CCl_4 dissociation on ice-Ih surface: An excess electron mediated process

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Abstract

Dissociation of chlorofluorocarbons in the atmosphere is a heterogeneous process that takes place mainly on the surface of ice particles. Recently an enhancement of the dissociation rate due to excess electrons has been shown theoretically and correspondingly measured experimentally. Our density functional theory calculations show that CCl_4 dissociates due to an excess electron with an energy gain of 0.8 eV on the ice surface as opposed to in the gas phase. Through the use of *ab-initio* molecular dynamics, an atomistic pathway for this dissociation has been elucidated, this pathway shows the capture of Cl^- by the ice surface through a partial solvation mechanism, in agreement with recent experimental findings.

Chlorofluorocarbons (CFCs), such as tetrachloro- (CCl_4) and dichloroflouro- (CF_2Cl_2) methane, are known to play a key role in the depletion of the ozone layer[1]. It has been shown that the photo-dissociation of CFCs, in gas phase[2] or supported by ice particles[3], is the main reaction pathway for the formation of active chlorine atoms which participate in the ClO_x catalytic cycle depleting the ozone layer in the Antarctic spring[3,4]. Extensive theoretical and experimental studies have been undertaken to elucidate the reaction pathways from an atomistic view point and to explain the appearance of the ozone hole during specific times of the year and within well defined geographical regions. It has been proposed that the dissociation could be catalysed by the presence of excess electrons (EE) left by galactic cosmic rays and trapped at the surface of ice particles in the polar stratospheric clouds[5–7]. Although the role of cosmic rays on ozone depletion has been the subject of a strong debate[8–11], several experiments have revealed that the dissociation of the CFCs induced by electron attachment is enhanced when it occurs on the ice surface, with respect to the gas phase[5,7,12]. Most CFCs, including CCl_4, undergo dissociative attachment of low energy electrons in the gas phase, so it has been argued that the enhancement of the dissociation rate on ice may be related to a partial or complete localisation of the EE at its surface[5].

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Ice is a large gap insulator with a negative electron affinity[13]. Penetration and stabilisation of EE in the bulk requires large molecular rearrangements, presumably similar to those required to solvate EE in bulk water. It has been shown that a competing stabilisation mechanism for the EE in pure ice is self-trapping at the surface[14]. Recent experiments and theoretical calculations have shown that surface trapping takes place through a rearrangement of the uppermost molecular layers or at pre-existing defects[15]. The goal of this paper is to investigate theoretically the mechanism that leads to the enhancement of the dissociation rate of CCl_4 in the presence of EE localised on the surface of ice.

Theoretical efforts to understand the role of EE on the dissociation of CFCs in water systems have been restricted to the study of CFCs with small water clusters[16]. To the best of our knowledge this work is reportedly the first *ab-initio* calculation describing the dissociation of CCl_4 on an ice surface in the presence of an EE. We show that dissociative electron attachment is energetically more favoured on the ice surface than in the gas phase, and that the Cl^- product remains bound to the ice surface. Our theoretical calculations agree with experimental findings and provide an atomistic pathway for the dissociation.

We perform density functional theory based molecular dynamics (MD) using the Car-Parrinello method as implemented in the Quantum Espresso package[17]. The electrons were attributed a fictitious mass of 200 a.u. and the Brillouin zone sampling was restricted to the Γ-point only. A time step of 6 a.u. was used to integrate the equations of motion. The valence electron-nuclei interactions were described by Troullier-Martins pseudopotentials. The electronic states were expanded in a plane wave basis set with an energy cutoff of 80 Ryd. The Becke-Lee-Yang-Parr (BLYP) exchange correlation functional was used, as it has been adopted for water systems in most previous works[18]. Calculations with an EE were carried out with the self-interaction correction (SIC)[14]. Based on the recent work of VandeVondele and Sprik[19] we used a modified version of the original SIC scheme[20] whereby the self interaction is only partially screened. For the correction of Hartree and exchange-correlation terms, respectively, we use the suggested[19] parameters $\alpha = 0.2$ and $\beta = 0.0$. Since periodic boundary conditions were applied, the electron affinities (EAs) were corrected for the Madelung contribution of the corresponding cell.slab 'A' contains four bilayers and eight molecules in each bilayer, and slab 'B' contains three bilayers and 32 molecules in each bilayer. Slab 'A' and 'B' corresponds to (2×2) and (4×4) surface cells of the ideal ice-Ih(0001) surface. Ice slabs were separated by a 20 Å vacuum layer. One of the slab surfaces was terminated with a full bilayer along with an 'ideal' (2×1) periodicity and the other surface was reconstructed in order to accommodate the EE in a long-lived surface state[14,15]. The CCl_4 molecule was deposited on the reconstructed surfaces. During the dynamics, the 'O' atoms of the ideal surface, the bottom layer of our slabs, were kept fixed and all other atoms were allowed to move.

