Supplemental material for Comment on "HCl adsorption on ice at low temperature: a combined X-ray absorption, photoemission and infrared study" P. Parent, J. Lasne, G. Marcotte and C. Laffon, *Phys. Chem. Chem. Phys.*, 2011, 13, 7142.

J. Paul Devlin, Department of Chemistry, Oklahoma State University, Stillwater, OK, 74078; devlin@okstate.edu

Heon Kang, Department of Chemistry, Seoul National University Gwanak-gu, Seoul 151-747(Republic of Korea); surfion@snu.ac.kr

Details for recognition of molecular adsorbate HCl from shifted bands of the surface d-H and d-O bending modes (the authors initials (PLML) will identify the article in question).

Unlike for ionized adsorbates, ***molecular adsorbates*** do not eliminate ice surface vibrational modes but merely shift the mode frequencies. For moderate-to-strong adsorbates, the downshifts, often > 100 cm^{-1}, are difficult to follow for d-H or d-O water ***stretch*** modes as they become obscured by the intense interior ice band. However, despite having <50% the intensity of the d-H stretch mode, the 10 to 40 cm^{-1} shifts of the bending modes of the d-O and d-H surface molecules [S-1a] can be followed and used to define the nature of the adsorbate state [S-1b]. Though not reported previously for adsorbed HCl, the sharp d-H and d-O bands are ideal for this purpose as we demonstrate here using hand-traced segments of the RAIR film spectra of PLML (Fig.S-1) along with smoothed D$_2$O nanocrystal transmission spectra (Fig.S-2).
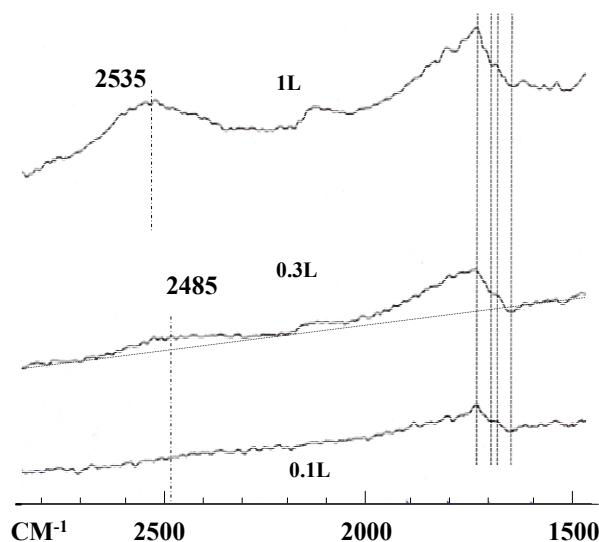

Fig.S-1 Hand-traced segments of the 50K ASW spectra from Fig.4 of PLML. The bands tabulated in Table S-1, as features of the shifted and unshifted modes of the d-O and d-H surface water bending vibrations, are highlighted using vertical lines. Also, a "horizontal" dotted line is added to aid recognition of the weak 2485 band of the 0.3L sample. (In fact, this is a composite of ~2450 and ~2550 bands).

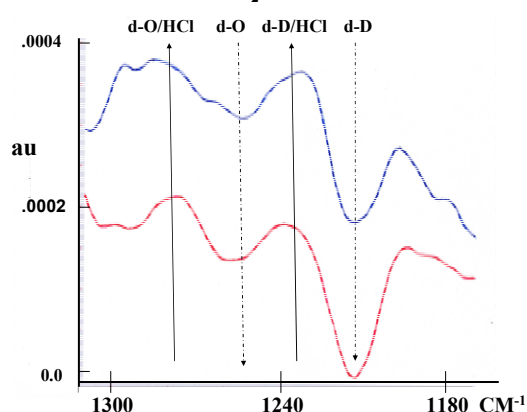**HCl-Shifted and Bare D$_2$O Ice Surface Bend Modes**

Fig.S-2 Two difference spectra for d-D and d-O surface bending modes of D$_2$O ice with the bare ice spectrum (negative bands) subtracted from that with ~0.2 ML of HCl adsorbate (positive bands). See text for details. Spectra have been smoothed to ~ 8 cm^{-1} resolution. Of the surface bending bands, the d-D/d-H are known to be most intense [S-1a].

