

Evaluation of Depth Profiling Using Laser Resonant Desorption as a Method To Measure Diffusion Coefficients in Ice

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Diffusion of gases in ice is involved in cloud, snow, and ice core chemistry, but few data exist on the relevant diffusion coefficients. A novel method to measure diffusion coefficients in ice has recently been proposed by Livingston et al. (*Anal. Chem.*, 2000, 72, 5590–5599). It is based on depth profiling of doped ice crystals epitaxially grown on Ru(001) by laser resonant desorption (LRD). Using this method, Livingston et al. obtained a value of the diffusion coefficient of the HCl hydrate in ice at 190 K of about $5 \times 10^{-11} \text{ cm}^2/\text{s}$. We argue here that this value is many orders of magnitude higher than what could be expected from literature values, which are not reported in sufficient detail by Livingston et al. We investigate the possibilities that their high value could be due to (1) diffusion in defects in the ice, which would be present in very high concentrations because of the ice growth method; and (2) the fact that diffusion of high concentrations of HCl in ice at 190 K forms an amorphous HCl:H₂O solid mixture, where HCl diffusion is fast. We present new infrared spectroscopic data on solid HCl:H₂O mixtures that confirm that such mixtures can indeed be formed in an amorphous state at 190 K. Our proposed interpretation is that by depositing large amounts of HCl on epitaxially grown ice, Livingston et al. created a superficial amorphous binary mixture and that fast diffusion of HCl in the ice, possibly accelerated by a high defect density, produced an amorphous HCl:H₂O mixture. We conclude that the processes studied by Livingston et al. are different from those involved in the atmospheric and cryospheric sciences, and that their data, obtained by depth profiling using LRD, probably cannot be applied to those fields.

OBJECTIVES

Understanding diffusion of species such as HCl in ice is important to elucidate aspects of atmospheric chemistry such as stratospheric ozone depletion¹, ice core analysis², and snow chemistry.^{3–4} Yet, few data are available on the diffusion of atmospheric trace gases in ice.

In a recent paper, Livingston et al.⁵ described a novel, elegant method to measure diffusion coefficients in ice films. Briefly, an ice film is grown epitaxially on a Ru(001) crystal. Doping by diffusion from the surface of the ice film is then performed, and the diffusion profile is measured by laser resonant desorption (LRD) depth-profiling using a radiation wavelength of 2.94 μm . The desorbed molecules are analyzed by a quadrupole mass spectrometer. The main stated purpose of this novel method is to provide data to the atmospheric and cryospheric sciences. Livingston et al.⁵ used LRD to measure the diffusion coefficient, D_{HCl} , of what is referred to as “HCl hydrate” in ice and obtain a value $D_{\text{HCl}} \approx 5 \times 10^{-11} \text{ cm}^2/\text{s}$ at $T = 190 \text{ K}$. They concluded that this result illustrates the potential of LRD depth-profiling to study diffusion in ice.

The first purpose of this paper is to note, after a brief review of Livingston et al.'s methods, that their value is much higher than previous measurements, some of which they do not discuss. Our second goal is to investigate the cause of these large disagreements and to propose (1) that the structure of the ice used is different from that of atmospheric ice and (2) that the dopant concentrations used are too high to duplicate atmospheric processes. The combination of both effects leads to our conclusion that although these measurements are probably interesting to study, some aspects of the physical chemistry of epitaxially grown ice, that is, their application to atmospheric problems, may not be possible.

DEPTH PROFILING METHOD AND RESULTS

To measure D_{HCl} , Livingston et al.⁵ used a sandwich structure. They first grew epitaxially a 10- μm -thick ice film, then deposited an unspecified thickness of HCl at 120 K and deposited a 7- μm -thick extra ice layer to encapsulate the HCl. Their LRD depth profiling, using a laser-pulse energy of 0.61 mJ, has a depth resolution of 0.5 μm . The profile of the HCl sandwich prior to diffusion (their Figure 12) shows that the HCl signal is concentrated on one pulse, suggesting that the HCl thickness is $\leq 0.5 \mu\text{m}$. There is, however, a weak signal on laser shots both before and after the strong HCl signal, suggesting that the HCl thickness might be $\approx 0.5 \mu\text{m}$. The maximum HCl signal is ~ 1200 counts,

