{-1} since their behaviour can be compared with the

experimental one. The adsorption through the double C=C bond (I) gives rise to a consistent red-shift of the C=C stretching and the CH₂ asymmetric in-plane wag modes, while the other vibrations change in a negligible way. The interaction by means the F atom (II) results in a large red-shift of the C-F stretching mode and of both the two CH₂ stretchings vibrations.

It is important to notice that the predicted shifts are in agreement with those observed from the experimental point of view. In particular, they are able to well reproduce the behaviour of the ν_3 and ν_5 modes: in fact, the vibrations connected to the molecular basic site interacting with the surface Lewis acid site (i.e. the double C=C bond or the F atom) are associated to a large red-shift of about 26 cm⁻¹ for the C=C stretching (ν_3) and of about 33 cm⁻¹ for the C-F stretching (ν_5). In addition, as it has been observed at the experimental level, the ν_5 and ν_3 result slightly affected when the interaction occurs through the double C=C bond or the F atom, respectively. According to the estimated vibrational frequencies of the modes associated to the CH₂ group, it can be inferred that the observed absorptions assigned to the ν_1 and ν_2 behave as the corresponding vibrations associated to the model in which the adsorption occurs through the F atom (II). In conclusion, basing on the calculated frequencies, it is possible to conclude that the two structures, which have been investigated by the calculations, are in agreement with those formulated at the experimental level. Moreover, an investigation on all the possible adsorption geometries has indicated that the two structures reported in the current work are the only ones which both are possible from the energetic point of view and give rise to calculated frequencies comparable with those experimentally observed.

Conclusions

The current work concerns the first infrared study of 1-bromo-1-fluoroethene (CH₂CBrF) both in gas phase and adsorbed on TiO₂ surface at room temperature. According to the observed shifts of the C=C and C-F stretching vibrations, it can be inferred that the investigated molecule can adsorb on the surface Lewis acid site (Ti⁴⁺) through the double C=C bond or by means the F atom. Moreover, the observed red-shifts of the two CH₂ stretchings suggest the presence of an H-bond between the CH₂ group and a

surface Lewis basic site (OH^- or O^{2-}). In order to achieve information about the variations occurring inside the molecule as consequence of the adsorption, the two adsorbate-substrate structures have been investigated by using periodic quantum-mechanical calculations at DFT/B3LYP level and the most stable surface of TiO_2 , i.e. the rutile (110). The interaction through the double $\text{C}=\text{C}$ bond results in an increase and a decrease of the $\text{C}=\text{C}$ and $\text{C}-\text{F}$ bond lengths, respectively, while an opposite behaviour for the two bonds occurs for the interaction by means the F atom. The $\text{C}-\text{Br}$ bond length decreases in both cases. The interaction energy arising from the adsorption through the double $\text{C}=\text{C}$ bond is smaller than that resulting from the interaction by the F atom and the H-bond. The shifts of the calculated vibrational frequencies associated to the adsorption have been found in good agreement with the experimental data.

Spectroscopic investigations on the adsorption of pollutants on photocatalytic surfaces can provide useful information for the comprehension of the adsorbate-substrate structure and for a better understanding of the photocatalytic degradation mechanisms.

ACKNOWLEDGMENT

Financial support by PRIN 2007 funds (project: "Trasferimenti di energia, carica e molecole in sistemi complessi") is gratefully acknowledged.

REFERENCES

- [1] A. L. Linsebigler, G. Lu and J. T. Yates Jr., *Chem. Rev.* **95**, 735 (1995).
- [2] J. Scaranto, A. Pietropolli Charmet, P. Stoppa and S. Giorgianni, *J. Mol. Struct.* **741**, 213 (2005).
- [3] J. Scaranto, G. Mallia, S. Giorgianni, C. M. Zicovich-Wilson, B. Civalieri and N. M. Harrison, *Surf. Sci.* **600**, 305 (2006).