Table S-1: FTIR bending frequencies (cm^{-1}) for outer surface layer water molecules (dangling-H & dangling-O) of ice unshifted and shifted by adsorbed HCl. From figures of PLML for HCl adsorbed on amorphous (ASW: Fig. S-1) and crystalline ice (CI) and Devlin (Fig. S-2) from HCl on D$_2$O nanocrystals (INC). Difference spectra are of bare ice subtracted from ice with a low dose of HCl so that unshifted bands are negative and shifted are positive in intensity. Frequencies apply to the indicated dosage levels. Shifted FTIR bands are absent for heavy dosing, particularly at 90 K, so are not included. Units of dosage are Langmuir (L) and monolayer (ML).

HCl Dose:	Degree K:	ice type:	d-H bare:	d-H/HCl:	d-O bare:	d-O/HCl:
0.0	100	INC	1651/1213	- - - -	1702/1244	- - - -
0.3L	50	CI	(1650)	1690	1710	1740
0.1, 0.3, 1.0 L	50	ASW	1650	1680	1700	1730
0.1 - 0.3 ML	50	INC[b]	1650	1680	1707	1739
0.1 L	90	ASW	1650	1680	1695	1730

a – Most frequency values were estimated from the sharp features in PLML Fig. 4 [S-1] and the CI spectra in the PLML Supplement as viewed in multifold expansion.

b – The INC spectral values were from average of two HCl – D$_2$O ice nanocrystal samples with no interfering absorptions in the pertinent 1200 cm^{-1} region. The D$_2$O frequencies (Fig. S-2) were then converted to H$_2$O values using 1.36 as the multiplier. Bare-ice surface bend values are from ref. S-1a. Typical shifts induced by adsorbates and assignments are given in ref. S-1.

The application of these data is simple and made more so by the relative sharpness of the surface bending mode bands, for which the <20 cm^{-1} bandwidths contrast strongly with the great breadth of the HCL[1] and HCl[2] bands as well as those of the HCl ion products. As Table S-1 indicates, the bands of the d-O (1702/1235) and d-H(D) (1651/1213) molecules of bare ice have been assigned [S-1a]. The magnitude of the shifts of these modes for several moderate and strong adsorbates have been determined for both D_2O and H_2O ice. For example, for D_2O ice (Fig. 3 of ref. S-1(b)), SO_2 shifts the d-D bend mode from 1213 to 1232 cm^{-1} while d-O moves from 1235 to ~1270. One expects a similar effect for HCl, which, like the adsorbed Lewis-acid SO_2, bonds more strongly to a d-O than d-H surface site.

The shifted values for SO_2 [S-1b], converted for H_2O ice, are 1676 (d-H) and 1727 (d-O), which compare well with the HCl shift values for ASW of Table S-1 of 1680 and 1730. Tabulated shift values are estimates taken from the PLML ASW 50K spectra (Fig. S-1), with the CI 50K values of the PLML Supplement included. Though not reported by PLML and difficult to recognize without expansion of the spectra, the PLML *low-dosage* spectra show these sharp features with nearly complete regularity (the 1651d-H negative band, which must to be there, is "missing" in the noise of the CI samples). Further, the peak positions of our smoothed difference spectra for ice nanocrystals of Fig.S-2 match well those of PLML.

As ionization takes over at higher dosages or temperatures and the ice surface loses it original identity, the sharp shifted bands disappear. The disappearance of these reproducible sharp positive features for all higher dosage (> 1L) and warmer sample spectra assures that they are not merely instrument noise. ***Thus, these surface bending mode bands confirm the largely molecular nature of the first ~20% of an ML of HCl adsorbed at 50 K***.