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about 10 times as strong as the signal coming from a 0.1- μm -thick H_2^{18}O layer. Although the mass spectrometer sensitivity to HCl and H_2^{18}O are certainly different, these observations appear to be consistent with a HCl deposit thickness of the order of 0.5 μm and in any case, probably thicker than 0.05 μm . The HCl signal is assigned to a HCl hydrate interlayer, suggesting that a mixed HCl– H_2O layer is formed by depositing pure HCl on ice, but the structure of this layer is not detailed.

Diffusion is then allowed to take place at 190 K. Gaussian depth profiles are obtained after 120 and 300 s. By fitting both profiles to the appropriate diffusion equation, D_{HCl} values of $(4.8 \pm 1.5) \times 10^{-11}$ and $(5.1 \pm 1.6) \times 10^{-11} \text{ cm}^2/\text{s}$ are obtained. These values are assigned to the HCl hydrate diffusion coefficient, not to D_{HCl} , but no details are given regarding the meaning of “HCl hydrate”. There are 4 known crystalline hydrates of HCl, the hexa-, tri-, di-, and monohydrates^{6,7} and it is not specified which one is involved. Note, by the way, that the tetrahydrate, which is mentioned by some authors,^{8,9} does not exist. The mechanism of diffusion is not discussed, and it may be of interest to know whether the HCl hydrate diffuses as the $\text{HCl}-n(\text{H}_2\text{O})$ entity, or whether the diffusion of HCl results in the transformation of ice into hydrates of HCl.

Comparison of Laser Depth Profiling Results with Literature Values. Livingston et al.⁵ briefly review part of the literature on the subject and state that “Quantitative measurements of diffusion in ice are almost non existent for species other than H_2O isotopes”. They mention that “HCl diffusion coefficients have varied dramatically and range from $D_{\text{HCl}} \approx 10^{-9} \text{ cm}^2/\text{s}$ to $D_{\text{HCl}} \approx 10^{-13} \text{ cm}^2/\text{s}$ at $T \approx 185 \text{ K}$.” They also note that D_{HNO_3} values “were ≈ 100 times greater than HCl at the same temperature”.

However, values lower than those are found in the literature, and the temperatures at which they were measured or determined were often around 250 K, not 185 K. Mentioning the correct temperature is important when comparing values, because diffusion coefficients decrease with decreasing temperature. Wolff et al.¹⁰ report $D_{\text{HCl}} < 10^{-13} \text{ cm}^2/\text{s}$ at 253 K. Barnaal and Slotfeld-Ellingsen¹¹ report $D_{\text{HCl}} = 4 \times 10^{-9} \text{ cm}^2/\text{s}$ at 258 K. Dominé et al.³ and Dominé and Thibert⁴ report values between $\sim 10^{-12}$ and $10^{-11} \text{ cm}^2/\text{s}$ in the range $T = 248\text{--}255 \text{ K}$. Krishnan and Salomon¹² obtained values between 2.2×10^{-8} and $16 \times 10^{-8} \text{ cm}^2/\text{s}$ in the range $T = 255\text{--}269 \text{ K}$. Koehler et al.¹³ report $D_{\text{HCl}} = 10^{-12} \text{ cm}^2/\text{s}$ at 158 K from measurements on microcrystalline ice films. Horn and Sully¹⁴ obtained $D_{\text{HCl}} = 1.5 \times 10^{-11} \text{ cm}^2/\text{s}$ at 150 K using polycrystalline ice films probably similar to those used by Koehler et al.¹³ Thibert and Dominé¹⁵ performed a detailed study of the diffusion of HCl in ice and obtained by serial sectioning 27 diffusion profiles of HCl in large single ice crystals that yielded

D_{HCl} values in the range of 1.1×10^{-12} to $1.45 \times 10^{-11} \text{ cm}^2/\text{s}$ in the range $T = 238\text{--}265 \text{ K}$. However, their measurements were perturbed by the presence of defects, probably small angle boundaries, that acted as diffusion short circuits, and their values must, therefore, be considered as upper limits.