We begin our discussion with the EE induced dissociation of the CCl_4 molecule in gas phase. The simulation was performed with a periodic box of size 20 Å which we find to be sufficient to achieve the energy convergence. The remaining simulation parameters are the same as used for surface calculations. Our calculated vertical and adiabatic electron affinities (VEA and AEA, respectively) and dissociation energy (DE) compare well with experiments as reported in Table 1. Both self-interaction corrected and uncorrected results predict a positive VEA in agreement with the experiments, but the SIC result describes the AEA and DE better. In order to determine the AEA, we first perform a MD run of the CCl_4^- ion starting from the atomic coordinates of the relaxed neutral molecule. The dynamics lead to spontaneous dissociation through the

Table 1: Electron affinities (vertical, VEA, and adiabatic, AEA) and dissociation energy (DE) of CCl_4 during the cleavage pathway in eV with SIC-BLYP. Local-spin-density (LSDA-BLYP, this work), B3LYP and experimental values are also reported for comparison.

Method	VEA	AEA	DE
SIC-BLYP	1.14	2.54	1.40
LSDA-BLYP	0.41	1.15	0.74
B3LYP[21]	0.48	1.5	
Exp.	> 0[22]	$\sim$2.0[23]	1.4[23]

stretching of a C-Cl bond and the formation of $CCl_3^\bullet$ and Cl^-, in agreement with the results of simulations on small water clusters[16]. Minimisation of the atomic coordinates along the MD trajectory at fixed C-Cl distances shows an energetic minima at a C-Cl distance of 3.5 Å. The AEA was calculated as the difference between the energy of this configuration and that of the neutral CCl_4 molecule.

We now consider the EE induced dissociation of CCl_4 on the ice surface. A CCl_4 molecule was added on top of the reconstructed surface. The surface along with the CCl_4 molecule was relaxed. Slab 'A' and 'B' gave similar results. For the neutral case, the equilibrium distance between the CCl_4 molecule and the surface was found to be 3.3Å and the binding energy was observed to be less than 0.1 eV. We calculated the dissociation energy by elongating a C-Cl bond, removing the CCl_3 molecule and leaving one Cl on the surface, and found it to be > 3 eV. Thus, in the neutral case, CCl_4 dissociation on the surface of ice is a highly endothermic process, as in the gas phase, even in the presence of surface defects. For the relaxed configuration found in the neutral case, an EE was added to the system. The EE was found to localise on the CCl_4 as shown in the panel (a) of Fig.1. We evolve the system with time, using MD. The CCl_4 molecule dissociated spontaneously into the $CCl_3^\bullet$ radical and a Cl^- anions in less than 0.1 ps.

After about 0.3 ps, the Cl^- ion forms two additional bonds to the surface, and the $CCl_3^\bullet$ radical moves away into the vacuum region. A rearrangement of the dangling hydrogen atoms surrounding the defect occurs in order to accommodate the Cl^- over the centre of the hexagonal ice surface ring (see Fig. 1). Three hydrogen bonds are formed between the surrounding dangling hydrogen atoms and the Cl^- ion, with bond distances of between 2.0 - 2.8 Å. The -1 charge state of chlorine, Cl^-, is confirmed by calculating the spin density difference, defined as $\rho_{SDD} = \rho_\uparrow - \rho_\downarrow$, where $\rho_\uparrow$ and $\rho_\downarrow$ are the spin up and spin down charge densities, respectively. The location of the unpaired electron as depicted by the peak in ρ_{SDD} , is spatially localised around the carbon atom of the $CCl_3^\bullet$ molecule, as shown in Fig.1 (b). Thus, the CCl_4 dissociation causes the chlorine atom left on ice surface to capture an extra electron and so becomes negatively charged, while the $CCl_3^\bullet$ remains neutral. The dissociation process is accompanied by an energetic release of 2.0 eV for slab 'A' and 2.15 eV for slab 'B', with a net energy gain of 0.7-0.9 eV with respect to the energy released in the gas phase dissociation of CCl_4^-. We attribute the difference in the energy gain between the two slabs to the fact that the Cl^- forms two hydrogen bonds on slab 'A' and three bonds on slab 'B'. Additionally, slab 'A' undergoes substantial reconstruction to accommodate the Cl^- ion. On the other hand, the reconstruction of slab 'B' is almost negligible and there are

