

Infrared Evidence for the Existence of the (HCl)*(H₂SO₄) Complex Trapped in Argon at 5 K[†]

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Infrared bands associated with the (HCl)*(H₂SO₄) complex were identified in argon matrices. In agreement with computation (Beichert, P.; Schrems, O. *J. Phys. Chem. A* **1998**, *102*, 10540), HCl is found to bridge between the OH and S=O groups of the H₂SO₄ monomer, but the hydrogen-bonded O—H and Cl—H stretches are more red shifted than predicted. No spectral evidence for the existence of an (HCl)*(SO₃) complex was found.

Introduction

Stratospheric H₂SO₄ aerosols provide a suitable site for the activation of chlorine which, in turn, catalyzes ozone destruction. Active chlorine may be produced via a reaction of HCl with HONO and subsequent photodissociation of the ClNO product,¹ or via the reaction of HCl with ClONO₂ followed by photodissociation of Cl₂.² In addition to ClONO₂, HCl thus constitutes the main reservoir of atmospheric chlorine.³ The simultaneous presence of gaseous HCl with pure as well as hydrated sulfuric acid implies a possible interaction between the two acidic molecules. Theoretical calculations by Beichert et al.⁴ have recently suggested the existence of the (HCl)*(H₂SO₄) dimer with a rather low stabilization energy (27.4 kJ mol⁻¹), similar to that of the (ClONO₂)*(H₂SO₄) complex (calculated stabilization energy of 25.3 kJ mol⁻¹), but significantly smaller than that calculated for the analogous (H₂O)*(H₂SO₄) and (H₂O₂)*(H₂SO₄) species (62.7 kJ mol⁻¹ and (60.1 kJ mol⁻¹, respectively). Bidental bonding of HCl to the OH and S=O moieties of H₂SO₄ was suggested, with the relevant bonding lengths of 2.29 Å for Cl...H— and 2.02 Å for H...O⁴ (Figure 1).

We have recently completed an infrared characterization of pure monomeric H₂SO₄ and SO₃ species as well as of their complexes with H₂O, (H₂O)₂, SO₃,⁵ CO, (OC)*(H₂O),⁶ NO, N₂O₂, and N₂.⁷ In addition, several weak bands related to (H₂SO₄)₂ dimers were identified,⁵ and a double H-bonded cyclic structure was proposed. For the latter the energy of a single H bond was estimated as 25.5 kJ mol⁻¹ on the basis of a correlation proposed by Iogansen,⁸ relating the hydrogen bond enthalpy, Δ*H*_{bond}, with the square root of the red frequency shift of the bonded OH stretching mode.

In the present contribution we discuss the infrared absorptions of the (HCl)*(H₂SO₄) complex formed by depositing gaseous Ar/HCl/H₂SO₄ mixtures onto a cold tip. The observations are related to the possible structure and the strength of the bonding of the two acid molecules forming the complex, a first step toward an understanding of the processes in which they are involved.

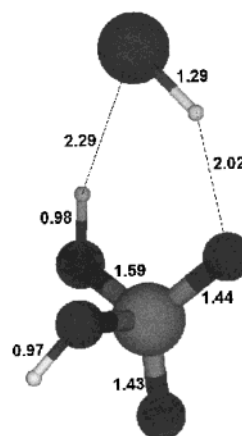


Figure 1. Structure of the (HCl)*(H₂SO₄) complex according to calculations by Beichert et al.⁴

Experimental Section

Most experimental details were given previously.^{5–7} HCl was produced by reacting NaCl and H₂SO₄, passing the gaseous products mixed with argon (AGA, 5.7) over a drop of sulfuric acid (Prolabo (p.A.)) placed in a quartz nozzle wrapped by a heating coil, and warming to a maximum of 38 °C. Typical samples of the ratios Ar:HCl:H₂SO₄ = 300:1:1 to 300:3:1, were sprayed onto the CsI window, cooled by an Air Products HS-4 Heliplex cryostat with deposition times of 1–3 h. Deposition rates were several millimoles per hour. Temperature cycling was conducted by a slow warming (1 K/min) of the sample up to 38 K, followed by quick recooling to 5 K. Infrared spectra were recorded at the latter temperature on a Bruker IFS 88 instrument, employing a DTGS detector and coadding 32–128 scans at nominal resolutions of 0.5–1 cm⁻¹.