Transition from the $H_3O^+Cl^-$ cation spectrum to the Zundel continuum:
PLML assigns the origin of the 2530 band as strictly molecular at 50 K, Ayotte as strictly ionic (20 K) ... and we argue that it is largely molecular (~2480) changing progressively to the $H_3O^+ Cl^-$ ion pair band (~2550) with increasing HCl dosage/temperature. The 2530 band does not appear in PLML's ***90 K series***, because the surface contact ion pairing is lost as the protons move to form Zundel-like cations with the underlying ice. That the latter occurs is known since, using D_2O ice, the transferred proton, that prefers the center position of the $HD_4O_2^+$ cation [S-3], displays 90 K spectra with an ~50% H rather than "all"-D Zundel continuum despite the dominant presence of the D isotope. This is demonstrated in Fig.S-3.
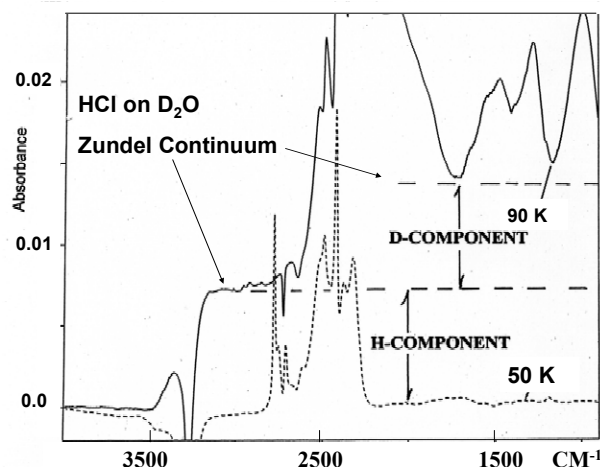
Fig.S-3 Difference spectra of HCl doped D_2O nanocrystals minus the bare ice spectrum showing the strong Zundel continuum at 90 K with its two components: the H component derived from the HCl and the D component from the D_2O ice. This continuum emerges as the ion-pair band weakens during warming.

Summary of RIS and LES observations for molecular HCl and hydronium ions on various ice samples:

Numerous literature reports over the past 20 years with seemingly conflicting observations hint that the chemical states of HCl adsorbed on ice surfaces are sensitive to the ice temperature as well as other parameters of the ice samples. In Table S-2, we list the RIS and LES observations for HCl adsorption states on various ice surfaces and summarize the results and the experimental conditions employed for sample preparation. It is now well established that HCl completely ionizes at 140 K. Therefore, we focus on the results obtained at lower temperatures (< 100 K). At ~90 K, molecular HCl and hydronium ion signals were observed on an amorphous ice film grown on a Pt(111) substrate [S-5]. This sample was prepared first by growing a thick (60 BL) crystalline D_2O film on Pt(111) at 140 K and then by adding an amorphous D_2O overlayer (3 BL) onto the CI film at 120 K. On a crystalline D_2O film (60 BL) grown on Pt(111), however, only hydronium ion signals were detected at ~90 K. These observations suggest that the ASW surface offers higher stability for molecular HCl adsorbates than the CI surface does. When HCl was adsorbed on a very thin (~2 BL) ice film grown on a Ru(0001) substrate, both molecular and ionized HCl states were observed on the surface at 80-100 K, regardless of whether the ice film was prepared in an amorphous or crystalline phase [S-6, S-7]. The different results depending on the thickness (~60 BL *vs*. ~2 BL) of the ice film may be attributed to several factors, including the unique structure of the ~2 BL ice film, the effect of the underlying metal substrate, and the different RIS detection efficiency for HCl on these surfaces. These observations suggest that HCl adsorption state is sensitive to subtle changes in the structure and electronic properties of ice sample. Studies with ASW films deposited on Si(111) [S-4] show that the relative portion of molecular HCl increases as the ice temperature is lowered to 50 K, and the ionized HCl portion decreases. A qualitatively similar temperature dependency may be expected for various types of ice samples, although quantitative features of this behavior may substantially vary with different ice samples.

