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The HCl hexahydrate: RAIR spectra and theoretical investigation

Ismael K. Ortega ^{a,b,*}, Rafael Escribano ^a, Delia Fernández-Torre ^a, Víctor J. Herrero ^{a,*}
Belén Maté ^a, Miguel A. Moreno ^a

^a Instituto de Estructura de la Materia, (CSIC), Serrano 123, Madrid, Spain

^b Departamento de Química Física y Analítica, Universidad de Jaén, Pasaje Las Lagunillas, 23071 Jaén, Spain

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Abstract

A combined theoretical and experimental study of crystalline hydrogen chloride hexahydrate $\text{HCl} \cdot 6(\text{H}_2\text{O})$ has been performed. This species is stable in the range of atmospheric pressure and temperature, and some apparent discrepancies existed between previous crystallographic and vibrational studies. This work presents theoretical calculations based on the SIESTA method that allow a refinement of the geometrical structure and a prediction of the vibrational modes of the crystal. The experimental part consists in new reflection–absorption infrared spectra, that are analysed and assigned with the help of the theoretical results, and compared to previous assignments of infrared transmission spectra. This research supports the equivalence of the samples prepared by different methods in previous experimental investigations.

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1. Introduction

The $\text{HCl}/\text{H}_2\text{O}$ solid system plays an important role in the physical chemistry of the stratosphere and of the upper troposphere. Mixtures of HCl and water can give rise to different solids, amorphous and crystalline, of variable composition depending on formation conditions [1,2]. The processes of HCl uptake by ice, the associated mechanisms of ionisation and solvation and the heterogeneous chemistry with atmospheric relevant compounds have been studied by many groups over the last 15 years (see e.g. [1–13] and references therein).

X-ray diffraction measurements have allowed the identification of four crystalline hydrates with one [14], two [15], three [16] and six [17] water molecules per HCl molecule. The structural constituents of these crystals are Cl^- anions, various forms of hydrated protons, and H_2O molecules. Vibrational spectra of HCl hydrates

in the mid IR have been measured since the 1950s [18]. In 1973, Gilbert and Sheppard [19] reported a systematic study of a series of crystalline hydrates of HCl and gave an interpretation of the observed bands in terms of the vibrations of H_2O , H_3O^+ and H_5O_2^+ units; however, a wrong identification of the 1:1 amorphous solid led to an incorrect assignment of the spectra of the lowest hydrates as shown in later spectroscopic studies performed by Devlin and co-workers in the nineties [20,21]. After a certain controversy [6,19,21], characteristic IR spectra have been assigned to the four HCl hydrates just mentioned [11,13].

Among the different hydrates, the hexahydrate is the one with stability conditions closer to the range of temperature and pressure of atmospheric relevance [1,2,22]. Its X-ray structure was determined by Taesler and Lundgren [17], who characterized the crystal as $\text{H}_3\text{O}_4^+\text{Cl}^- \cdot 2(\text{H}_2\text{O})$ from consideration of the positions of the H atoms and of the hydrogen-bond distances between the water molecules. Ritzhaupt and Devlin [20] provided the first IR spectrum of a sample attributed to $\text{HCl} \cdot 6(\text{H}_2\text{O})$, together with an empirical band

* Corresponding authors. Fax: +34915855184.

E-mail addresses: ikortega@iem.cfmac.csic.es (I.K. Ortega), vherrero@iem.cfmac.csic.es (V.J. Herrero).

assignment based on the vibrational modes of the water molecules and hydronium ions. However, this hydrate is difficult to nucleate and, taking into account the fact that the samples used in the X-ray and IR experiments were generated by different procedures, there remain some doubts about the actual nature of the solid characterized by its IR spectra alone [2]. The clarification of this point is an important issue, especially considering that IR spectra are often used for the identification of the different hydrates in atmospheric, thermodynamic or kinetic studies.

We have undertaken the present investigation as an attempt to shed more light on this problem. On the one hand, an *ab initio* study of the solid has been performed using the SIESTA method and computer programs. This allows a refinement of the geometrical structure of the crystal and a prediction of its vibrational modes. On the other hand, we have prepared samples of annealed HCl hexahydrate and recorded its spectrum using reflection–absorption infrared spectroscopy (RAIRS). The combination of these two methods provides an appropriate tool for the analysis of the spectrum, and, as far as we know, has never been applied to this species.