Results and Discussion

The yield of the dimeric (HCl)*(H₂SO₄) complex in gaseous mixtures is expected to be rather low. It competes with the reactions of both HCl and H₂SO₄, primarily with H₂O, but also with themselves, to form pure and mixed complexes. In addition, most complexes formed by diffusion, both during deposition and by temperature cycling, contain a water component due to

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TABLE 1: Bands Attributed to (HCl)*(H₂SO₄) in Argon Matrix (cm⁻¹)

(HCl)*(H ₂ SO ₄)	assignments	comparison to (H ₂ SO ₄)*(H ₂ SO ₄)
3393 (vw)	bonded OH stretch	3180 (w)
1436.4 (w)	S=O ₂ antisymmetric stretch	1432.5 (w)
1212 (w)	S=O ₂ symmetric stretch	1211 (w)
861, 854.8 (vw)	S-(OH) ₂ stretches	892.5, 869.4
[561 (vw)]	S=O ₂ rock	
[549.5 (vw)]	S=O ₂ bend	
2636.5 (w)	H-Cl stretch	

the inevitable presence of H₂O species (ca. 19% in the equilibrium H₂SO₄ ↔ SO₃ + H₂O at the experimental temperatures⁵) and its being the species of highest mobility. Thus, the low (HCl)*(H₂SO₄) concentration results in weak infrared bands, similar to those reported by us for the (H₂SO₄)₂ dimer,⁵ hidden in a rather complicated spectrum. The various regions of the relevant vibrational modes have, therefore, to be carefully compared with neat Ar/H₂SO₄ frozen vapors in order to identify the pertinent (HCl)*(H₂SO₄) complex absorptions. It may be noted that deuteration is, in this case, a complication rather than a help, due to the large variety of partly and fully, binary and mixed, monomeric, dimeric, and higher species produced. In the following text we shall not deal with the spectral lines already attributed and discussed in our previous work,⁵ and not pertaining to the formation and characterization of HCl/H₂SO₄ species. Table 1 summarizes the discernible bands attributed to this (HCl)*(H₂SO₄) complex, which are compared with those recorded for the analogous (H₂SO₄)₂ interacid dimer. An indication of the band intensities is given in parentheses. All figures comprise three traces: traces A are spectra of H₂SO₄ vapor species in solid Ar at 5 K;⁵ traces B are spectra of an HCl/H₂SO₄/Ar mixture deposited and recorded at 5 K; traces C result from sample B, after its annealing to 20 K. All bands assigned to the binary complex HCl*H₂SO₄ show similar behavior upon temperature cycling. In particular, they do not show the intensity enhancement upon temperature cycling, a characteristic of complexes involving one or more water molecules.

The HCl stretch region comprises the previously assigned bands;⁹⁻¹⁷ the 2887.9 cm⁻¹ line of the R(0) HCl vib-rotor monomer, the weak Q branch doublet at 2870.5, 2868.3 cm⁻¹, all losing intensity upon temperature cycling. In addition, the doublet band at 2863.2, 2861.2 cm⁻¹ related to the (N₂)*(HCl) complex was observed, as well as a distinct line at 2663.7 cm⁻¹ (Figure 2) of the (H₂O)*(HCl) complex.¹⁵⁻¹⁷ The latter three bands gain intensity upon temperature cycling. An additional new weak (~0.01 au) absorption, at 2636.5 cm⁻¹ (Figure 2, traces B, C), only observed for HCl containing deposits and very slightly enhanced upon temperature cycling, is assigned to the HCl stretch of the (HCl)*(H₂SO₄) complex.