Thibert and Dominé¹⁵ stressed the difficulty of obtaining coefficients of heterodiffusion in ice and pointed out many artifacts in previous studies. For example, they suggested that the high D_{HCl} values of Krishnan and Salomon¹² were due to surface diffusion, that the low value (which is only a lower limit) of Wolff et al.¹⁰ is due to an insufficient detection limit that prevented them from observing diffusion, and that the high value of Koehler et al.¹³ applied to polycrystalline ice films, in which diffusion in grain boundaries and on the grains surfaces that extend inside the macroscopic surface, could take place. The same suggestion may also apply to the result of Horn and Sully.¹⁴

Recently, Fluckiger et al.¹⁶ obtained several values of D_{HCl} at 190 K using several methods to prepare ice samples. They obtained $D_{\text{HCl}} = (1\text{--}4) \times 10^{-14} \text{ cm}^2/\text{s}$ for single-crystal ice, $5.6 \times 10^{-13} \text{ cm}^2/\text{s}$ for ice condensed from the gas phase, and $\sim 2 \times 10^{-12} \text{ cm}^2/\text{s}$ for ice obtained by the rapid freezing of liquid water. These authors mention that they lacked optical methods to characterize their ice samples, but their data show that changing the mode of preparation of the ice can result in D_{HCl} values varying by a factor of about 100.

Regarding D_{HNO_3} , Livingston et al.⁵ omit the detailed study of Thibert and Dominé¹⁷ who obtained 18 diffusion profiles of HNO_3 in large single ice crystals, and derived D_{HNO_3} values in the range 1.1×10^{-11} to $2.6 \times 10^{-10} \text{ cm}^2/\text{s}$ in the range $T = 238\text{--}265 \text{ K}$, i.e., $\sim 3\text{--}100$ times greater than D_{HCl} values at the same temperature.

Most D_{HCl} values available in the literature are, therefore, in the range 10^{-12} to $10^{-9} \text{ cm}^2/\text{s}$ at temperatures usually above 238 K. At lower temperatures, D_{HCl} is expected to be much lower in single ice crystals. Dominé et al.,¹⁸ in fact, pointed out that from their measurements and using a diffusion activation energy of 50 to 70 kJ/mol, a value of $D_{\text{HCl}} \approx 10^{-16}$ to $4 \times 10^{-18} \text{ cm}^2/\text{s}$ should be expected at $T = 190 \text{ K}$. Fluckiger et al.¹⁶ found D_{HCl} in the $10^{-14} \text{ cm}^2/\text{s}$ range at 190 K, but this was an indirect measurement obtained by modeling HCl uptake by ice. Moreover, no ice characterization was performed, and defects that could accelerate diffusion may have been present. Fluckiger et al.¹⁶ themselves point out that “because of the large uncertainties, these values have to be considered as upper limits”.

The value obtained by Livingston et al.,⁵ $D_{\text{HCl}} \approx 5 \times 10^{-11} \text{ cm}^2/\text{s}$ at $T = 190 \text{ K}$, therefore appears to be orders of magnitude higher than what could be expected from previous measurements, and we will attempt to suggest some reasons that may explain such high values.

Interpretation of High D_{HCl} Values Obtained by Depth Profiling. Two possibilities that may contribute to the actual explanation will be explored: (1) diffusion takes place essentially in defects, not in the ice crystalline lattice; and (2) the high HCl concentrations employed perturbed the ice lattice, and the solid may not even have been ice.

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Diffusion in Defects. Epitaxial growth on a substrate that has a 4% lattice mismatch with ice will generate dislocations near the interface. Lattice mismatch is not the only factor that could lead to perturbations of the ice structure. Held and Menzel¹⁹ have shown that the adsorption of a water bilayer on Ru(001) led to a striped structure, with gaps in the H₂O coverage of the Ru surface. Such gaps, which are observed in the [010] direction every 6.5 Ru lattice constants, are very likely to lead to defects when subsequent layers are adsorbed. Thus, both the misfit and the striped structure will lead to a very high defect density near the interface. It is difficult to predict the impact of these defects on the surface of a 10- μ m ice film, but the possibility that these will lead to the emergence of dislocations, small angle boundaries, or even grain boundaries on the surface seems a reasonable possibility. In addition, the orientation of Ru crystals is done with an accuracy of about 0.5°^{20,21} so that steps are present that can also generate defects.

