Cl2p, O1s PSD-NEXAFS study of the adsorption of HCl on ice: A direct experimental evidence of the HCl ionization

5 AUTHORS, INCLUDING:

P. Parent

French National Centre for Scientific R...

119 PUBLICATIONS **1,261** CITATIONS

Cl2p, O1s PSD–NEXAFS study of the adsorption of HCl on ice: a direct experimental evidence of the HCl ionization

F. Bournel [a], C. Mangeney [a], M. Tronc [a], C. Laffon [b], Ph. Parent [b,*]

[a] *Laboratoire Chimie Physique, Université P. et M. Curie, et CNRS UMR 7614, 11 rue Pierre et Marie Curie, 75231 Paris Cedex 05, France*
[b] *LURE, Bât. 209d, B.P. 34, Université Paris-Sud, F-91898 Orsay Cedex, France*

Abstract

We have used NEXAFS and photo-stimulated desorption (PSD)–NEXAFS spectroscopy at the O1s and at the Cl2p edges to study H_2O and HCl ices, as well as the adsorption of HCl on water ice. The PSD–NEXAFS provides a clear fingerprint of the dangling OH bond at the water ice surface. We evidence the H–Cl fragmentation at the $2p \rightarrow \sigma^*(H–Cl)$ excitation of condensed HCl. Last, we directly observe the ionization of HCl when adsorbed on H_2O ice, both at the surface and after diffusion in the bulk of ice.
© 2002 Published by Elsevier Science B.V.

Keywords: Water; Halides; Surface chemical reaction; Near edge extended X-ray absorption fine structure (NEXAFS); Photon stimulated desorption (PSD)

1. Introduction

The study of the electronic and atomic structures of the ice surface is of fundamental importance for the understanding of the heterogeneous chemistry of the earth stratosphere [1,2]. For instance, most of the chemical reactions involved in the seasonal depletion of the stratospheric ozone take place at the surface of the polar stratospheric icy clouds that form when temperature drops during the winter. Those clouds are made of crystalline ice I_h, the phase naturally found on earth; one important reaction catalyzed by the surface of ice and leading to the release of Cl_2 occurs between $ClONO_2$ and HCl, following [1]:

$$HCl + ClONO_2 \rightarrow Cl_2 + HNO_3$$
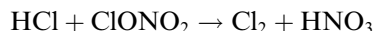
HCl is also involved in reactions with many other reservoir species, and the reactivity of HCl with ice is therefore a key issue in this chemistry. The interaction process of HCl with ice is often seen as a complex phenomenon described in a two-step mechanism [3]: first, the adsorption of HCl through a hydrogen bond with a surface water molecule, and then its incorporation within the lattice to form hydrates of various compositions, depending on the ice temperature and on the HCl concentration [4,5]. HCl is supposed to be ionized on those hydrates [5], but there is so far no experimental work that have directly evidenced such ionization. In addition, the presence of molecular HCl have been detected in some experimental studies [6]. Last, little is known about the HCl diffusion mechanism in ice [7], the hydrates structures

[8] and the surface species [9]. To better understand the HCl–ice chemistry, we have studied the adsorption of HCl at 120 K on crystalline ice using X-ray absorption spectroscopy (or NEXAFS for near-edge X-ray absorption fine structures) at the Cl2p and O1s edges. In addition to the conventional NEXAFS technique, that probes the bulk of ice, we have also used the photo-stimulated desorption NEXAFS (PSD–NEXAFS) signal which is sensitive only to the surface.

