

Acidity of hydrogen chloride at the surface of low-temperature (40–150 K) water-ice films

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We use near-edge x-ray absorption spectroscopy (NEXAFS) at the chlorine 2*p* levels with two detection modes: total electron yield and total ion yield to obtain direct information on chemical states of HCl molecules at the surface and in the bulk of thin water-ice films at low temperature (40–150 K). NEXAFS spectra show that HCl species are the same at the surface and in the bulk, and that when HCl is adsorbed in excess of a monolayer at $T > 90$ K, transitions from the Cl 2*p* levels to the antibonding $\sigma_{\text{H-Cl}}^*$ are totally suppressed as a result of HCl dissociation into an $\text{H}_3\text{O}^+\text{Cl}^-$ ion-pair complex.

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It is well known that HCl molecules are poorly reactive with many molecules in the gas phase, but that HCl is a very strong acid ($pK_A = -7$) fully dissociated to chloride anion (Cl^-) and hydronium cation (H_3O^+) in aqueous solution. But the interaction (solvation, ionization, and dissolution) of HCl with water ice is still not well known although it is of fundamental importance for the understanding of strong acid and base problem^{1,2} and has practical and considerable implications in many areas such as heterogeneous chemistry in the atmosphere and interstellar space, biological transformations on icy dusts and particulates, physical chemistry, in particular because HCl is one of the major products resulting from dissociation of chlorofluorocarbons.^{3,4} Starting with the 1985 discovery of large seasonal loss of total ozone in the Antarctic stratosphere⁵ due to the presence of polar stratospheric cloud ice particles and their active role in heterogeneous catalytic reactions^{6–8} extensive efforts have been made both from the theoretical side with molecular-dynamics simulations,^{9,10} hybrid quantum-classical Monte Carlo simulations,¹¹ *ab initio* density-functional molecular-orbital methods,^{12,13} and with laboratory experimental approaches including Fourier transform infrared spectroscopy,^{1,2} reactive ion scattering and secondary ion mass spectroscopy,¹⁵ temperature programmed desorption,¹⁶ pulsed molecular beam and mass spectroscopic techniques,^{14,17} and laser resonant desorption depth profiling technique¹⁸ to better understand the nature and properties of HCl-ice interface. The more recent results show that at submonolayer coverage^{14,19,20} covalently adsorbed molecular HCl may exist at the surface of ice, but at higher coverage and for temperature above 110 K, ionized HCl prevails on ice, the ionization being even probably complete above 140 K.¹⁵ However, our understanding of HCl-ice interaction at the molecular level is still very limited and a clear picture and detailed mechanisms for solvation, ionization, and penetration of HCl in ice is still lacking. In this Rapid Communication we show directly and at the molecular level the adsorption and dissociation of HCl molecules at the surface of thin ice films, and its diffusion into the bulk ice.

In recent high-resolution x-ray absorption spectroscopy measurements on ice we have shown that the

morphology^{21,22} and phase transitions²³ of thin ice films could be studied both in the bulk ice when the total electron yield (TEY) detection technique was used because the Auger electrons coming from the decay of inner-shell photoexcited molecules have a large mean free path (>50 Å), and at the topmost and near surface layer of ice when using the total ion yield (TIY) desorption technique²⁴ because of the low kinetic energy and consequent low escaping depth of fragment cations issuing from the inner-shell hole excited states, which have to overcome the polarization induced barrier energy to escape into vacuum.^{22,23} In these experiments the x-ray absorbing atom is not only sensitive to its local environment, but also to very faint modifications of local geometric and electronic structure. Moreover, thanks to the high atomic energy selectivity of the inner shells, the interaction and reaction of low-pressure gas phase molecules with ice films can be followed^{25,26} both for the adsorbed (absorbed) molecule itself and for the ice substrate water molecule, and both at the surface layer by measuring the TIY desorption induced by Cl 2*p* (≈ 200 eV) (in the present experiment) and O 1*s* (≈ 500 eV) excitation, respectively, and in the bulk by measuring the TEY following X-ray irradiation around the Cl 2*p* or O 1*s* edges.

The experiments were performed at the Super-ACO storage ring in Orsay. The near edge X-ray absorption spectroscopy (NEXAFS) measurements have been achieved with a plane grating monochromator having a resolution of ≈ 60 meV full width at half maximum around 200 eV photon energy. Photon energies were calibrated using the 284.70 eV feature on the incoming photon beam due to low carbon contamination adsorbed on the optics. Exposures are given in units of monolayer equivalents²⁷ (1 ML = 10^{-4} Pa s assuming a sticking coefficient of unity). Ice films were prepared by dosing 100 ML (370 Å thickness) of ultra pure water vapor at a rate of 0.1 ML s^{-1} on a Au (111) substrate in an ultrahigh vacuum chamber. Water was degassed via several freeze-pump-thaw cycles. The substrate was maintained at 150 K to obtain crystalline ice, in the form of nanocrystals giving rather rough surfaces, or at 120 K to get dense amorphous ice films, or at 40 K to have microporous amorphous