Diffusion in defects is much faster than in the crystalline lattice, and diffusion profiles in crystals with defects will be the result of a combination of both processes. Harrison²² separates 3 diffusion regimes in which different equations should be used to extract diffusion coefficients. The C diffusion regime applies when $(Dt)^{1/2} \ll h$, where h is the thickness of the defect (dislocation, grain boundary...). This means that the diffusion distance in the crystalline lattice is much less than the defect thickness. In this case, a diffusion profile will yield the diffusion coefficient in the defect. Using $D_{\text{HCl}} = 10^{-16}$ cm²/s at 190 K (upper estimate of Dominé et al.,¹⁸ obtained by extrapolating data from higher temperature using an activation energy of 50 kJ/mol), $t = 100$ s, and $h = 10^{-7}$ cm, one finds that $(Dt)^{1/2} = h$. Using the lower estimate of Dominé et al.,¹⁸ $D_{\text{HCl}} = 4 \times 10^{-18}$ cm²/s at 190 K, obtained using a diffusion activation energy of 70 kJ/mol, one finds that $(Dt)^{1/2} = h/5$, so that the C regime conditions are met.

If the range of values suggested by Dominé et al.¹⁸ at 190 K is correct, it then appears plausible that the conditions of Livingston et al.⁵ are in, or close to, the C diffusion regime. If this is indeed the case, then what Livingston et al.⁵ measured is the diffusion coefficient in the defects, D'_{HCl} .

How D_{HCl} and D'_{HCl} are related is unknown. In metals, D'/D is usually in the range 10^3 – 10^7 (refs 23,24), depending on the system considered and the proximity of the melting point. 190 K is far from the melting point, and if data obtained on metals has any validity here, a large value of $D'_{\text{HCl}}/D_{\text{HCl}}$ would be expected. This would then be consistent with $D'_{\text{HCl}} \approx 5 \times 10^{-11}$ cm²/s at $T = 190$ K, but D_{HCl} may be $\sim 10^{-17}$ cm²/s or lower.

In further support of the hypothesis that diffusion takes place in defects, we note that the self-diffusion of HDO in ice, studied by the same group²⁵ using a similar method and ice grown on Ru(001) yielded a diffusion coefficient at 160 K that is at least 150

times higher than the values derived from serial sectioning of large single ice crystals. The authors suggested that their near-surface measurements may be indicative of diffusion in the quasi-liquid layer of ice, but recent measurements using atomic force microscopy²⁶ indicate that this layer is essentially non-existent below ~ 233 K. Thus, in that self-diffusion study, high defect concentrations that may be intrinsic to their method may also have affected their results.

Nature of the Diffusion Medium. To obtain their diffusion profiles, Livingston et al.⁵ use a pure, or highly concentrated, HCl deposit formed at $T \leq 120$ K and encapsulated between two ice layers. It is not possible to determine the absolute HCl concentration of their diffusion profiles from the data shown. It is known, however, that above 110 K, HCl adsorbed on ice dissociates into Cl⁻ and H₃O⁺ (ref 27). Molecular HCl can be maintained on the ice surface at T up to 120 K, or even more, if a sufficient HCl pressure is applied,⁹ but even under those conditions, dissociated HCl predominates. Banham et al.⁹ showed that the HCl–H₂O mixture formed by exposing ice to high HCl pressures at 140 K resulted in the formation of an amorphous binary mixture, often referred to as amorphous mono-, di-, tri-, and hexahydrates. These names are not adequate, because amorphous mixtures need not be stoichiometric, but we will retain them here for consistency with previous publications. In any case, it is very likely that Livingston et al.⁵ formed an amorphous HCl–H₂O mixture by depositing HCl on their ice at $T \leq 120$ K. Considering the work of Banham et al.⁹ and the HCl–H₂O phase diagram^{6,7,15}, the most likely stoichiometry of their amorphous mixture is 1:1.