2. Experimental

The NEXAFS measurements have been done on the LURE-SuperACO SA22 beamline, with a resolving power of 5000. The energy was calibrated at the Cl2p and the O1s edges using the absorption features due to the first order K excitation of the oxygen and the third order $L_{2,3}$ excitations of the chromium contaminations of the optics. The preparation and measurements on the H_2O ice films have been done under UHV. The H_2O gas phase spectrum was previously recorded in partial ion yield using the same energy resolution and calibration than for ice. This calibration was set to match that of the H_2O gas phase data published in Ref. [10]. The NEXAFS measurements have been recorded in total electron yield (TEY), by doing the ratio of the photocurrent of the sample on that of the beam monitor. The PSD–NEXAFS measurements have been done in total ion yield (TIY), using a 5 cm^2 two-stages microchannel plate (Galileo) biased at −2.0 kV, and the spectra are the ratio of the sample TIY on the beam monitor photocurrent. The crystalline ice films were deposited at 150 K on a clean Au(1 1 1) single crystal. The substrate temperature was measured using a platinum resistance clamped on the back of the crystal. After the ultra pure H_2O was degassed by several freeze-pump-thaw cycles, thick ice films were prepared by dosing from the background 100 Langmuirs (1 L = 10^{-6} Torr s) of H_2O vapour at a rate of 0.1 L s^{-1} using a diffuser outlet located at the back of the substrate. Assuming a sticking coefficient of unity for ice at 150 K [11], 1 L is equivalent to 1 monolayer (ML), and the films are therefore 100 ML thick. Then, the films were

cooled at 120 K for a further background-dosing of 1 L (jauge corrected) of HCl (Air Liquide, electronic grade). A HCl multilayer was also prepared by dosing on a clean Au(1 1 1) substrate 45 L HCl at 50 K.

3. Results and discussion

3.1. Pure water ice

The Fig. 1 presents the O1s TEY and TIY spectra of a crystalline H_2O ice film, compared to the gas phase spectrum of H_2O. The TEY spectrum is representative of the bulk of the film, because of the large escape depth of the Auger/secondary electrons (∼50 Å). On the contrary, photo-ions (for ice, mostly H$^+$ [12]) have a very low kinetic energy, and the fragments emitted from the bulk are readily stopped by inelastic collisions. Only the ions emitted at the very surface
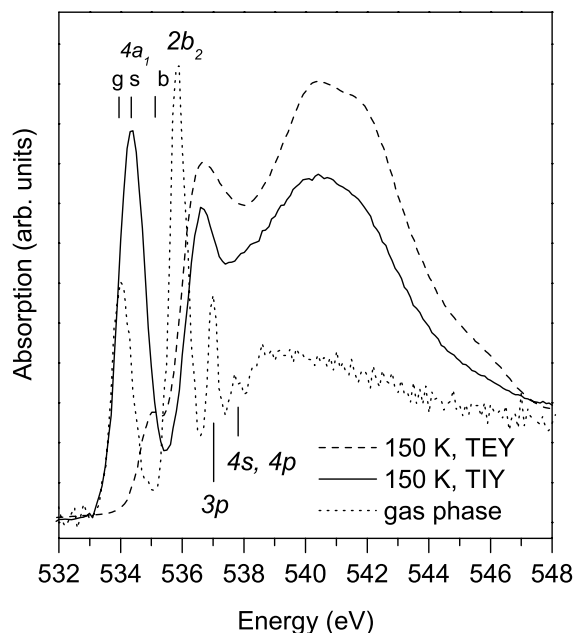

Fig. 1. Oxygen 1s NEXAFS spectra of a 100 L crystalline water ice film deposited at 150 K, recorded simultaneously in TEY (TEY, representative of the bulk) (---) and TIY (TIY, representative of the surface) (—). The gas phase spectrum of water (···) is reported for comparison. The vertical ticks indicate the energy position of the O1s → 4a$_1$ transition in the gas phase (g), at the surface (s) and for the bulk (b).

