

# ***Interactive comment on “The Influence of HCl on the Evaporation Rates of H<sub>2</sub>O over Water Ice in the Range 188 to 210 K at small Average Concentrations” by C. Delval et al.***

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(Throughout we will recognize references from Duval and Rossi using the first name with an asterisk)

Having given the authors rather high rankings and favored the publication of their manuscript, I will now concentrate on a few aspects where some weaknesses need attention. In particular, I do not feel nearly as congratulatory toward the group of Laffon and Parent as the authors appear to be on page 5. The new data and some of the insights from the Parent group may be useful, but it is difficult to be sure when they are careless in other respects; for example, refusing to expand their data where there

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are clearly uncertainties; even when a useful expansion can be had quite simply, as by replacing H by D (see later). For that reason in 2011 I collaborated with Heon Kang to produce a 2011 Comment (PCCP 06-2011-022007) on their 2011 publication, i.e. “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) and will use our “Comment” as a partial base for points made here in light of the praise on page 5. I will focus on the comparison of the infrared data and assignments from our lab with that of Parent’s. The insights of Kang with respect to the comparative data from other methods can be found in our earlier Comment noted above. This is not easy as in the new 2011 paper Parent quietly makes a complete assignment reversal on what we have always regarded as the major band, a strong one at 2480 cm<sup>-1</sup> that was 1st viewed and assigned as singly-hydrated molecular HCl in our 2002 Nature paper. This band first emerges at 2480 but shifts to 2520 with warming from 50 K to above 60 K or the addition of HCl beyond ~20% of an ML. Parent has never acknowledge a second band or this shift, but in 2011 changes the identity of the “single band”, for all temperatures and dosages, from what he had regarded as an 100% ionized HCl band to a single band assigned strictly to molecular HCl. Had he vertically expanded the 50 K 0.15 ML figure near the bottom in Fig.4 he may have been forced to accept that the band starts below 2500. The assignments of most other significant bands were left unchanged; in particular retaining 1740 as assigned as hydronium ion rather than our long-term assignment as doubly hydrated molecular HCl.

In an aside from the older data, it may be helpful to realize that we now have spectra for HX/DX molecules bound to oxygen of H<sub>2</sub>O on the small-cage walls of gas clathrate hydrates. Bonding to this oxygen becomes available when an ether in a neighbor cage steals a hydrogen from an oxygen of the intervening wall. These relatively new (2015) data in Fig.1 have been made accessible through the recent (2010) development of an all-vapor premixture methodology that commonly reduces the clathrate formation process from hours to sub-seconds. Paired with the corresponding adsorbate case

for the ice surface we find: HCl – 2482/2480; DCI – 1880/1870; HBr - 2350/2300. These are all broad bands with some manageable interference from other bands. The published spectra are available in the literature for all six cases; for discussion of the three clathrate spectra see DOI: 10.1021/acs.jpca.5b07019; J. Phys. Chem. A 2015, 119, 9018–9026. The close comparisons of the clathrate-wall and ice-surface values of bonded HX were surprising, but they support the new 50 K molecular assignment of Parent as well as our continuing assignment of the 2480 ice-surface band to molecular HCl. Most importantly they seem to show conclusively that one must expect a band near 2500 for molecular HCl with a single-bond to surface oxygen. Parent assumes that and assigns the 2500 band, the strongest band in the spectrum at 50 K and 0.5 ML, to the molecular HCl. Then he goes fully off-track by a) first suggesting that continued growth at 2500 reflects increasing single-bonded molecular HCl and then near the end of the paper criticizing Kang and myself for suggesting the concept of a very limited amount (0 -15%) of ionized HCl for low-dosages at 50 K. This seems to have been a required statement flowing from his insistence that there is only a single band near 2500. However, it fully inverts the generally accepted view that molecular HCl is prominent at 50 K while ionic versions, including the Zundel ion, dominate at higher temperatures /higher dosages. Keep in mind that we do report, in the 1998 paper of Uras\*, a figure showing molecular DCI on ice at 125 K close to a much stronger ion band. The 2520 ion band (our assignment) does weaken at higher temperature as the ions switch to Zundel forms (see the top of Figure 2 of Devlin\*).

Now let's focus on the 1740/1710 band that is agreed to be present in all cases below 90 K for doses less than 0.15 ML. Here we can make a simple molecular switch, one of several choices that we have shown in Buch\* and Devlin\*, to attack the Parent assignment as an ionic band in all cases. That switch is to retain HCl while replacing H<sub>2</sub>O by D<sub>2</sub>O as in the bottom section of Fig. 1 of Devlin\*. The figure-caption states correctly that "The use of D<sub>2</sub>O ice also eliminates possible contamination of this band by protonated-water absorption" since the ionic band should downshift by a factor of ~1.36 because of mass and anharmonic effects. The figure shows that our 1710 band

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is largely unaffected by the isotopic switch so that it cannot be exclusively an ionic band. This apparently eliminates the Parent-group strictly ionic assignment; but let's consider an all-deuteration switch to also eliminate the very unlikely possibility that a different ion-band shifted into the 1740 cm<sup>-1</sup> position. With complete deuteration, we can predict the shifted HCl band position by dividing the molecular 2480 band frequency by 1.36, obtaining 1824. Figure 2 of Devlin\* shows the band is in fact at 1870. This seems to be an acceptable match that would be even closer (1853) had we used the Parent new molecular-value of ~2520. So I stop here rather than going on to a comparison with data for HBr as in Buch\*, Fig.9 which also works quite well in establishing the one and two HX coordinations with the ice surface at low temperatures and dosages.