2. Theoretical method

The theoretical method employed in this investigation has been used in previous works [23–25]. It is based on the SIESTA suite of programs, a method recently developed for the study of periodic systems of large size. A detailed description can be found elsewhere [26,27] and only the most important features are briefly given here. The program, based on DFT theory, optimizes the geometry of a number of molecular species within a simulation cell, by a method that scales linearly in time and computer memory with the number of atoms in the cell. The wave functions are constructed as linear combinations of atomic orbitals (LCAO). Norm conserving pseudo-potentials are used for the core electrons, and valence wave functions are replaced by pseudo-wave functions that do not oscillate markedly in the core region. The PBE functional [28] and the conjugated gradient method were used for the optimization with a double-zeta polarized (DZP) basis functions, and a cut-off radius of 100 meV for the localization of the orbitals. The Hartree and exchange correlation potentials were calculated at the grid points of a mesh, with a mesh cut-off value of 150 Ry.

The starting coordinates for the calculation were taken directly from the X-ray data [17]. The crystal is orthorhombic with unit cell dimensions $a = 6.330$ Å, $b = 6.453$ Å and $c = 17.898$ Å. The simulation was performed keeping the cell dimensions fixed to the experimental values. After optimization of the equilibrium

geometry of the molecular species contained in the cell, atomic forces were evaluated, and the vibrational frequencies and the corresponding atomic displacements per vibrational mode were calculated. The frequencies were estimated at the gamma point only, which has proved to be a good approximation in similar systems [24]. The calculated atomic Cartesian displacements were visualized with MOLDEN [29] software. They provided an excellent tool for the assignments.

3. Experimental

The experimental set-up has been described elsewhere [30–32] and only the details relevant to the present work will be given here. The measurements were performed in a cylindrical chamber evacuated by a turbo-molecular pump. The chamber contained an Al deposition substrate, whose temperature was controlled by balancing the heat flow between a liquid nitrogen Dewar and a power transistor. Pressure and gas composition within the deposition chamber were monitored with a capacitance manometer, a cold ionisation gauge and a quadrupole mass spectrometer (INFICON, Transpector-2).

An amorphous H_2O layer was formed by exposing the substrate, held at 97 K, to a pressure of water vapour of 1.0×10^{-4} m bar (as measured with the capacitance manometer) for about 6 min. Under these (fast) deposition conditions the ice formed is expected to be very porous. The ice film was then exposed to a pressure of 1.0×10^{-4} m bar HCl for about 3 min. This created an excess amount of HCl adsorbed on the surface of ice.

The temperature of the substrate was then gradually raised to 180 K, where the sample was annealed for 50 min to complete crystallization. Most of the more volatile HCl in excess was evaporated during this time. An approximate pressure of 2×10^{-6} m bar HCl was maintained in the chamber until the end of the annealing. These conditions are within the reported stability range of the HCl hexahydrate [1,2,22]. The precise thickness of the $\text{HCl} \cdot 6(\text{H}_2\text{O})$ layer formed is not known, but it is estimated to be in the hundreds of nanometers range.

RAIR spectra were recorded with a FTIR spectrometer Bruker IFS66. The IR light was focused on the sample by means of a KBr lens at an incidence angle of 75° and the reflected IR radiation was focused with a curved mirror onto a Mercury Cadmium Telluride (MCT) detector cooled with liquid nitrogen. Each spectrum was obtained by addition of 512 scans, recorded with an apodized resolution of 8 cm^{-1} .

4. Results and discussion

The optimized atomic structure within the unit cell of the $\text{HCl} \cdot 6(\text{H}_2\text{O})$ crystal is shown in Fig. 1. In agree-

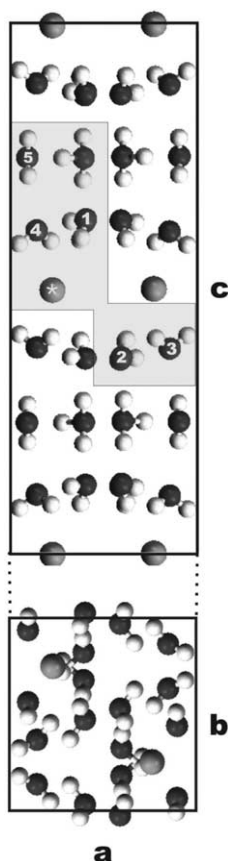


Fig. 1. Schematic atomic disposition in the refined structure of the $\text{HCl} \cdot 6(\text{H}_2\text{O})$ unit cell [17] ($a = 6.330 \text{ \AA}$, $b = 6.453 \text{ \AA}$, and $c = 17.898 \text{ \AA}$). See text and Table 1 for a discussion of the numbered molecules.