are able to escape, and the TIY signal is thus representative of the surface ($\sim$2 Å). On the gas phase spectrum, the first two sharp resonances are attributed to the O1s $\rightarrow$ 4a$_1$ transition (534 eV, Γ(FWMH) = 0.78 eV) and to the O1s $\rightarrow$ 2b$_2$ transition (535.9 eV, Γ = 0.62 eV). Then follow transitions to pure Rydberg states. On the TEY spectrum, the shoulder at 535 eV is assigned to the 4a$_1$ state, shifted by +1.0 eV and broadened (Γ = 0.98 eV) compared to the gas phase. This upwards shift shows that the 4a$_1$ state becomes more antibonding upon condensation, a result of an increase in the bonding character of the valence states caused by the hydrogen bonding between water molecules. On the TIY spectrum, the O1s $\rightarrow$ 4a$_1$ transition is at 534.3 eV, between the gas phase value (534 eV) and the TEY value (535 eV). Its linewidth (0.98 eV) is broader than for H$_2$O gas (0.78 eV) and is equal to the TEY value. Its intensity is strongly enhanced with respect to the continuum region. This enhanced H$^+$ emission at the O1s $\rightarrow$ 4a$_1$ excitation is due to the fact that the breakage of the OH bond is more efficient at this resonance than on others, thanks to the dissociative nature of the O1s^{-1}4a1^{+1} excited state and/or of the Auger decay final states [12,13]. The enhancement of the 4a$_1$ transition is also strongly maximized when the electric field ε of the synchrotron beam is directed along the surface normal n of the ice film, as reported in detail by Coulman in Ref. [12]. Our experiments have also been done in such grazing geometry. Coulman has suggested that this polarisation dependence is related to a preferred orientation of the molecules at the surface, and that the peaking of the H$^+$ signal around the surface normal is due to the breaking of the molecules having one of their OH bond oriented along n. The molecules in this configuration are those with one of the OH bond participating to the hydrogen bonding with the neighbouring molecules and keeping the other OH bond free, sticked up out the surface and directed toward the vacuum. This former bond is usually called the "dangling" OH bond (noted d_{OH}) [14]. In the idealized hexagonal I_h [0 0 0 1] surface, a third of the sites are occupied by those d_{OH} molecules, an other third by three-coordinated dangling O molecules (those having their two OH groups

hydrogen bonded with two other molecules, noted d_O), and the last third by normal four-coordinated molecules located at the bottom of the ice bilayer (noted s-4). Those two latter configurations are not expected to contribute to the enhancement of the ion yield at the 4a$_1$ transition, since the OH bonds of these molecules are not oriented along n. Indeed, when fragmentation occurs at the d_O or s-4 sites, the escape probability of the H$^+$ fragment is likely weak, since the OH axis are directed toward the bulk or at most parallel to the surface, and not toward the vacuum as for the d_{OH} molecules. We therefore assume that the fragmentation of the dangling OH bond is the dominant contributor to the enhanced ion yield at the 4a$_1$ resonance, which can be thus considered as a fingerprint of the d_{OH} molecules. The -0.7 eV energy shift of the 4a$_1$ resonance on the TIY spectrum compared to the TEY then mostly reflects the differences in the electronic structure of the surface d_{OH} molecules compared to the bulk molecules. It is noteworthy that the 4a$_1$ state of the d_{OH} molecules is close (+0.3 eV) to the gas phase value, indicating that they own an electronic configuration close to the free molecule, less antibonding than in the solid, as expected since one hydrogen bond is missing.

The transition to the 2b$_2$ level, which has a strong Rydberg character in the gas phase [15], and the transitions to the pure Rydberg states (ns, np) have collapsed in a continuum of state, the conduction band of ice. Those diffuse levels have lost their molecular character because they strongly overlap the neighbouring water molecules, the oxygen–oxygen intermolecular distance in ice (2.76 Å) being comparable to their Rydberg radii [15, 16].