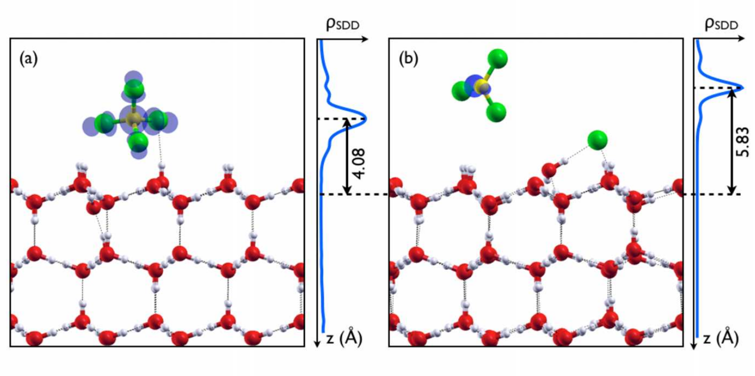

Figure 1: Spin density difference of the unpaired electron, shaded area, for the reconstructed (4x4) ice surface with CCl_4 (a) before and (b) after the dissociation. In-plane spin density difference, ρ_{SDD} in arbitrary units, is plotted versus the distance from the surface in both cases. The bottom dashed line refers to the mid distance between oxygen in the outermost bilayer. After the dissociation ρ_{SDD} is peaked on the carbon atom of the $CCl_3^\bullet$ radical. Oxygen atoms are in red, hydrogen in white, carbon in yellow, chlorine in green while H-bonds are represented by dashed black lines.

small changes around the defect. In fact, this existing defect, which acts as a trap for the EE providing an extra floating H-bond, as visible in Fig.1 (a), is easily attracting one chlorine atom on top of the hexagonal oxygen ring with three free OH groups.

Although subsequent solvation of Cl^- may occur at longer time scales, our calculations provide an atomistic pathway for the early stages of the dissociation that clearly shows the formation of Cl^- species on the surface.

The presence of Cl^- on the surface of ice as a product of the EE induced dissociation of CCl_4 is consistent with the experimental evidence. Using a variety of surface science techniques, Faradzhev *et al.*[24] proposed that the first step of the reaction pathway in the EE stimulated reaction of CFCs on ice surface is the formation of Cl^- which remains bound to the surface. Similar conclusions were reached earlier on by Lu and Sanche[25], who were however unable to distinguish conclusively between different negatively charged species. Our results confirm the findings of Faradzhev *et al.*[24] and provide a detailed atomistic picture of the Cl^- solvation mechanism, in agreement with experimental suggestions.

The presence of Cl^- on the surface was also hypothesised by Bertin *et al.*[12] in their time resolved photoemission experiments. The detection was based on the measured increase of the work function, ϕ, of the ice surface after CCl_4 exposure in the presence of photo-generated electrons. An increase of the work function is expected upon formation of negative species[26]. Here we confirm that the negative species resulting from the EE induced dissociation is Cl^-. Moreover, we provide a simple model to explain the strength of the work function change in the experimental observation[12]. The model is based on the formation of a dipole layer between the anion at the surface and their images in the metal substrate. In this model, the change in ϕ, denoted by $\Delta\phi$ is given by :

$$\Delta\phi = -\frac{4\pi d N q}{\varepsilon_{ice}} \tag{1}$$

where d is the thickness of the ice slab, q the charge of the species, ε_{ice} is the dielectric constant of ice and N is the surface density of the charged species. In their experiment, Bertin *et al.*[12] considered a surface of thickness of 4.5 bilayers ($d \sim 20$Å), a surface density of 2.3×10^{12} cm^{-2} (corresponding to CCl_4 coverage of 0.004 monolayers). Considering q = -1 and ε_{ice} = 4 we obtain for $\Delta\phi$ a value of 210 meV which is very close to the experimental value of $\Delta\phi$ = 250 meV.