ment with the X-ray structure, the hydronium ions of this refined geometry are hydrogen bonded to three water molecules in a pyramidal arrangement giving rise to a H_9O_4^+ symmetrical complex. Besides the H_3O^+ group there are five water molecules within the irreducible unit, numbered in the figure. Of these, number 5 is unique, as it is linked to H_3O^+ with the strongest hydrogen bond. Numbers 3 and 4 are equivalent, and they have the weakest bonding, to units 1 and 2, respectively. Numbers 1 and 2 are also equivalent, and they support three hydrogen bonds, to H_3O^+ , water units 3 and 4, and the chlorine anion.

The interatomic distances and angles corresponding to the geometry optimized in the present calculations are compared with those from the X-ray measurements of [17] in Table 1. Values are quoted only for the species contained in an irreducible chemical unit, formed by a chlorine anion, a hydronium and five water molecules. There is a very good accordance between the refined and experimental Cl–O distances. The calculated O–H distances are systematically longer (by 10–20%) than those estimated in the X-ray experiment. A similar pattern was obtained in previous calculations for nitric acid hydrates [23], performed by the same method. It seems

Table 1

Summary of interatomic distances (in \AA) and angles (in $^\circ$) within the irreducible chemical unit (containing Cl^- , H_3O^+ , and 5 (H_2O) molecules), of the unit cell of $\text{HCl} \cdot 6(\text{H}_2\text{O})$

Distances			Angles		
H ₃ O ⁺	X-ray	Calculated	H ₃ O ⁺	X-ray	Calculated
O'–H ⁺	0.976	1.061	H ⁺ –O'–H	110.484	112.768
O'–H	0.872	1.057	H ⁺ –O'–H	110.483	112.798
O'–H	0.872	1.056	H–O'–H	112.892	115.013
<i>H₂O</i>			<i>H₂O</i>		
O ¹ –H	0.771	0.999	H–O ¹ –H	105.348	105.033
O ¹ –H	0.823	1.010			
O ² –H	0.771	0.999	H–O ² –H	105.348	105.020
O ² –H	0.823	1.010			
O ³ –H	0.795	1.001	H–O ³ –H	115.681	104.029
O ³ –H	0.815	0.997			
O ⁴ –H	0.795	1.001	H–O ⁴ –H	115.681	104.019
O ⁴ –H	0.815	0.997			
O ⁵ –H	0.781	0.998	H–O ⁵ –H	107.261	109.468
O ⁵ –H	0.781	0.997			
<i>Cl...O</i>					
Cl–O'	4.620	4.637			
Cl–O ¹	3.142	3.136			
Cl–O ²	3.571	3.652			
Cl–O ³	4.470	4.459			
Cl–O ⁴	4.478	4.488			
Cl–O ⁵	4.714	4.684			

X-ray diffraction data from [17]; calculated results from this work.

that the PBE functional leads to an overestimation of the O–H lengths and, on the other hand, it may be argued that X-ray measurements tend to underestimate them. In fact, the vibrational frequencies of the water O–H stretching normal modes, are quite well reproduced in the calculation (see below) for the estimated bond distances. The calculated HOH angles in the H_3O^+ ions reproduce satisfactorily those derived from the crystallographic data, with a minor positive deviation of less than 2%. For the H_2O molecules, the calculations yield values lower than 110° and mostly close to the $104\text{--}105^\circ$ characteristic of free H_2O . Two of the experimental X-ray angles, corresponding to units 3 and 4 in Fig. 1, are larger than 115° , which would imply a clear distortion of the water molecules, not reproduced in the calculation.