3.2. Pure HCl; HCl/H$_2$O

The spectra a and b on the Fig. 2 present the Cl2p TEY and TIY, respectively, of a 45 L HCl multilayer. First, we interpret the TEY spectrum (Fig. 2a) following Ref. [17]. The broad peak around 201 eV results from the 2p$_{3/2}$, 2p$_{1/2}$ excitations to the σ^*(H–Cl) valence orbital (200.83 and 202.15 eV, respectively), and is therefore a fingerprint of the H–Cl valence bond. Then follows the L$_3$4s (203.1 eV, Γ = 0.6 eV) Rydberg state, the
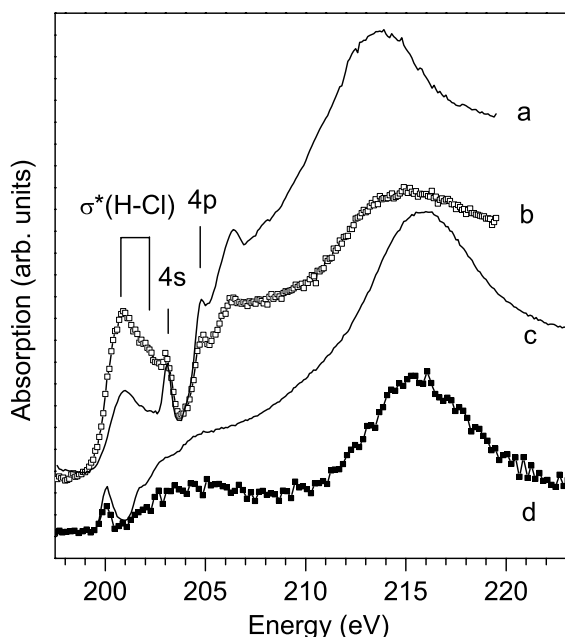
Fig. 2. Chlorine 2p NEXAFS spectra for (i) 45 L of pure HCl condensed at 50 K: (a) TEY, (b) TIY and (ii) 1 L of HCl adsorbed at 120 K on 100 L of a crystalline water ice film (150 K): (c) TEY, (d) TIY.

only resolved transition of the L_3ns serie in condensed HCl. We set the ionisation threshold at 204.8 eV (the inflexion point of the continuum), which is almost superimposed to the $L_3$4p state (204.8 eV) of the L_3np serie. The broad resonance centered at 213.7 eV is assigned to the intermolecular scattering of the 2p photoelectron by the Cl atoms of the surrounding HCl molecules. The TIY spectrum (Fig. 2b) has the same overall shape than the TEY spectrum, except the enhancement of the ion yield at the σ^*(H–Cl) state—as observed at the $O1s^{-1}4a_1^{+1}$ excitation of H_2O–, and the shift of the scattering resonance towards high energy. This enhancement could come from the H–Cl bond ultrafast dissociation (UFD) in the $2p^{-1}\sigma^*$(H–Cl)$^{+1}$ core excitation, as found in the gas phase [18]. However, the TIY should not be enhanced if a pure UFD process is the cause of the H–Cl fragmentation, because only neutral fragments are expected from such neutral core excitation. In the case of the $4a_1$ state of water, UFD has been indirectly evidenced for the gas phase [19], but not

on condensed water, where no H° emission has been detected [20]. It has been then suggested in Ref. [20] that interactions with the surrounding water molecules during the fragmentation could lead to the production of H$^+$ instead of H°. By extension, it could be that such processes are also involved in the photo-ion production at the $2p^{-1}\sigma^*$(H–Cl)$^{+1}$ excitation of condensed HCl, leading to desorption of charged ions rather than neutral fragments. It is to note that, in addition to the H–Cl dissociation in the photoexcited state, the bond fragmentation can also occur in Auger decay final states, which are thus expected to contribute also to the ion yield.

Contrary to ice, we do not observe any shift in the σ^*(H–Cl) energy of HCl. This indicates that, in the bulk, the binding interactions between HCl molecules (or their effect on the intramolecular σ(H–Cl) and σ^*(H–Cl) valence orbitals) are weak. In consequence, the disruption of those interactions at the surface does not induced any perturbation of the σ^*(H–Cl) energy. The only surface effect detected is for the Cl–Cl resonance, upwards shifted from 213.7 eV (TEY) to 215.1 eV (TIY). The shift of this resonance indicates that the Cl–Cl distances at the surface are a slightly lower than in the bulk, as also observed on ice [21].