- [4] J. Scaranto and S. Giorgianni, *J. Phys. Chem. C* **111**, 11039 (2007).
- [5] U. Diebold, *Surf. Sci. Rep.* **48**, 53-229 (2003).
- [6] M. Primet, P. Pichat, and M.-V. Mathieu, *J. Phys. Chem.* **75**, 1216 (1971).
- [7] K. E. Lewis, and G. D. Parfitt, *Trans. Faraday Soc.* **62**, 204 (1966).
- [8] K. I. Hadjiivanov, and D. G. Klissurski, *Chem. Soc. Rev.* **25**, 61 (1996) and references therein.
- [9] V. R. Saunders, R. Dovesi, C. Roetti, R. Orlando, C. M. Zicovich-Wilson N. M. Harrison, K. Doll, B. Civalleri, I. J. Bush, P. D'Arco, and M. Llunell, *CRYSTAL03 User's Manual*, University of Torino (2003).
- [10] R. Dovesi, V. R. Saunders, C. Roetti, R. Orlando, C. M. Zicovich-Wilson F. Pascale, B. Civalleri, K. Doll, N. M. Harrison, I. J. Bush, P. D'Arco, and M. Llunell, *CRYSTAL06 User's Manual*, University of Torino (2006).
- [11] J. Muscat, Ph. D. Thesis, University of Manchester (1999).
- [12] P. C. Hariharan, and J. A. Pople, *Theoret. Chim. Acta* **28**, 213 (1973).
- [13] V. A. Rassolov, M. A. Ratner, J. A. Pople, P. C. Redfern, and L. A. Curtiss, *J. Comput. Chem.* **22**, 976 (2001).
- [14] K. Doll, V. R. Saunders and N. M. Harrison, *Int. J. Quantum Chem.* **82**, 1 (2001).
- [15] B. Civalleri, P. D'Arco, R. Orlando, V. C. Saunders and R. Dovesi, *Chem. Phys. Lett.* **348**, 131 (2001).
- [16] F. Pascale, C. M. Zicovich-Wilson, F. Lopez, B. Civalleri, R. Orlando and R. Dovesi, *R. J. Comput. Chem.* **25**, 888 (2004).

- [17] C. M. Zicovich-Wilson, F. Pascale, C. Roetti, V. C. Saunders, R. Orlando, and R. Dovesi, J. Comput. Chem. **25**, 1873 (2004).
- [18] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian 03, Revision A.1, Gaussian, Inc., Pittsburgh PA (2003).
- [19] J. Scaranto, Ph. D. thesis, University of Venice (2006).
(Available from the web site <http://venus.unive.it/molspectragroup/LowResolutionTiO2/TiO.htm>)
- [20] <http://srdata.nist.gov/cccbdb/vibscalejust.asp>.
- [21] A. Kokaly, J. Mol. Graphics Modelling **17**, 176 (1999).

Table 1. Fundamental frequencies (cm^{-1}) of isolated CH_2CBrF .

Band	Symmetry Species	Observed Envelope	Relative intensities ^a	Approx. description	Experimental wavenumber ^b	Calculated wavenumber ^c
ν_1	A'	B	vw	CH_2 asym. stretch	3154.2 ± 0.5	3209.3
ν_2	A'	B / A	w	CH_2 sym. stretch	3068.8	3101.7
ν_3	A'	B / A	vs	C=C stretch	1647.3	1602.0
ν_4	A'	A / B	vw	CH_2 asym. in-plane wag	1368.6	1372.4
ν_5	A'	A / B	vs	C-F stretch	1168.6	1151.8
ν_6	A'	A / B	s	CH_2 planar rock	946.4	932.9
ν_7	A'	A / B	s	C-Br stretch	617.9^d 617.3^e	622.4
ν_8	A'	A / B	vw	CFBr bend	364.0 ± 0.5^d 362.6 ± 0.5^e	367.5
ν_9	A'	A / B	vw	CCBr bend	321.1 ± 0.5	326.8
ν_{10}	A''	C	s	CH_2 out-of-plane wag	838.9	830.4
ν_{11}	A''	C	vw	C=C torsion	707.8	716.6
ν_{12}	A''	C	w	CFBr out-of-plane wag	476.2	481.8

a: abbreviations used are as follows: vs = very strong, s = strong, w = weak, vw = very weak.

b: the experimental error is $\pm 0.1 \text{ cm}^{-1}$ unless otherwise quoted.

c: calculated using Gaussian 03 program [18] at the MP2/6-311++G(3d,2pd) level of theory and basis set.

d: $\text{CH}_2\text{C}^{79}\text{BrF}$.

e: $\text{CH}_2\text{C}^{81}\text{BrF}$.

Table 2. Fundamental frequencies (cm⁻¹) of CH₂CBrF adsorbed on TiO₂ at room temperature.

CH ₂ CBrF/TiO ₂ ^a		
Band	Approx. description	Wavenumber
ν ₁	CH ₂ asym. stretch	3135 (-19)
ν ₂	CH ₂ sym. stretch	3036 (-33)
ν ₃	C=C stretch	1643 (-4)
		1632 (-15)
ν ₄	CH ₂ asym. in-plane wag	1348 (-21)
ν ₅	C-F stretch	[1166 (-3), 1156 (-13)] ^b
		[1122 (-47), 1112 (-57)] ^b

a: the shift with respect to the compound in gas phase is given in parenthesis (see Table 1).

b: the two frequencies refer to the presence of two surface Lewis acid sites.

Table 3. Optimized structural parameters for the free and adsorbed CH₂CBrF.