According to the calculations of Beichert et al.,⁴ the expected complex bonding scheme in H₂SO₄ affects the S=O bonds, as evidenced by the Cl-H...O=S bond length. In our experiments also, the ν₁₀(b) antisymmetric S=O₂ stretch shows the most clear (although weak) complexation effect. In the ν₁₀(b) S=O₂ antisymmetric stretch mode region (Figure 3) a new weak (~0.03 au) HCl dependent band emerges at 1436.4 (2.5) cm⁻¹ (trace B), close to the (H₂SO₄)₂ dimeric line at 1432.5 cm⁻¹ (2 cm⁻¹) and of similar intensity. This (H₂SO₄)*(HCl) complex band does not appear in the HCl free sample (trace A) and its relative intensity is very slightly increased by cycling to 20 K (trace C). It is, however, clearly distinct from both the strong monomeric H₂SO₄ band (1452.4 cm⁻¹) and the absorptions of the water complexes, (H₂O)₁₋₂*(H₂SO₄), around 1449 and 1442

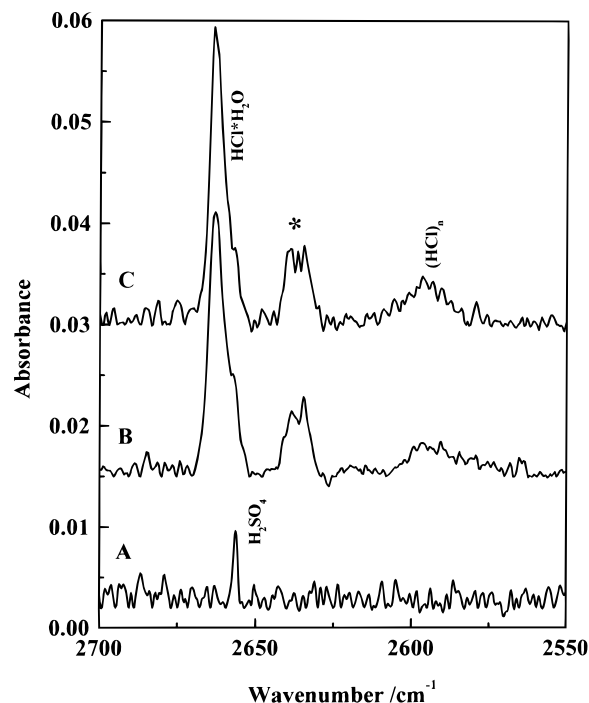


Figure 2. Bonded H-Cl stretch region of the (HCl)*(H₂SO₄) and (HCl)*(H₂O) complexes. Recorded on solid Ar/HCl/H₂SO₄ mixtures deposited at 5 K. The * marked band is attributed to the (HCl)*(H₂SO₄) complex. (A) Ar/H₂SO₄ = 500/1. As deposited at 5 K. (B) Ar/HCl/H₂SO₄ = 300/1/1. As deposited at 5 K. (C) Sample B after temperature cycling to 20 K.

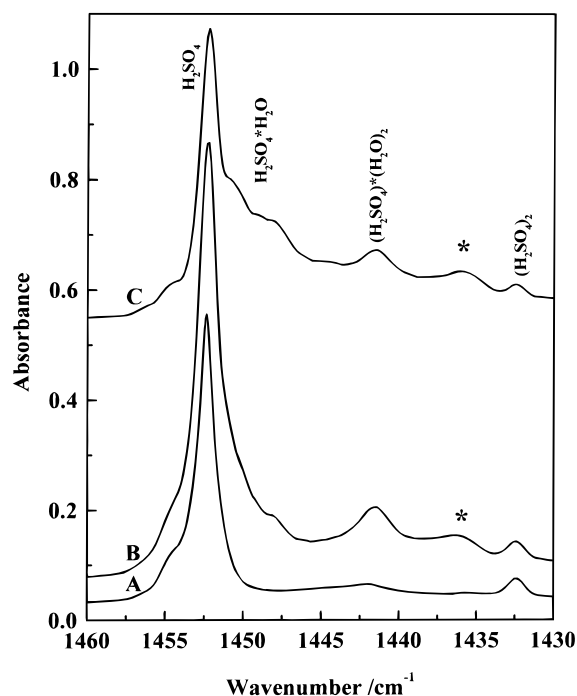
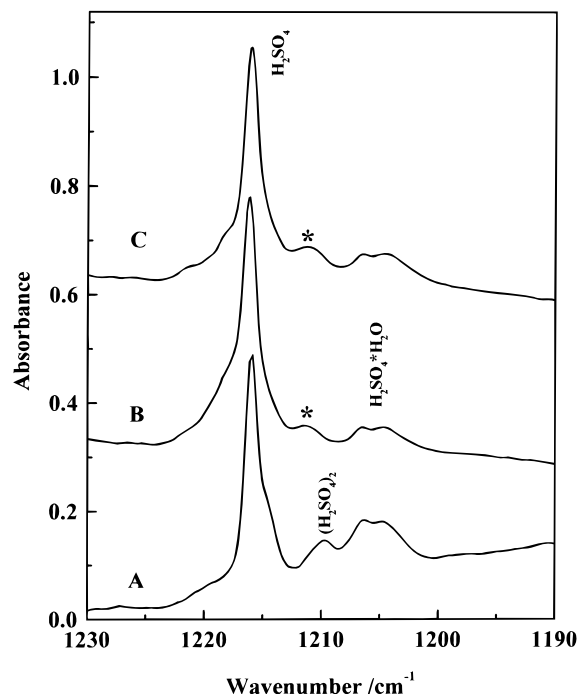