The spectra c and d on the Fig. 2 show the Cl2p TEY and TIY spectra, respectively, of 1 L HCl adsorbed at 120 K on a 100 L crystalline ice film. Those spectra are strongly different from condensed HCl, clearly showing that the HCl adsorption is not molecular, both in the bulk (TEY) and at the surface (TIY). On the two spectra, we observe a narrow ($\Gamma = 0.65$ eV) peak at 200.1 eV, followed at 201.4 eV by the onset of the ionisation threshold, shifted of −3.4 eV with respect to HCl (204.8 eV). The intermolecular shape resonance is now located at 216.0 eV (TEY) and 215.5 eV (TIY). The direct evidence of the ionization of HCl is the *disappearance of the* σ^*(H–Cl) *state*, both in the bulk and at the surface [22]. We assign the remaining peak at 200.1 eV to the lowest excitation of the Cl$^-$ ion, $2p^63s^23p^6 \rightarrow 2p^53s^23p^64s$. Its narrowness, similar to that of the $L_3$4s Rydberg state in HCl, evidences the atomic character of this line. The downwards shift of the ionization threshold compared to HCl is a result of the additional

negative charge localized at the Cl atom, increasing the repulsive character of the ion at the ionization threshold and thus decreasing the necessary energy for ionization. We also observe on the TEY spectrum weak features just above the ionization threshold, likely the unresolved multiplets open by the 2p excitation to highest electronic states of the Cl^- ion, for instance $2p^63s^23p^54s^1$ and $2p^63s^23p^54p^1$ [23]. Last, the intermolecular resonance is strongly shifted upwards compared to HCl. This is a consequence of the change in the atomic neighbouring of the excited chlorine, both in nature and in structure. Indeed, water molecules now surround chlorine. Due to the change in atomic number, the amplitude and phase of the Cl 2p photoelectron wave function scattered by H_2O is not the same than when scattered by HCl, and due to the differences in the interatomic distances between HCl–HCl in condensed HCl and HCl–H_2O in the adsorbate, the scattering resonance is not at the same energy [24]. Self-consistent field multiple scattering X_α calculations are now under progress to determine the local molecular arrangement of the solvation cage around the Cl ions. Qualitatively, the small shift in the resonance energy between the TEY and TIY signal show that the Cl–O distance at the surface is slightly longer than in the bulk, a possible consequence of the surface relaxation.

4. Conclusion

We have shown that the O1s PSD–NEXAFS data provide a fingerprint of the OH dangling bonds of the ice surface, opening promising perspectives for studying the role of this adsorption site on the ice-adsorbate reactions. We have shown directly, in situ and for the first time that HCl adsorbed on crystalline ice is dissociated both at the surface of the film and in the bulk of ice. This study also shows that the NEXAFS and PSD–NEXAFS techniques, together with the high energy selectivity of innershell levels are very powerful tools to study the interaction of adsorbate with ice, since they allow to follow geometric and chemical state changes both at the surface and in

the bulk and for both the interacting and the substrate molecules.

References

[1] S. Solomon, R.R. Garcia, F.S. Rowland, D.J. Wuebbles, Nature 321 (1986) 755.

[2] M.J. Molina, T.L. Tso, L.T. Molina, F.C.-Y. Wang, Science 238 (1987) 1253.

[3] B.J. Gertner, J.T. Hynes, Science 271 (1996) 1563;
S. Casassa, Chem. Phys. Lett. 321 (1999) 1.

[4] N. Uras-Aytemiz, C. Joyce, J.P. Devlin, J. Phys. Chem. A 105 (2001) 10497.

[5] K. Foster, M.A. Tolbert, S.M. George, J. Phys. Chem. A 101 (1997) 4979;
V. Sadchenko, C.F. Giese, W.R. Gentry, J. Phys. Chem. B 104 (2000) 9421.