Conclusions: The Parent group data is mostly reliable but the interpretations are not. The 50 K low dosage spectra clearly include bands for both single (2480) and doubly (1710) hydrated molecular HCl. Clathrate-hydrate data for HX and DX are a surprising source of relevant data. There seems no basis to reject band assignments from 2002 (Buch\* and Devlin\*).

1. Perhaps it should be clarified that RAIR FTIR data often cannot be compared directly with absorbance data. 2. This current review of the data convinces me that at least between 40 and 130 K the Bartels-Rausch recent HCl-on-ice publication may be right about the presence of molecular HCL on ice surfaces to some extent at most temperatures (but not all conditions). Is there a reason that paper was not included in the review? 3. The Zundel ion is important in understanding the evolution of the changes that follow warming after HCl has been adsorbed on ice at low levels at low T. Also the basic characteristics of the Zundel ion vs its environment have been thoroughly examined in the last 10 years. I particularly recommend an older joint review paper of Buch, Parrinello and others on the hydrates of HCl; J. Phys. Chem. A 2008, 112, 2144-2161 that highlights the Zundel ion. 4. On page 5 the authors question the importance of the dangling O=H bonds during the early uptake of HCl at low temperature. Is this consistent with the Parent infrared data in their 2011 paper in which they show/remark that

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the dH-band is gone after 0.15 ML at 50 K. Why did you make the statement WITHOUT GIVING A REASON?

Fig,1 HX spectra in clathrate hydrates.

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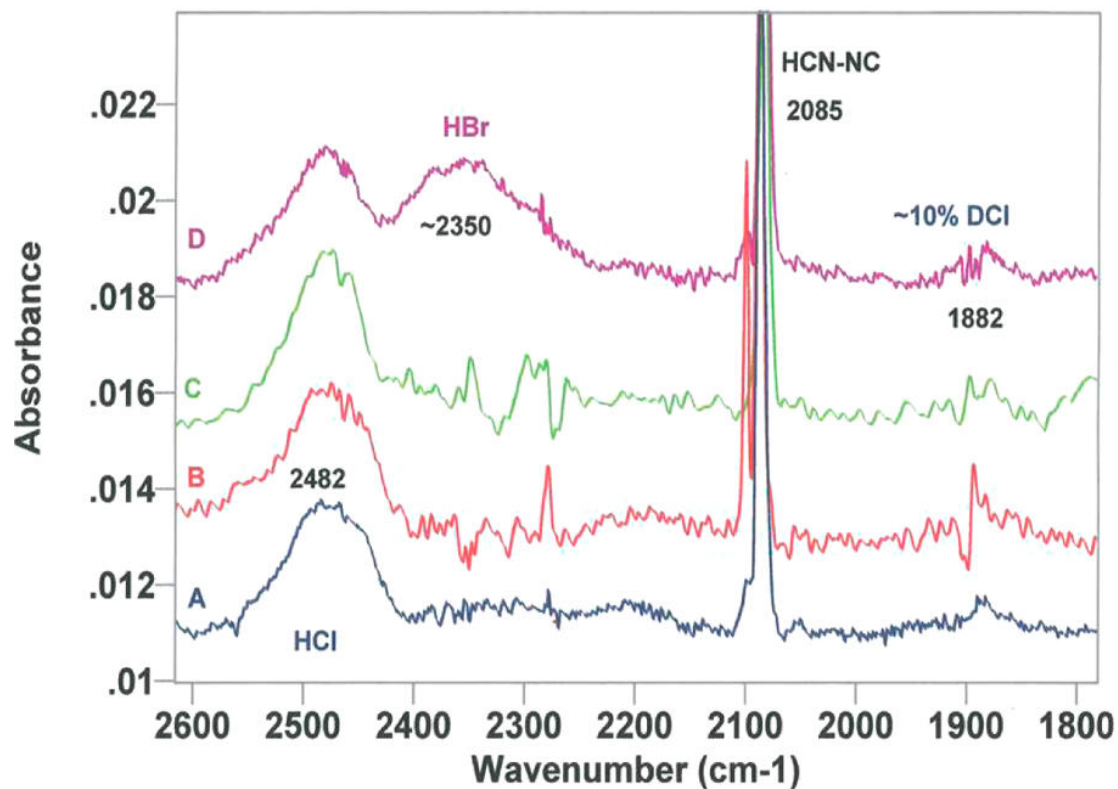
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**Fig. 1.** Fig,1 HX spectra in clathrate hydrates.

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