Fig. 2 displays the RAIR spectrum of the $\text{HCl} \cdot 6(\text{H}_2\text{O})$ crystalline film recorded in our laboratory. In the same figure, the calculated normal mode vibrational frequencies are represented as vertical lines of unitary height. The assignment of the spectrum in terms of molecular vibrations is given in Table 2. As already mentioned in previous works [23,24], the description of the crystal normal modes in terms of molecular vibrations is only approximate. These crystal modes correspond usually to the in- or out-of-phase vibrations of more than one molecule within the unit cell. Sometimes only one type of molecular vibration is involved, but

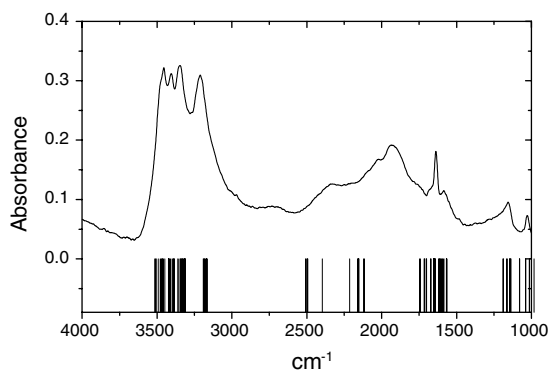


Fig. 2. RAIR infrared spectrum of a crystalline HCl hexahydrate at 97 K. The sample was annealed at 180 K and then cooled down to that temperature.

Table 2

Wavenumber range (in cm^{-1}) of the calculated normal modes of crystalline $\text{HCl} \cdot 6(\text{H}_2\text{O})$, with a proposed assignment to the predominant molecular vibrations in each range

Wavenumber range ^a	Predominant vibrations
3514–3421 (12)	ν_3 (H_2O) asym. stretch
3420–3312 (20)	ν_3 (H_2O) + ν_1 (H_2O) asym. + sym. stretch
3190–3165 (8)	ν_3 (H_2O) + ν_1 (H_2O) asym. + sym. stretch ^b
2507–2494 (4)	ν_1 (H_3O^+) sym. stretch
2395–2117 (8)	ν_3 (H_3O^+) asym. stretch
1744–1670 (8)	ν_4 (H_3O^+) asym. 'scissors'
1653–1615 (10)	ν_2 (H_2O) sym. bend + ν_4 (H_3O^+) asym. 'scissors'
1611–1565 (10)	ν_2 (H_2O) sym. bend
1189–1162 (4)	ν_2 (H_3O^+) sym. 'umbrella' + ν_L libration
1145–1013 (10)	ν_L libration

^a Numbers in brackets indicate number of vibrations in the corresponding wavenumber range.

^b This vibration takes place between two H_2O molecules linked by a strong H bond.

often more than one molecular mode and even different molecules participate. This is especially noticeable in the low frequency libration modes.

Previously reported IR transmission spectra of vapour deposited samples attributed to crystalline $\text{HCl} \cdot 6(\text{H}_2\text{O})$ [4,20], prepared using somewhat different procedures, display equivalent spectral features, but the intensities do appear different. Our aim in the present work is to discuss the vibrational assignment of the spectrum, and we will not comment in the following on the observed intensity discrepancies, which arise as a consequence of the different infrared techniques used, namely transmission or reflection-absorption.

Ritzhaupt and Devlin [20] proposed an empirical assignment of the spectrum of the HCl hexahydrate. With the help of the present theoretical calculations, we can now carry out a more detailed analysis of this spectrum. A large set of calculated frequencies matches the location of the intense absorption observed above 3000 cm^{-1} . It is interesting to note that the calculated

frequencies are grouped in blocks that correspond approximately to the experimental peaks. These frequencies are unquestionably assigned to O–H stretching vibrations of the water molecules. The theoretical results show that symmetric (ν_1) and antisymmetric (ν_3) stretching vibrations appear usually mixed in the various crystal modes. The larger gap between the peak at 3212 cm^{-1} and the rest is well reproduced in the calculations, which indicate that the corresponding vibrations involve a H atom strongly hydrogen-bonded to a neighbouring water molecule and oscillating along a nearly straight line between the two oxygen atoms. Note that the detachment of this O–H peak at the lower frequency end of the OH band is a characteristic of the hexahydrate spectra [4,20,21].

In the interval between ≈ 2500 and 1500 cm^{-1} the experimental spectra exhibit a wide absorption band with broad maxima at about 2330 and 1930 cm^{-1} and a narrow peak at 1638 cm^{-1} . The shape of this band is also distinctive of the IR spectra attributed thus far to the hexahydrate of HCl. The calculated crystal vibrations associated with the ν_1 and ν_3 modes of H_3O^+ lie between 2500 and 2100 cm^{-1} and those with predominant H_3O^+ ν_4 bending character between 1744 and 1670 cm^{-1} , but no vibrations are predicted close to the prominent absorption maximum at 1930 cm^{-1} .