The process observed by Livingston et al.⁵ then appears to be interdiffusion of H₂O and HCl between two phases: ice and a 1:1 H₂O:HCl amorphous mixture. Diffusion of HCl into ice can lead to the formation of a solid solution of HCl in ice, the formation of crystalline HCl hydrates, or the formation of amorphous HCl–H₂O mixtures of various compositions. These 3 possibilities are tested below.

Thibert and Dominé¹⁵ have studied in detail the solid solution of HCl in ice and have proposed a phase diagram. They concluded by extrapolating data obtained at $T \geq 238$ K that the maximum solubility of HCl in ice at thermodynamic equilibrium was about 6×10^{-5} mole fraction, reached on a univariant line in the T – P_{HCl} (=HCl partial pressure) phase diagram that starts at $T = 200$ K and extends to lower temperatures. A change in the incorporation mechanism of HCl in ice over the extrapolated temperature range is possible, and this may lead to an error in the maximum solubility value, but it is difficult to imagine that this error could reach a factor of 10.

It is important to evaluate the HCl concentrations observed by Livingston et al.⁵ in their doped ice. As mentioned above, Livingston et al.'s HCl deposit probably had an HCl mole fraction of ~ 0.5 . If this is indeed the case, and if the deposit is 0.5 μ m thick, then their signal of 1200 counts may be used as a semiquantitative calibration. Their profile after 120 s of diffusion has a concentration at half the maximum of their Gaussian diffusion curve of the order of 0.05 mole fraction. Of course, the actual concentration might be significantly lower. But even then, this is much greater than the maximum solubility of HCl in ice of

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6×10^{-5} mole fraction, and reconciling this value with that of Livingston et al.⁵ requires an unrealistic combination of errors and incorrect assumptions. If a solid solution is formed in the experiment of Livingston et al.,⁵ then it must be very supersaturated. The implications are that it is very unlikely to form for thermodynamic reasons, because there would be no driving force to supersaturate the ice. Even if it did form, the incorporation site of HCl would probably be different from that of the equilibrium solid solution, which would lead to a concentration-dependent diffusion coefficient.

The profiles of Livingston et al.⁵ do not show any indication of such a dependence. It is true that since their HCl detection limit is not known, it is possible that the low HCl mole fractions characteristics of the equilibrium solid solution either form an unimportant part of their diffusion profiles, or were not at all detected. In any case, we conclude that the formation of a solid solution of HCl in crystalline ice is unlikely to have taken place in the experiments discussed here.

Interdiffusion of H₂O and HCl between ice and a H₂O:HCl mixture may lead to the formation of one or several HCl hydrates of lower and lower HCl content as the distance from the original HCl layer is increased. Banham et al.⁹ observed that annealing amorphous HCl–H₂O mixtures at $T < 170$ K could lead to the formation of the hexahydrate of HCl, depending on the initial composition of the amorphous mixture. The formation of a stoichiometric crystalline phase would not result in a Gaussian diffusion profile, however. Indeed, in such a system consisting of several crystalline phases, diffusion will lead to the equalization of the chemical potential of the diffusing species, but not to the equalization of the concentrations.²⁸ Thus, one would then expect a sharp discontinuity in the diffusion profile on one side of which would be ice and on the other side of which would be the hexahydrate. It is also possible that successive hydrates would form, with a HCl concentration discontinuity at each boundary between successive hydrates. This is frequently observed in metals and alloys.²⁸ Again, this is not observed by Livingston et al.,⁵ and we conclude that crystalline HCl hydrates are not formed in their experiments.

Banham et al.⁹ observed that exposing crystalline ice to HCl at 140 K led to the formation of an amorphous HCl–H₂O mixture of a finite thickness. Thus, the interaction of HCl with ice can lead to the formation of an amorphous mixture, and diffusion of HCl in ice has to take place at some point to lead to the formation of a new solid of finite thickness. Annealing at 160 K leads either to the formation of the crystalline hexahydrate, with the release of some of the HCl to the gas phase, or to the preservation of an amorphous HCl–H₂O mixture, depending on the HCl pressure that had been applied.⁹ From the data of Banham et al.,⁹ it does not seem certain that an amorphous mixture could be maintained at 190 K. However, transitions between amorphous and crystalline phases are thermally activated and depend on conditions that could, for example, influence crystal nucleation. Banham et al. used microcrystalline ice films that were exposed to various HCl pressures, but Livingston et al.⁵ used epitaxially grown ice crystals, with HCl encapsulated between 2 ice layers. These different

conditions may have led to different temperatures for the amorphous-to-crystalline transition in HCl–H₂O mixtures.