In summary our results, together with recent experimental evidence, confirm the original proposal of Sanche *et al.* that EE enhance the dissociation rate of CFCs on ice. The atomistic picture of the process that emerges from the simulations clearly indicates the role played by the presence of surface trapped states for the EE[14,15]. The energy gain in the dissociation of the CCl_4 on the ice surface shows the surface is capable of stabilising the charged products through their partial solvation. Our simulations also indicate that CCl_3 is the main product of the first step of the electron stimulated reactions of CFCs on ice surface.

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References

[1] P. Martinerie, E. Nourtier-Mazauric, J. M. Barnola, W. T. Sturges, D. R. Worton, E. Atlas, L. K. Gohar, K. P. Shine and G. P. Brasseur, *Atmospheric Chemistry and Physics*, 2009, **9**, 3911–3934.

[2] M. Molina, L. Molina and C. Kolb, *Annual Review of Physical Chemistry*, 1996, **47**, 327.

[3] S. Solomon, *Reviews of Geophysics*, 1999, **37**, 275.

[4] M. J. Molina and F. S. Rowland, *Nature*, 1974, **249**, 810.

[5] Q. B. Lu and T. E. Madey, *Phys. Rev. Lett.*, 1999, **82**, 4122.

[6] Q.-B. Lu, *J. Chem. Phys.*, 1999, **111**, 2861.

[7] Q.-B. Lu and T. E. Madey, *J. Phys. Chem. B*, 2001, **105**, 2779.

[8] R. Muller and J.-U. Grooss, *Phys. Rev. Lett.*, 2009, **103**, 228501.

[9] S.-B. Lu, *Phys. Rev. Lett.*, 2009, **102**, 118501.

[10] P. Patra and M. Santhanam, *Phys. Rev. Lett.*, 2002, **89**, 219803.

[11] Q.-B. Lu and L. Sanche, *Phys. Rev. Lett.*, 2001, **87**, 078501.

[12] M. Bertin, M. Meyer, J. Stahler, C. Gahl, M. Wolf and U. Bovensiepen, *Faraday Disc.*, 2009, **141**, 293.

[13] V. Petrenko and I. Ryzhkin, *Phys. Rev. Lett.*, 1993, **71**, 2626.

[14] F. Baletto, C. Cavazzoni and S. Scandolo, *Phys. Rev. Lett.*, 2005, **95**, 176801.

[15] U. Bovensiepen, J. Stahler, M. Bockstedte, F. Baletto, X. Y. Zhu, S. Scandolo, A. Rubio and M. Wolf, *J. Phys. Chem. C*, 2009, **113**, 979.

[16] H. Tachikawa and S. Abe, *JCP*, 2007, **126**, 194310.

[17] P. Giannozzi and et al., *Journal of Physics-Condensed Matter*, 2009, **21**, 395502.

[18] M. Boero, M. Parrinello, K. Terakura, T. Ikeshoji and C. C. Liew, *Phys. Rev. Lett.*, 2003, **90**, 226403.

[19] J. VandeVondele and M. Sprik, *Phys. Chem. Chem. Phys.*, 2005, **7**, 1363.

[20] M. D'Avezac, M. Calandra and F. Mauri, *Phys. Rev. B*, 2005, **71**, 205201.

[21] N. Zhang, P. Bowlers and J. Farrell, *Env. Sci. Tech.*, 2005, **39**, 612.

[22] P. D. Burrow, A. Modelh, N. S. Chiu and K. D. Jordan, *Chem. Phys. Lett.*, 1981, **82**, 270.

[23] K. Lacmann, M. J. P. Maniera, A. M. Moutinho and U. Weigmann, *J. Chem. Phys.*, 1983, **78**, 1767.

[24] N. S. Faradzhev, C. C. Perry, D. O. Kusmierek and T. E. Madey, *J. Chem. Phys.*, 2004, **121**, 8547.

[25] Q. B. Lu and L. Sanche, *Phys. Rev. B*, 2001, **63**, 153403.

[26] A. Zangwill, *Physics at Surfaces,*, 1988, **Cambridge Univ. Press**, Cambridge.