Matrix Isolation Infrared Spectrum of the Sulfuric Acid−Monohydrate Complex: New Assignments and Resolution of the "Missing H-Bonded *ν*(OH) Band" Issue

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The matrix isolation infrared spectra of "dry" and "wet" vapors of sulfuric acid have been investigated as trapped in solid argon matrices. The availability of a spectrum of trapped anhydrous acid vapor and its comparison with the spectra of trapped water containing vapors of the acid allowed the identification of the hydrogen-bonding shifted hydroxyl bands for both the acid and the water moieties of the monohydrated $H_2SO_4 \cdot H_2O$ complex. The experimental results are compared to the various theoretically calculated wavenumber values of the acid and its monohydrated complex. The complex stabilization energies, as obtained from calculations and empirical correlations, are compared.

Introduction

Recent years have seen a growing interest in the hydration process of sulfuric acid at the molecular level. This interest stems from sulfuric acid and its hydrates being the major component of stratospheric aerosols and the important role the latter play in atmospheric processes. A good survey of available experimental data and theoretical calculations is given in the Introduction of ref 1.

The number experimental studies of monomeric H_2SO_4 and its first hydrates is limited. We reported the infrared matrix isolation spectra of H_2SO_4, D_2SO_4, and $HDSO_4$[2] and of the monohydrate $H_2SO_4 \cdot H_2O$.[3] Fiacco[4] et al. reported the microwave spectrum of $H_2SO_4 \cdot H_2O$ in the gas phase.

All concurrent and following theoretical studies[1,5−11] as well as chemical intuition suggest that the most stable structure for the $H_2SO_4 \cdot H_2O$ complex would involve a configuration where the O−H hydroxyl hydrogen of the H_2SO_4 moiety forms a strong hydrogen bond with the H_2O oxygen. A secondary, weaker interaction between one H_2O hydroxyl hydrogen and the oxygen of a doubly bonded S═O group of the acid was also predicted.[1,6,7,9,11] Fiacco[4] et al. also deduced this structure from their microwave spectral results.

From the predicted hydrogen-bonding energy and red shifts of the hydrogen-bonded hydroxyl *ν*(O−H) stretching mode, a strong band was expected and calculated to be positioned at over 600 wavenumbers below the corresponding vibrational band of unbound H_2SO_4. However, in our previous matrix isolation study,[3] no such band could be reliably discerned and assigned, although other spectral features could safely be attributed to the monohydrate complex. Moreover, a band somewhat blue shifted from the *ν*(OH) modes of free H_2SO_4 seemingly showed the characteristics associated with a complex mode, by being dependent upon the H_2O contents of the matrix layer and sensitive to temperature cycling of the sample.

This contradiction between our experimental findings and the accumulating bulk of calculated predictions motivated us to a reinvestigation of matrix isolated sulfuric acid and its monohydrate complex. In the present study, we overcame the major difficulty complicating the assignments of the spectral bands: the inherent presence, due to the thermodynamic equilibrium in the vapor, of water, $(H_2O)_n$, species in the sample layer and the ensuing multitude of bands originating from the pure and binary species (cf. Table 1 in ref 3). The present availability of a "dry" matrix layer of H_2SO_4, on the one hand, and a comparison with the spectrum of matrix-isolated water vapors, taken under the same experimental conditions, allow us to reliably reassign some of the $H_2SO_4 \cdot H_2O$ bands observed previously as well as to report new bands, showing the effects of hydrogen bonding for both the H_2SO_4 and the H_2O moieties of the $H_2SO_4 \cdot H_2O$ complex.

Experimental Section

Materials. The sulfuric acid used was supplied by Frutarum, Israel, and was of Analytical grade (98%). Deuterated sulfuric acid of 98% purity and 99% isotopic enrichment was supplied by Aldrich. ^{18}O-enriched sulfuric acid in $H_2{}^{18}O$ was supplied by ICON with a claimed isotopic enrichment of 85% (our spectra indicate an enrichment closer to only 50%).

The argon matrix gas (5.7 purity) was supplied by AGA.

Sample Preparation: An acid drop was placed in a glass tube ending with a 2 mm pinhole and then pumped for up to 100 h before deposition to minimize water and dissolved gas content. Additional drying of the deposited vapors was attained by placing phosphorus pentoxide powder near the acid drop. For sample layer deposition, the matrix gas was introduced by flowing it over the acid sample. To achieve the desired vapor pressure of the acid, the acid drop was heated by irradiating it with by a small electrical bulb controlled by a 7−12 VDC power supply. Sample temperature was not measured directly, and the extent of heating was determined by monitoring the recorded spectral band intensities.

No additional water was added to the matrix gas. The water content of the matrix layers was determined by the natural abundance of water, most of which is due to the inherent equilibrium in the vapor phase above the liquid sulfuric acid. With this procedure, we could obtain matrices which ranged from "dry" showing no traces of water spectral lines to "wet", with prominent water monomeric and dimeric bands. The wettest matrices also showed spectral evidence of water cluster bands.