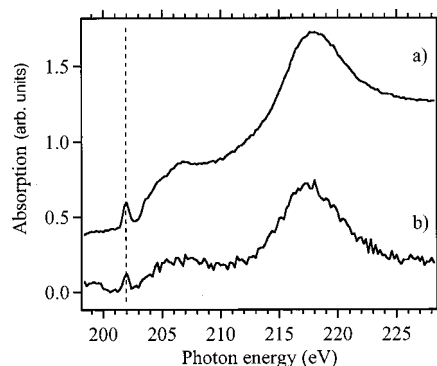


FIG. 1. Chlorine $2p$ NEXAFS spectrum for (a) the TEY detection mode and (b) the TIY desorption mode for 2.5 ML of HCl adsorbed at 120 K on 100 ML of crystalline water ice condensed at 150 K. The absorption scale is for spectrum (b), spectrum (a) on a different scale has been shifted vertically for clarity.

ice layers. Crystalline ice can be cooled down to a very low temperature without phase transformation, but annealing of low temperature amorphous microporous ice results in the collapse of the micropores to give dense amorphous ice starting around 90 K and then the formation of crystalline ice at 140–150 K. Hydrogen chloride (Air Liquide, electronic grade, with $\text{H}_2\text{O} < 10$ ppm) was introduced with a fixed dynamic partial pressure of 10^{-6} Pa at temperature in the range 40–120 K and the TEY and TIY were measured at the temperature of HCl deposition on the ice film. The TEY spectra correspond to the ratio between the signal from the sample and the signal I_0 from a Au grid located upstream of the sample, measured simultaneously. The TIY spectra were obtained on a wide (5 cm^2) two-stage microchannel plate detector positioned at 5 cm in front of the sample.²¹

Figure 1 shows Cl $2p$ TEY and TIY NEXAFS spectra for 2.5 ML of HCl adsorbed at 120 K on 100 ML of crystalline water ice deposited at 150 K. The two spectra are quite similar with a low-energy peak at 202 eV, some unresolved ns and md Rydberg structures between 203 and 207 eV, and a broad resonance centered at 220 eV in the Cl $2p_{3/2,1/2}$ continua. The great resemblance and the same peak energies [except for a small shift of the continuum resonance around 220 eV (Ref. 25)] for these two spectra which probe empty levels of HCl molecules present in the bulk of ice film and at the top and near surface layer, respectively, reveal that HCl species are the same at the surface and in the bulk. The adsorption of HCl on the O-H dangling bonds at the surface of ice, followed by its encrustation into the bulk ice is shown in Fig. 2. Figure 2(a) is the TIY (mainly H^+) desorption spectrum after excitation at the oxygen $1s$ for a pure crystalline water-ice film with a prominent $\sigma_{\text{O-H}}^*$ peak at 532 eV.^{21,28} Figure 2(b) shows the same TIY spectrum measured 30' after dosing with 2.5 ML of HCl at 120 K on the ice film. The O-H dangling bonds are now blocked up by hydrogen-bonded HCl and no more active in ion desorption. The TIY spectrum in Fig. 2(c) was obtained 150' after dosing with HCl; it shows a partial restoration of the O-H dangling bonds at the surface of ice after HCl (as Cl^- anion) diffusion into the film. The same observations (not shown) were done for HCl molecules adsorbed on dense amorphous ice condensed

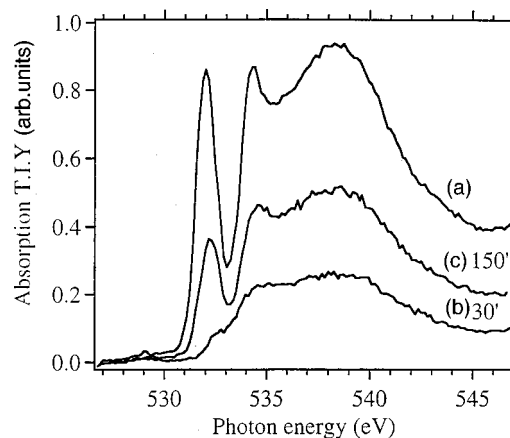


FIG. 2. Oxygen $1s$ TIY NEXAFS spectrum for (a) 100 ML of crystalline pure water ice condensed at 150 K, (b) 100 ML of crystalline ice dosed with 2.5 ML of HCl at 120 K, spectrum measured 30' after dosing, and (c) 100 ML of crystalline ice with 2.5 ML HCl at 120 K, 150' after dosing.