Figure 3. Antisymmetric S=O₂ stretch region of solid Ar/HCl/H₂SO₄ mixtures. The * marked band is attributed to the (HCl)*(H₂SO₄) complex. (A) Ar/H₂SO₄ = 500/1. As deposited at 5 K. (B) Ar/HCl/H₂SO₄ = 300/1/1. As deposited at 5 K. (C) Sample B after temperature cycling to 20 K.

cm⁻¹, respectively.⁵ Its red shift from the free H₂SO₄ band is 1.1%, a shift larger by a factor of 3-10 of those affected by complexations with H₂O,⁵ CO,⁶ N₂, and N₂O₂⁷ (cf. Table 2), for which complexations involving the O-H bonds of H₂SO₄,

TABLE 2: Bonded $\nu(\text{OH})$ and ν_{10} Antisymmetric O=S=O Stretching Modes of Several H₂SO₄ Complexes Trapped in Solid Argon (cm⁻¹)

	$\nu(\text{OH})$	$\Delta\nu$	$\Delta\nu/\nu$, %	ν_{10}	$\Delta\nu$	$\Delta\nu/\nu$, %	ref
Ar matrix	3566.7			1452.4			5
(OC)*(H ₂ SO ₄)	3371.1	-195.6	-5.48	1448	-4.4	-0.3	6
(N ₂)*(H ₂ SO ₄)	3547	-19.7	-0.55	1450.9	-1.5	-0.1	7
(NO)*(H ₂ SO ₄)	3452.3	-114.4	-3.21				7
(N ₂ O ₂)*(H ₂ SO ₄)	3446.5	-120.2	-3.37	1445.7	-6.7	-0.46	7
(HCl)*(H ₂ SO ₄)	3393	-173.7	-4.87	1436.4	-16.0	-1.1	this work
(H ₂ SO ₄) ₂	3180	-386.7	-10.84	1432.5	-19.9	-1.37	5

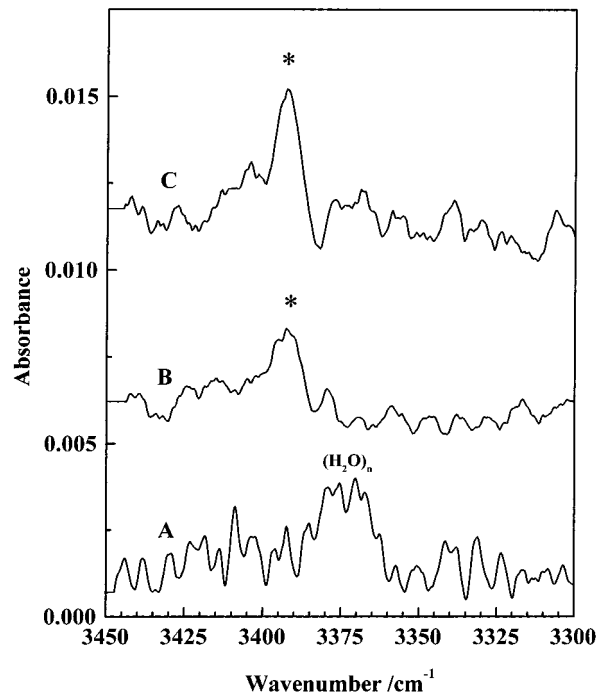
**Figure 4.** Symmetric S=O₂ stretch region of solid Ar/HCl/H₂SO₄ mixtures. The * marked band is attributed to the (HCl)*(H₂SO₄) complex. (A) Ar/H₂SO₄ = 500/1. As deposited at 5 K. (B) Ar/HCl/H₂SO₄ = 300/1. As deposited at 5 K. (C) Sample B after temperature cycling to 20 K.

were suggested. On the other hand bonding with the more acidic H₂SO₄ molecule affects a larger red shift of 1.37%.