[6] H. Kang, T.-H. Shin, S.-C. Park, I.K. Kim, S.-J. Han, J. Am. Chem. Soc. 122 (2000) 9842;
J.D. Graham, J.T. Roberts, J. Phys. Chem. 89 (1994) 5974;
N. Uras, M. Rahman, J.P. Devlin, J. Phys. Chem. B 102 (1998) 9375.

[7] F.E. Livingston, S.M. George, J. Phys. Chem. A 105 (2001) 5155.

[8] L. Delzeit, B. Rowland, J.P. Devlin, J. Phys. Chem. 97 (1993) 10312.

[9] R.S. MacTaylor, J.J. Gilligan, D.J. Moody, A.W. Castleman Jr., J. Phys. Chem A 103 (1999) 4196.

[10] J. Schirmer, A.B. Trofimov, K.J. Randall, J. Feldhaus, A.M. Bradshaw, Y. Ma, C.T. Chen, F. Sette, Phys. Rev. A 47 (1993) 1136.

[11] D.E. Brown, S.M. George, C. Huang, E.K.L. Wong, K.B. Rider, R. Scott Smith, B.D. Kay, J. Chem. Phys. 100 (1996) 4988.

[12] D. Coulman, A. Puschmann, U. Höfer, H.-P. Steinrück, W. Wurth, P. Feulner, D. Menzel, J. Chem. Phys. 93 (1990) 58.

[13] D.E. Ramaker, Chem. Phys. 80 (1983) 183.

[14] J.P. Devlin, V. Buch, J. Phys. Chem. B 101 (1997) 6095, and references therein.

[15] W.A. Goddard III, W.J. Hunt, Chem. Phys. Lett. 24 (1974) 464.

[16] R.A. Rosenberg, P.R. LaRoe, V. Rehn, J. Stöhr, R. Jaeger, C.C. Parks, Phys. Rev. B 28 (1983) 3026.

[17] K. Nonomaya, E. Ishiguro, S. Iwata, A. Mikuni, T. Sasaki, J. Phys. B: At. Mol. Phys. 14 (1981) 1777;
C.D. Cadwell, M.O. Krause, R.D. Cowan, A. Menzel, S.B. Whitfield, S. Hallman, S.P. Frigo, M.C. Severson, Phys. Rev. A 59 (1999) R926.

[18] O. Björneholm, S. Sundin, S. Svensson, R.R.T. Marihno, A. Naves de Brito, F. Gel'mukhanov, H. Ågren, Phys. Rev. Lett. 79 (1997) 3150.

[19] M.N. Piancastelli, A. Hempelmann, F. Heiser, O. Gessner, A. Rüdel, U. Becker, Phys. Rev. A 59 (1999) 300;

I. Hjelte, M.N. Piancastelli, R.F. Fink, O. Björneholm, M. Bässler, R. Feifel, A. Giertz, H. Wang, K. Wiesner, A. Ausmees, C. Miron, S.L. Sorensen, S. Svensson, Chem. Phys. Lett. 334 (2001) 151.

[20] R. Romberg, S.P. Frigo, A. Ogurtsov, P. Feulner, D. Menzel, Surf. Sci. 451 (2000) 116.

[21] Ph. Parent, C. Laffon, C. Mangeney, F. Bournel, M. Tronc, J. Chem. Phys. 117 (2002) 10842.

[22] F. Bournel, C. Mangeney, M. Tronc, C. Laffon, Ph. Parent, Phys. Rev. B 65 (2002) R20140.

[23] J.J. Matese, S.P. Rountree, R.J.W. Henry, Phys. Rev. A 8 (1973) 2965;
D.L. Cunningham, A.K. Edwards, Phys. Rev. A 8 (1973) 2960.

[24] J. Stöhr, in: NEXAFS Spectroscopy, Springer Series in Surface Science, Springer, Berlin (1992), p. 252.