	Free	Adsorbed ^a			
		Structure I	%	Structure II	%
C ₁ -C ₂	1.325	1.330	0.4	1.320	-0.4
C ₁ -Br	1.906	1.900	-0.3	1.895	-0.6
C ₁ -F	1.332	1.331	-0.1	1.362	2.3
C ₂ -H ₁	1.081	1.082	0.1	1.081	0.0
C ₂ -H ₂	1.084	1.085	0.1	1.087	0.3
Br-C ₁ -C ₂	125.0	125.1	0.1	126.3	1.0
F-C ₁ -C ₂	123.3	123.1	-0.2	122.4	-0.7
H ₁ -C ₂ -C ₁	121.2	120.5	-0.6	119.4	-1.5
H ₂ -C ₂ -C ₁	119.1	118.5	-0.5	120.0	0.8
C ₁ -Ti		3.857			
C ₂ -Ti		3.290			
F-Ti				2.583	
H ₂ -O				2.058	
Ti-C ₁ -C ₂		55.4			
Ti-C ₂ -C ₁		105.1			
Ti-F-C ₁				157.5	
O-H ₂ -C ₂				163.0	
E _{int}		-12.80		-29.91	

Lengths and angles are reported in Å and degrees, respectively. The interaction energy (E_{int}) is given in kJ·mol⁻¹.

a: % refers to the isolated optimized molecule (Free); structures **I** and **II** refer to the adsorption through the double C=C bond and the F atom, respectively (see also text).

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

Table 4. Calculated vibrational frequencies (cm^{-1}) of the free and adsorbed CH_2CBrF .

Free			Adsorbed ^a	
			Structure I	Structure II
Band	Approx. description	Wavenumber	Wavenumber	Wavenumber
ν_1	CH_2 asym. stretch	3175	3177 (+2)	3152 (-23)
ν_2	CH_2 sym. stretch	3077	3072(-5)	3034 (-43)
ν_3	$\text{C}=\text{C}$ stretch	1660	1634 (-26)	1657 (-3)
ν_4	CH_2 asym. in-plane wag	1364	1355 (-9)	1365 (+1)
ν_5	$\text{C}-\text{F}$ stretch	1147	1142 (-5)	1114 (-33)
ν_6	CH_2 planar rock	934	936 (+2)	911 (-23)
ν_7	$\text{C}-\text{Br}$ stretch	581	584 (+3)	591 (+10)
ν_8	CFBr bend	346	349 (+3)	361 (+15)
ν_9	CCBr bend	310	313 (+3)	325 (+15)
ν_{10}	CH_2 out-of-plane wag	824	826 (+2)	908 (+84)
ν_{11}	$\text{C}=\text{C}$ torsion	693	699 (+6)	730 (+37)
ν_{12}	CFBr out-of-plane wag	473	486 (+13)	456 (-17)

a: Structures **I** and **II** refer to the adsorption through the double $\text{C}=\text{C}$ bond and the F atom, respectively (see also text). For clearness, the shift with respect to the free compound is given in parenthesis.

FIGURE CAPTIONS

Figure 1. Low-resolution IR spectra of CH_2CBrF in gas-phase (a) and adsorbed on TiO_2 (b-c). (a) Room temperature, $P \sim 1.0$ Torr, 16 cm cell; the spectrum in the region $3800\text{--}2850\text{ cm}^{-1}$ has been multiplied by a factor of 10. Infrared spectrum of TiO_2 taken after being in contact with ~ 0.6 (b) and ~ 1.2 (c) Torr of CH_2CBrF at room temperature.

Figure 2. Representation of the two formulated models of CH_2CBrF adsorbed on TiO_2 surface at room temperature. (I) and (II) correspond to the adsorption through the double $\text{C}=\text{C}$ bond and the F atom, respectively. The two types of interaction can occur on the same kind of surface Lewis acid site. Bonds between CH_2CBrF and TiO_2 are represented by dashed lines. LB in Structure (II) indicates surface Lewis basic site (O^{2-} or OH^-).

Figure 3. (a) Model of the rutile (110) surface and the CH_2CBrF molecule: Ti(5f) and Ti(6f) correspond to fivefold and sixfold coordinated titanium ions while O(2f) and O(3f) indicate twofold and threefold coordinated oxygen ions. (b) Model of the $\text{CH}_2\text{CBrF}/\text{TiO}_2$ system resulting from the interaction by means the double $\text{C}=\text{C}$ bond. (c) Model of the $\text{CH}_2\text{CBrF}/\text{TiO}_2$ system obtained from the adsorption through the F atom. In (b) and (c) only the outermost surface ions are depicted; the dashed lines represent the bonds between CH_2CBrF and TiO_2 . (a), (b) and (c) have been obtained by using the XCRYSDEN program [21].

Figure 1.

Figure 2.

Figure 3.

(b)

(c)