To illustrate this possibility, we studied the crystallization of HCl–H₂O mixtures under a third set of conditions. HCl–H₂O gaseous mixtures of various molar ratios were condensed on a silicon window at 190 K and studied by infrared spectroscopy. Figure 1 shows the spectra recorded during the growth of a HCl–H₂O film from the condensation of a HCl:H₂O 1:50 gas mixture. These spectra are not those of crystalline HCl hydrates.⁸ Figure 2 compares the spectrum obtained after a deposition time of 53 min to those reported by Delzeit et al.⁸ and that are attributed to amorphous HCl:H₂O mixtures of molar ratios 1:4 and 1:6. From this comparison, we deduce that we formed an amorphous HCl mixture of composition intermediate between 1:4 and 1:6. From these data, we believe that conditions can be found under which amorphous HCl hydrates can be maintained at 190 K for time scales greater than those involved in Livingston et al.'s experiments.

To sum up our interpretation, we then suggest that by depositing HCl on epitaxially grown ice films at $T < 120$ K, Livingston et al.⁵ formed an amorphous HCl–H₂O mixture on top of the ice. This mixture was then encapsulated, which prevented the degassing of HCl when the film was heated to 190 K to observe diffusion. At 190 K, high concentrations of HCl diffused in ice to form an amorphous, or at least highly disordered, HCl–H₂O mixture. Diffusion was probably facilitated by a high defect density. This is suggested by the results on H₂O self-diffusion obtained with a similar method,²⁵ but ice disordering by HCl may also have played a role to produce the observed very fast diffusion. Obtaining IR spectra of the ice–HCl mixtures that were used would provide a good test of these suggestions. We also suggest that a quantitative determination of the actual HCl concentration present in the samples would yield useful data.

Relevance of the Depth Profiling Experiments to Atmospheric Problems. The physical and chemical conditions present in Livingston et al.'s experimental setup are very different from those prevalent in the atmosphere and cryosphere. Dislocation densities in atmospheric ice are very low, usually $<10^2$ cm⁻², but in glacier ice, this density is of the order of 10^4 cm⁻² (ref 29). Exceptionally, dislocation densities as high as 10^9 cm⁻² have been locally observed in heavily deformed crystals in deep ice cores,³⁰ but this is atypical, so that the density of dislocations, and of defects in general, are certainly much lower in natural ice than in epitaxially grown ice.

P_{HCl} values above, and concentrations in, natural ice are also much lower than those used by Livingston et al.⁵ Typical P_{HCl} values near the ground and in the lower troposphere are of the order of a few times 10^{-6} Pa (refs 3,31), and similar values are observed in the polar stratosphere.³² Cl⁻ mole fractions in snow is of the order of 10^{-8} (refs 3, 33), and HCl (measured as Cl⁻ by ion chromatography) in natural snow is usually undersaturated with respect to atmospheric HCl. The phase in which HCl is present in atmospheric ice is then a solid solution of HCl in ice,