In the vicinity of the $\nu_2(\text{a})$ H₂SO₄ symmetric S=O₂ stretch (1216.1 cm⁻¹), for the HCl containing sample, a weak band (Figure 4, traces B and C) at 1212 cm⁻¹ is observed and is ascribed to the result of complexation of H₂SO₄ with HCl. Its position is very close to that of the (H₂SO₄)₂ dimer at 1211 cm⁻¹.⁵ The clearer effect of complexation on the $\nu_{10}(\text{b})$ mode, described in the previous paragraph, is in accord with the higher sensitivity of antisymmetric stretching modes to environmental changes.¹⁸

The S=O₂ rock and bend modes region also reveals two shoulders at 561 cm⁻¹ (rock mode) and 549.5 cm⁻¹ (bend mode), on the respective free argon isolated monomeric H₂SO₄ absorptions (Figure 5, trace B) not found in the absence of HCl (Figure 5, trace A). They show slight intensity gains upon temperature cycling (Figure 5, trace C). However, their proximity to the (H₂O)*(H₂SO₄) modes⁵ makes their assignment to (HCl)*(H₂SO₄) less reliable.

The OH stretching modes region reveals a very weak band at 3393 cm⁻¹ (Figure 6, trace B) not discerned in the HCl free samples (Figure 6, trace A). Its position is close to the polymeric water band at 3370 cm⁻¹.¹⁹ Its intensity resembles that of the 3180 cm⁻¹ (H₂SO₄)₂ line⁵ attributed to the bonded OH stretch of the sulfuric acid dimer and it is assigned to the bonded OH

**Figure 5.** S=O₂ rock and bend region of solid Ar/HCl/H₂SO₄ mixtures. The * marked band is attributed to the (HCl)*(H₂SO₄) complex. (A) Ar/H₂SO₄ = 500/1. As deposited at 5 K. (B) Ar/HCl/H₂SO₄ = 300/1. As deposited at 5 K. (C) Sample B after temperature cycling to 20 K.

stretch of (HCl)*(H₂SO₄). For this OH stretch frequency our observations yield values of $\nu_{\text{complex}}/\nu_{\text{sulfuric acid}} = 0.951$ and of $\nu_{\text{complex}} - \nu_{\text{sulfuric acid}} = -173.7$ cm⁻¹, in comparison with +0.972 and -106.3 cm⁻¹, respectively, calculated by Beichert et al.⁴

For the sulfuric acid dimer, a cyclic configuration was suggested,⁵ in analogy to the structures for other acid dimers such as (HNO₃)₂,^{20,21} (CH₃COOH)₂, and (HCOOH)₂.²² It is instructive to compare the red shifts of the complexed O—H bonds and relate them to the H-bonding strength. The 173.7 cm⁻¹ (4.87%) red shift of the bonded OH absorption of (HCl)*(H₂SO₄) from the monomeric H₂SO₄ free OH stretch, is about half the value observed for the doubly bonded structures of (H₂SO₄)₂ and (HNO₃)₂ dimers (Table 3). This lower value points to a weaker hydrogen bond between the HCl chlorine and the OH moiety of H₂SO₄ than that in the acid dimers between the OH moieties and the oxygen lone pairs. It is, however, stronger, and produces larger OH red shifts, than in sulfuric acid complexes with N₂, NO, N₂O₂,⁷ and resembles the (OC)*(H₂SO₄) species⁶ (Table 2). The OH stretch red shift is also much larger than that found for the HCl acceptor in the (HCl)₂ dimer (52 cm⁻¹, 1.8%).⁹

In the S—(OH)₂ stretching modes region (Figure 7), two new weak (~0.02 au) bands were discerned at 861 and 854.8 cm⁻¹. These bands, too weak to demonstrate significant changes upon temperature cycling, are positioned approximately at the average