Broad absorptions like this one are usually found in bulk phases containing hydrated protons (see for instance the discussion in [11,33–35]). In solid phases this effect is explained as due to the interaction, via dispersion forces, of neighbouring hydrogen bonds with large proton polarizability. As a result the proton oscillates within a very anharmonic potential modulated by the O–O distance [35]. In the case of the HCl hexahydrate, the H_3O^+ cation is fully solvated by three water molecules forming an H_9O_4^+ Eigen ion. The present calculations and normal mode analysis do not contemplate such a complicated anharmonic system, but are restricted to small atomic motions. Although the calculated modes for ν_1 , ν_3 and ν_4 of H_3O^+ all lie within the broad band between 2500 and 1500 cm^{-1} , the estimated frequencies are shifted with respect to the observed maxima. It may be assumed that the stretching vibrations of the solvated H_3O^+ ions, significantly affected by the strong H-bonding with the solvating water molecules, experience an appreciable redshift with respect to the values of the predicted harmonic frequencies. A 200 – 300 cm^{-1} (10–15%) displacement toward lower frequencies would thus lead to a good agreement between the calculated ν_1 and ν_3 stretching modes, and the experimental main absorptions between 2500 and 1750 cm^{-1} . The influence of H-bonding on the bending vibrations of H_3O^+ should be smaller. The calculated asymmetric ν_4 bending lies between 1744 and 1670 cm^{-1} , and this range corresponds approximately to the lower frequency portion of the broad absorption mentioned

above (2500–1500 cm^{-1}). The ν_4 bending was previously assigned [20] to the 1930 cm^{-1} peak, giving a reasonable frequency ratio agreement with a peak at about 1450 cm^{-1} measured later on the transmission spectrum of a deuterated sample [11]. With the present knowledge it is difficult to make an unambiguous assignment for this mode.

The narrow experimental peak at about 1638 cm^{-1} is assigned to the ν_2 bending mode of H_2O [20], calculated between 1611 and 1553 cm^{-1} , mixed with low frequency components of ν_4 of H_3O^+ . Ritzhaupt and Devlin [20] attribute the small width of this peak and of the water O–H stretch bands beyond 3000 cm^{-1} , to an ordered arrangement of the water molecules of hydration within the crystalline network. In general, these water modes are fairly tightly packed together also in the calculations.

The predicted ν_2 ‘umbrella’ vibrations of H_3O^+ between 1189 and 1161 cm^{-1} are in good agreement with an observed experimental peak and corroborate the empirical assignment of [20]. Finally, the small experimental peak at about 1027 cm^{-1} can be assigned to the highest frequency librational modes of the crystal, predicted between \approx 1145 and 1000 cm^{-1} .

5. Summary and conclusions

We have carried out a combined experimental and theoretical investigation of crystalline $\text{HCl} \cdot 6(\text{H}_2\text{O})$. The RAIR spectra, which had never been recorded before within our knowledge, show the same features as those from former IR transmission measurements of films deposited under different conditions, but annealed at similar temperatures. The results suggest that the crystalline solid can be formed in a reliable way from amorphous $\text{H}_2\text{O}/\text{HCl}$ deposits of different composition by annealing them under the stability conditions reported for this hydrate in the published phase diagrams. This point supports the equivalence of the samples as prepared in the X-ray experiment [17] and in the infrared laboratories.

We present here, also for the first time, a theoretical calculation of the geometrical structure and vibrational frequencies of the crystalline HCl hexahydrate, based on the SIESTA method and programs. The refined structure is in good agreement with crystallographic data although the calculated O–H bonds tend to be somewhat longer than those from X-ray measurements. The calculated crystal modes involving predominantly vibrations of water molecules appear in groups that match approximately the location and width of observed experimental peaks. In particular the location of the experimental peaks at about 3200 (O–H stretch with strong hydrogen-bonding) and 1600 cm^{-1} (H_2O bend), characteristic of all the available spectra attributed to the HCl hexahydrate, are well rendered in the calculations.

The predicted modes with predominant participation of H_3O^+ vibrations lie within the broad band attributed empirically to vibrations of this ion, but are shifted by 10–15% with respect to the main absorptions. This discrepancy may be attributed to large anharmonic motions of hydrated protons, which are not dealt with in the present theoretical treatment, based on a harmonic approximation.

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