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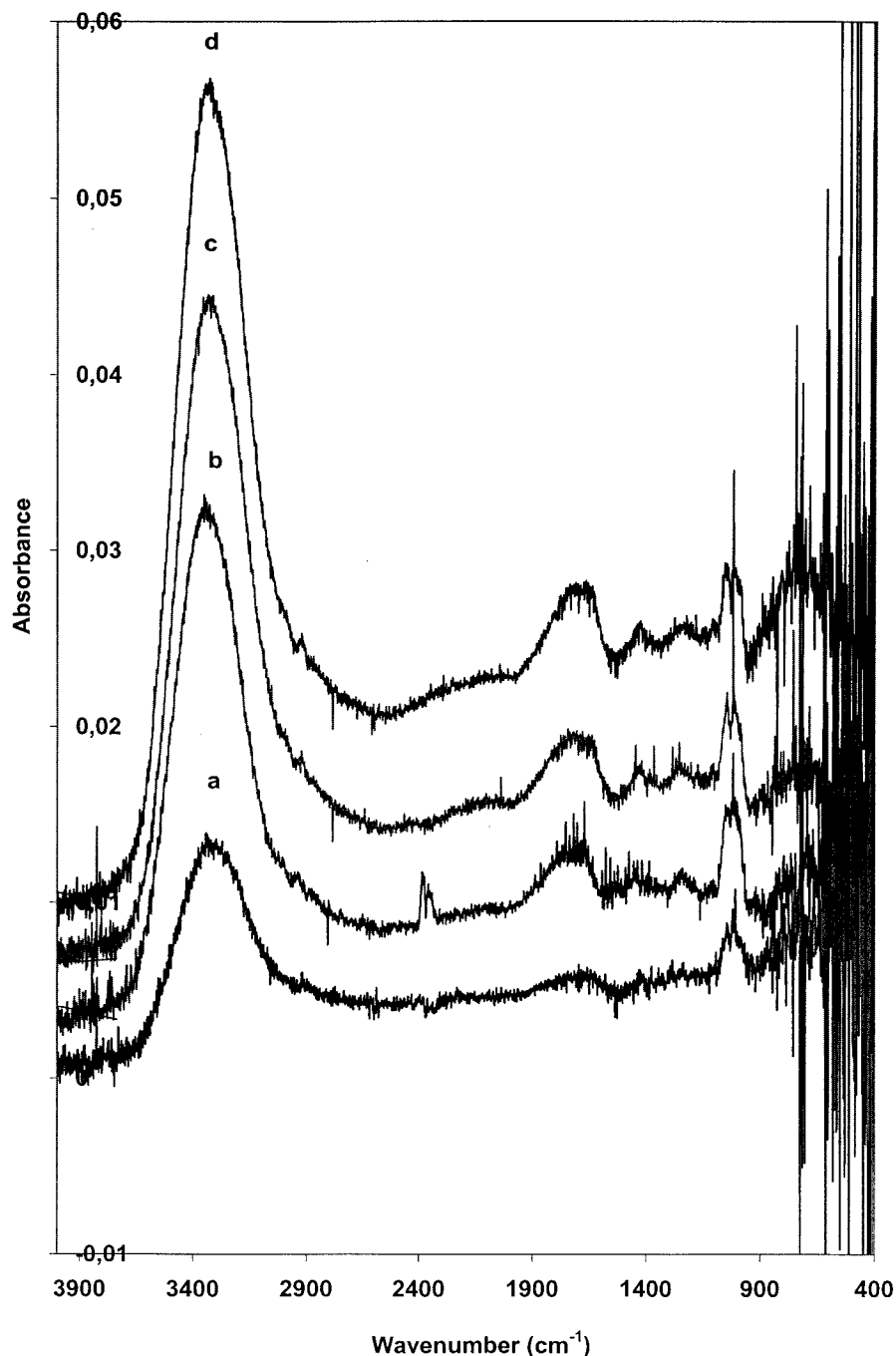


Figure 1. Infrared spectra of a solid formed by the condensation of a HCl:H₂O gaseous mixture of composition 1:50. The solid is growing on a Si window at 190 K. Growth time: (a) 2 min, (b) 11 min, (c) 19 min, and (d) 53 min.

and HCl occupies its thermodynamically stable crystallographic site, which Thibert and Dominé¹⁵ argued was interstitial. The partial pressures used by Livingston et al.⁵ are not specified, but local pressures above the surface during gas deposition are doubtless higher than atmospheric values. For the reasons detailed in the previous section, concentrations obtained by Livingston et al.⁵ in their ice are, beyond a reasonable doubt, much higher than those observed under atmospheric conditions, and they probably did not form a solid solution of HCl in ice. This is because (1) the low concentrations of HCl in an ice solid solution seem to be below their detection limit, (2) the diffusion coefficient measured is too high to be that of HCl in the ice crystalline lattice,

and (3) IR spectroscopic data strongly suggest that they formed an amorphous HCl–H₂O mixture.