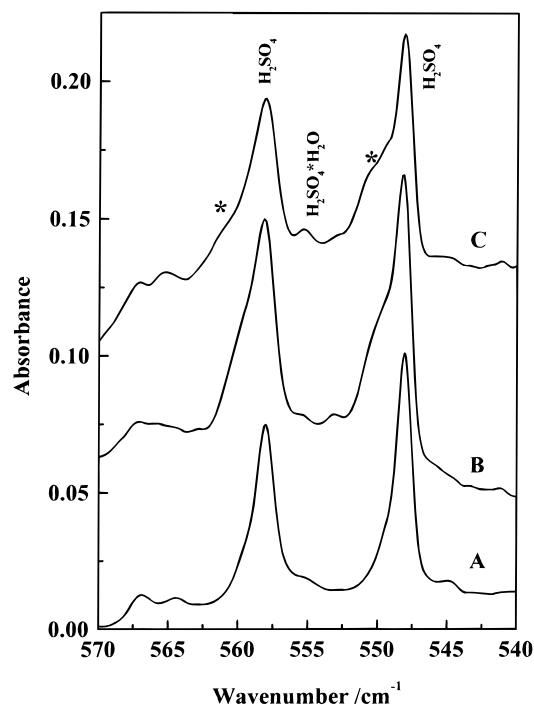


Figure 6. Bonded OH band of $(\text{HCl})^*(\text{H}_2\text{SO}_4)$. Recorded on Ar/HCl/ H_2SO_4 mixtures deposited at 5 K. The * marked band is attributed to the $(\text{HCl})^*(\text{H}_2\text{SO}_4)$ complex. (A) Ar/ H_2SO_4 = 500/1. As deposited at 5 K. (B) Ar/HCl/ H_2SO_4 = 300/1/1. As deposited at 5 K (spectral smoothing applied). (C) Sample B after temperature cycling to 20 K (spectral smoothing applied).

TABLE 3: Red Shifts of Bonded $\nu(\text{X}-\text{H})$ Stretches and Bond Energies of Double Acid Species Trapped in Argon Matrices

species	$\Delta\nu$ (cm^{-1})	bond energy (kJ mol^{-1})
$(\text{HCl})_2$	-52^a 9	-9.4^c
$(\text{HNO}_3)_2$	-306^b 21	$-45.4^{b,c}$
$(\text{H}_2\text{SO}_4)_2$	-386.7^b 5	$-51.0^{b,c}$
$(\text{HCl})^*(\text{H}_2\text{SO}_4)$	-173.7	$-27.4^{a,4}-37.0^c$
$(\text{HNO}_3)^*(\text{H}_2\text{SO}_4)$	-46.1^b 4	$-46.1^{b,4}$
$(\text{HCOOH})_2$	-427^{20}	$-53.7^{b,c}-58.6^{b,22}$

^a Calculated from the Q branch. ^b Cyclic structure suggested,^{4,5,20} two hydrogen bonds. ^c By correlation suggested in ref 8.

wavenumber value of the $\nu_4(\text{a})$ symmetric and $\nu_{12}(\text{b})$ antisymmetric S-(OH)₂ stretches of the free argon isolated H_2SO_4 , and are assigned to these modes of the $(\text{HCl})^*(\text{H}_2\text{SO}_4)$ complex.

As noted above, the complexed HCl stretch exhibits a large red shift of 233.5 cm^{-1} (8.1%), from the Q branch position of the argon isolated HCl monomer, and strongly indicates that here HCl is the electron acceptor, via its hydrogen atom. For comparison, in the $(\text{HCl})_2$ dimer the acceptor HCl band is red shifted by 52.2 cm^{-1} (observed at 2855.5 cm^{-1}) the donor is far less shifted (14.5 cm^{-1} , observed at 2817.8 cm^{-1} ⁹). Other results of large red shift of $\nu(\text{HCl})$ due to interactions of its hydrogen with oxygen or nitrogen lone pairs are found for complexations with water,^{15–17} alcohols,²³ and HCN.²⁴ The shift and related comparisons are, then, conclusive evidence for an $\text{Cl}-\text{H}\cdots\text{O}=\text{S}$ interaction to be the major factor in the $(\text{HCl})^*(\text{H}_2\text{SO}_4)$ complexation. The spectral results yield an experimental ratio of $\nu_{\text{complex}}/\nu_{\text{trace gas}} = 0.919$ and a wavenumber difference of $\nu_{\text{complex}} - \nu_{\text{trace gas}} = -233.5 \text{ cm}^{-1}$ as compared with $+0.965$ and -110.3 cm^{-1} , the computed values.⁴