Table S-2: Summary of the detection of HCl molecules and hydronium ions on various ice films in RIS and LES experiments

Temp.	Ice surface morphology	
	ASW	CI
~50 K	Molecular HCl and hydronium ion (10-20 BL D_2O film grown on Si(111) at 120 K; HCl exposure ~0.3 L at 50 K) [S-4].	
80-100 K	Molecular HCl and hydronium ion (~60 BL D_2O film grown on Pt(111) at 120 K; HCl exposure = 0.2-0.4 L at 90 K) [S-5]	Hydronium ion (~60 BL D_2O film grown on Pt(111) at 140 K; HCl exposure = 0.2-0.4 L at 90 K) [S-5]
	Molecular HCl and hydronium ion (~20 BL D_2O film grown on Ru(0001) at 120 K; HCl exposure ~0.3 L at 80 K) [S-5]	
	Molecular HCl and hydronium ion (~2 BL D_2O film grown on Ru(0001) at 135 K; HCl exposure ~1 L at 100 K) [S-6]	Molecular HCl and hydronium ion (~2 BL D_2O film grown on Ru(0001) at 140 K; HCl exposure ~0.3 L at 80 K) [S-7]
~140 K		Hydronium ion [S-4, S-6, S-7]

Summary of points emphasized in the Comment:
- A revised interpretation of the PLML ASW and CI RAIR spectra attributes the 0.3L 50K data to primarily adsorbed molecular HCl. This revision is based on subtle changes in the ~1740 and 2500 cm^{-1} bands in the PLML spectra together with extensive published results for HCl, DCl, and HBr on H_2O and D_2O ice nanocrystals. Further, infrared bands that indicate the response of the d-H and d-O surface water bending modes to adsorbed HCl seem to require the presence of molecular HCl.
- One should be careful about possible radiation damages in the use of high-energy radiation spectroscopies for investigating the HCl/ice system because of the apparent metastability of the adsorbed molecular acids that can be readily nudged to a more stable ionized state.

- The presence of molecular HCl adsorbates for low HCl dosing at low T is supported harmoniously by IR, RIS, and our quantum chemical calculations with a greater meta-stability of molecular HCl on an oxygen disordered ice surface than a CI surface.
- The temperature dependency of HCl adsorption states on ice, as reported in ref. S-4, may be applicable to various types of ice samples in a qualitative but not quantitative respect, as the chemical state of HCl adsorbate is sensitive to several ice surface parameters.

Supplement References:

S-1. a) J. P. Devlin, J. Sadlej and V. Buch, *J. Phys. Chem. A*, 2001, **105**, 974, and b) J. Hernandez, N. Uras and J. P. Devlin, J. Chem. Phys. 1998, 108, 4525.

S-2. P. Parent, J. Lasne, G. Marcotte and C. Laffon, *Phys. Chem. Chem. Phys.*, 2011, **13**, 7142.

S-3. J. P. Devlin, M. W. Severson, M. W. Mohamed, J. Sadlej, V. Buch and M. Parrinello, *Chem. Phys. Lett.*, 2005, **408**, 439.

S-4. H. Kang, T.-H. Shin, S.-C. Park, I. K. Kim and S.-J. Han, *J. Am. Chem. Soc.*, 2000, **122**, 9842.

S-5. S. Kim, Y. Kim and H. Kang, unpublished result.

S-6. S. C. Park and H. Kang, *J. Phys. Chem. B*, 2005, **109**, 5124.

S-7. P. R. Lee, C. W. Lee, J. K. Kim, E. S. Moon, and H. Kang, *Chem.-Asian J.,* 2011*, **6**, 938.

S-8. A. Hodgson and S. Haq, *Surface Sci. Rep*. 2009, **64**, 381.