To the best of our knowledge, HCl hydrates or HCl–H₂O amorphous mixtures have never been observed in the atmosphere or the cryosphere. Results obtained by the formation of amorphous or crystalline hydrates of HCl by fast diffusion of high concentrations of HCl into epitaxially grown ice, probably accelerated by a high defect density, then cannot be used to understand atmospheric or cryospheric processes.

We suggest that, at present, methods used in previous studies are more suited to yield data applicable to atmospheric or cryospheric processes. Such methods include the serial sectioning

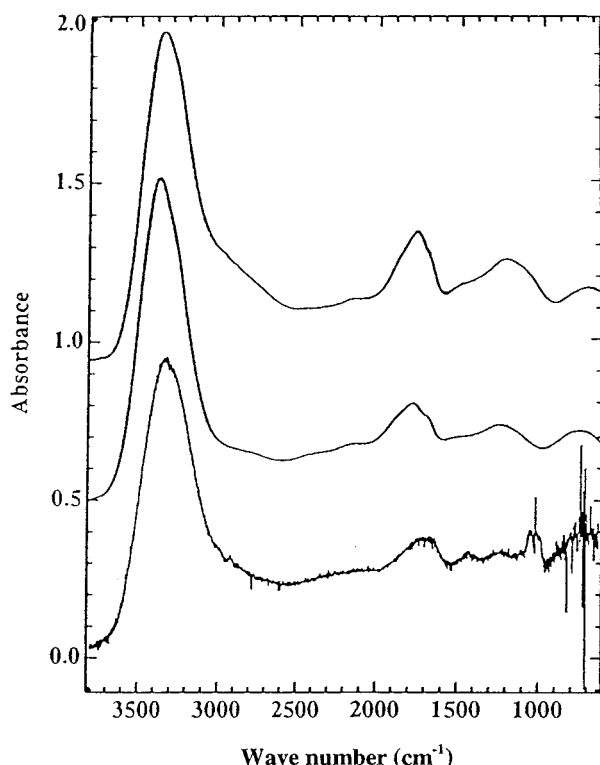


Figure 2. Comparison of the infrared spectra of solid amorphous HCl:H₂O mixtures of compositions 1:4 (top) and 1:6 (middle), after Delzeit et al.,⁸ with spectrum (d) of Figure 1 (bottom).

of large single ice crystals exposed to P_{HCl} sufficiently low to guarantee that the system is in the solid solution domain. Dominé et al.³ and Dominé and Thibert⁴ have used the D_{HCl} and D_{HNO_3} values obtained with such a method to discuss chemical equilibria between snow and the atmosphere. They found that the disequilibrium between Cl^- in snow and P_{HCl} in the atmosphere was consistent with their D_{HCl} values. Similarly, Thibert and Dominé¹⁷ mentioned that their D_{HNO_3} values were consistent with the observed diffusion of the NO_3^- signal in ice cores. On the contrary,

the very high value of D_{HCl} obtained by Livingston et al.⁵ at 190 K imply a yet higher value at temperatures typical of ice sheets or the lower troposphere. These high values cannot be reconciled with the observation that Cl^- in snow is not in equilibrium with the atmosphere.

Livingston et al.⁵ state that microtoming or lathing to obtain serial sections is prone to contamination effects, but this issue has been specifically addressed, and it has been demonstrated that careful work totally eliminated such contamination.³⁴ It is true that doping large ice crystals with gases takes days or weeks, and that defects in large ice crystals can perturb measurements, and the method does have its weaknesses; however, it yields data that appear useful to solve atmospheric and cryospheric problems, although the error bars on some of those data can sometimes be large. Moreover, the ice used in this method seems to be similar to atmospheric ice, and this is a crucial point, considering the impact of the ice structure on the measured D values.¹⁶ The clear advantage of LRD is that doping takes only a few minutes, and this technique may have a great potential. At this point, however, we suggest that significant improvements in the characterization of the phases formed and in the detection limit are necessary before this method can yield data that can be used in the atmospheric and cryospheric sciences.

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