at 90–120 K but with a faster diffusion of HCl into the bulk.²⁵

Information on the chemical state of HCl both at the surface and in the volume of water-ice films can be obtained by the comparison of TEY (or TIY) spectra of pure HCl films with that of HCl adsorbed on ice, and this is shown in Fig. 3. Figure 3(a) is the TEY spectrum of a pure multilayer HCl film (100 ML) condensed on a Au substrate maintained at 50 K. This spectrum is comparable, with some broadening, with the gas phase Cl $2p$ spectrum of HCl.^{29–31} The broad and asymmetric peak around 203 eV results from transitions from Cl $2p$ into the antibonding and dissociating³⁰ $\sigma_{\text{Cl-H}}^*$ molecular orbital (MO). The 205 eV peak is the $4s$ Rydberg final state, and the structures between 206 and 210 eV are unresolved ns , md Rydberg states. The two broad resonance structures in the $2p$ continua, which are not present in the isolated HCl molecule³² result from resonance scattering of

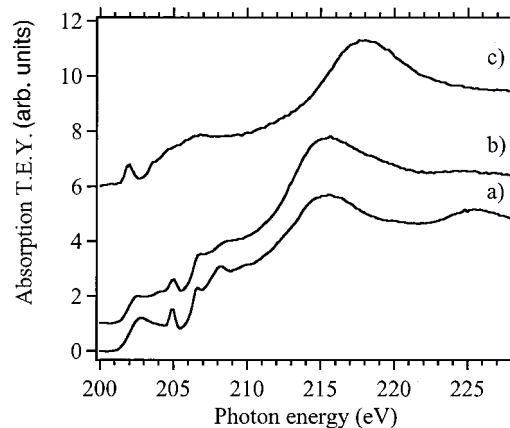


FIG. 3. Chlorine $2p$ TEY NEXAFS spectrum for (a) 100 ML of pure HCl condensed at 50 K, (b) 4 ML of HCl condensed at 40 K on 100 ML of crystalline water-ice film deposited at 150 K, and (c) 2.5 ML of HCl adsorbed at 120 K on 100 ML of a crystalline water-ice film (150 K). The absorption scale is for spectrum (a), spectra (b) and (c) have been shifted vertically for clarity.

the excited electron between the core excited chlorine atom and its neighboring molecules in the hydrogen bonded solid film. Note that the very low electron density at proton will not cause noticeable backscattering intensity.

When 4 ML of HCl is adsorbed at 40 K on crystalline ice [Fig. 3(b)] the Cl $2p$ TEY NEXAFS spectrum is essentially unchanged, which means that HCl species in the pure HCl film and on water ice are identical and undissociated in these conditions of multilayer growth. But when HCl is adsorbed at 120 K on crystalline ice the TEY spectrum changes dramatically [Fig. 3(c)] in both the $2p$ preedge and postedge region. In the preedge the $2p_{3/2,1/2} \rightarrow \sigma_{\text{Cl-H}}^*$ transitions around 203 eV are suppressed, just as in the recently observed atomic chlorine $2p$ spectrum,³³ and this is a direct evidence for the dissociation of HCl molecules with the suppression of the $\sigma_{\text{Cl-H}}$ molecular orbital and of its antibonding counterpart $\sigma_{\text{Cl-H}}^*$. The remaining narrow peak at 203 eV is then assigned to the $\text{Cl}^- 2p \rightarrow 4s$ excitation, the -3 eV energy shift compared to HCl resulting from the additional charge localized on the chlorine atom. In the $2p$ continua the broad resonances are shifted as a result of a modification of the $2p$ excited Cl atom environment and distances with neighbors in going from $(\text{Cl} \cdots \text{H}-\text{Cl})$ in condensed pure HCl to $\text{H}_3\text{O}^+ \text{Cl}^-$ in the dissociated ion-pair complex. A correlation has been established³⁴⁻³⁶ between continuum resonance energies and bond lengths or interatomic separations, and with the sum Z of the atomic numbers of the two nearest-neighbor atoms,

the absorbing and the scatterer in play in the resonance formation. A linear relationship has been shown adequate to describe the resonance energy referenced to the corresponding ionization threshold with Z and with interatomic distances, respectively.^{34,36} Our observations of ionized HCl not only in the bulk of ice films requiring at least four surrounding water molecules according to different calculations,^{9,11,13} but also at the surface is probably connected to the high density of dangling OH groups at the surface of rough nanocrystal and amorphous ice films in agreement with recent Car-Parrinello molecular-dynamics simulations³⁷ showing that dissociation of HCl is thermodynamically favorable and kinetically rapid when surface HCl interacts with at least two dangling OH groups at the surface of ice.

We have shown *in situ*, and directly, that HCl adsorbed above 90 K on crystalline and amorphous ice films is dissociated both at the surface of the film and in the volume of ice for coverage in excess of a monolayer. Moreover, it is shown that TEY and TIY NEXAFS spectra, together with the high energy selectivity of inner-shell levels are very powerful tools to study the interaction of low-pressure gas phase molecules with condensed molecular substrates as 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. This technique appears also quite promising³⁸ to follow photoinduced and electroinduced chemical reactions between cocondensed molecules.

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