The red shift in the ν_{10} antisymmetric S=O₂ stretch in the $(\text{HCl})^*(\text{H}_2\text{SO}_4)$ complex indicates that the complexation with HCl affects an S=O bond polarization. The red shifts listed in

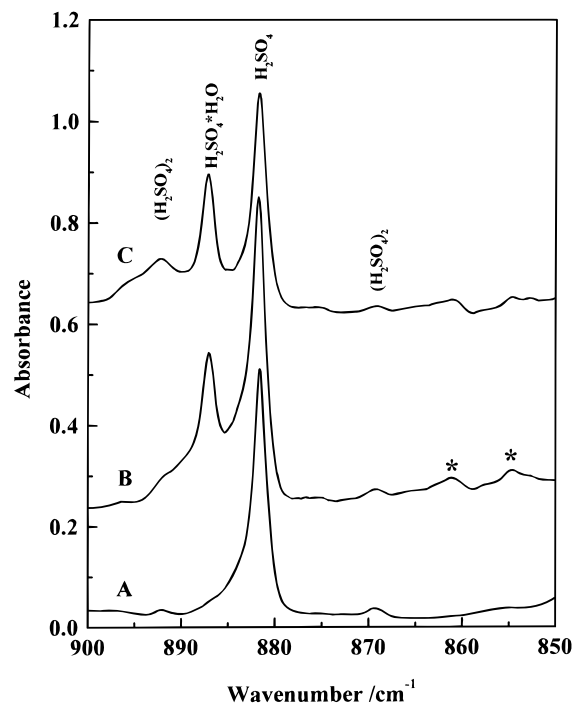


Figure 7. Antisymmetric and symmetric S-(OH)₂ stretch region of solid Ar/HCl/ H_2SO_4 mixtures. The * marked band is attributed to the $(\text{HCl})^*(\text{H}_2\text{SO}_4)$ complex. (A) Ar/ H_2SO_4 = 500/1. As deposited at 5 K. (B) Ar/HCl/ H_2SO_4 = 300/1/1. As deposited at 5 K. (C) Sample B after temperature cycling to 20 K.

Table 2 for other complexants are in accord with their relative capacities of introducing ionic character and the ensuing slight weakening of this bond.

In summary, three $(\text{HCl})^*(\text{H}_2\text{SO}_4)$ absorptions at 2636.5 , 1436.4 , and 1212 cm^{-1} , originate in an $\text{H}(\text{HCl})\cdots\text{O}(\text{H}_2\text{SO}_4)$ complexation, whereas the three very weak bands at 3393 , 861 , and 854.8 cm^{-1} bands are indications of a secondary $\text{Cl}(\text{HCl})\cdots\text{H}(\text{H}_2\text{SO}_4)$ interaction. In principle, the two frequency groups could belong to either two discrete isomers of the $(\text{HCl})^*(\text{H}_2\text{SO}_4)$ type or to a single isomer in which a single HCl molecule forms both bridging bonds, as proposed by Beichert et al.⁴ and illustrated in Figure 1. A conversion from the less stable to the more stable configuration would imply a growth of one group of bands at the expense of the other. The fact that neither group disappears upon temperature cycling points to the bridging configuration indicated by the theoretical computation.

Comparing our spectroscopic experimental results to the theoretical calculation,⁴ we find an agreement as to the predicted cyclical configuration of the complex. However, we note that the observed frequency shifts are considerably larger than those calculated, indicating a stronger bonding between the two acid molecules. Probably, the level of calculation (MP2) is not high enough to accurately reproduce the spectral shifts and bonding energy. Indeed, even a simple dipole-dipole interaction would render a somewhat higher bonding enthalpy. We hope that our present experiments would pose a challenge to a higher level calculation. An empirical correlation⁸ between the shifts of the hydrogen-bonded O-H and Cl-H stretch frequencies and the ΔH of bonding suggests a value of -37 kJ mol^{-1} (Table 3).

Similar to our previous studies with other ligands,^{5–7} no evidence was found in any of the SO_3 vibrational modes for its complexation with HCl in low-temperature argon matrices.

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