Deposition rates ranged from 10−1000 mM of Ar/h. It is noteworthy that the faster deposition rates tended to produce

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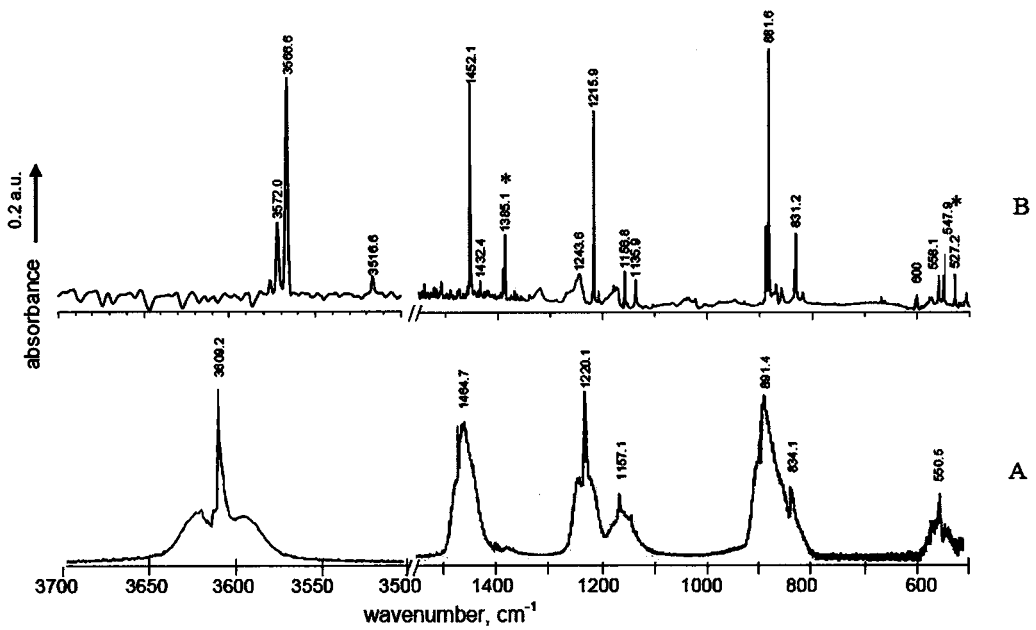

Figure 1. Spectra of sulfuric acid in the gas phase (A)[12] and an Ar matrix (B). The asterisk (*) indicates SO_3 bands.

matrices with lower water content, presumably because the equilibrium conditions above the acid drop were not fully achieved. Samples were deposited on a CsI window, with deposition temperatures in the 17−24 K range, and cooling was provided by an Air Product Displex model 202A closed cycle helium refrigerator. Deposition temperatures were monitored by an Au-0.007%Fe/Chromel thermocouple and controlled with an APDE temperature controller. To protect the window from the aggressive acid vapors, a pure Ar layer was deposited for several minutes before the first warming of the acid drop.

Deposited samples were temperature cycled to up to 40 K, but the spectra were not much affected by this procedure. This is in contrast to previous experiments,[3] where samples were deposited at lower temperatures, and band assignment could then rely upon the changes induced by the warming of the layer. Most probably, the present higher temperature depositions produced layers which were already inherently annealed.

Spectra were recorded on a Bruker Equinox 55 FTIR spectrometer, equipped with a DTGS detector at a resolution of 0.5 cm^{-1} and generally coadding 128 scans.

Results and Band Assignments

In presenting our results, the spectra will be categorized in accordance with the water content of the deposited matrix samples. As noted above, we present for the first time spectra of “dry” matrix layers which show intense acid bands but in which water bands cannot be discerned. On the other extreme, we recorded spectra of “wet” matrices in which not only the bands of water monomers and dimers are present but some spectral features of small ice clusters could be observed in the 3 μm range.

ν(O−H) Range (3800−2500 cm^{-1}). ***“Dry” Sulfuric Acid Matrices.*** Figure 1 reproduces an overview spectrum of “dry” sulfuric acid. The observed bands can be roughly divided into two ranges: (a) the higher wavenumber range, above 2700 cm^{-1}, where the ν(O−H) stretching modes are active and the spectral changes due to intermolecular interactions and hydrogen bonding are expected to be evident, and (b) the lower frequency range below 1600 cm^{-1}, where the skeletal mode bands appear but their positions remain mostly unaffected by the molecular environment. For comparison, we reproduced (by permission) the respective gas-phase spectra.[12] A matrix shift (of the order of 1%) is quite evident in the higher wavenumber range of the trapped species. In the lower wavenumber range, except for the weak SO_3 bands at 1385.1 and 527.2 cm^{-1}, the spectrum of the matrix layer contains no other bands than those already recorded for the vapor phase of H_2SO_4. The absence of bands of the various H_2O species, in both ranges, is especially noteworthy.

In the higher wavenumber range of 3000−3800 cm^{-1}, three bands are initially recorded at 3572.0, 3566.6, and 3516.6 cm^{-1}, as listed in Table 1. Taking the very strong, generally unaffected, ν(S=O) symmetric stretch at 1215.9 cm^{-1} as a reference, the relative intensities of these bands can be monitored quite reliably. The two higher wavenumber bands at 3572.0 (not resolved in previous experiments[3]) and 3566.6 cm^{-1} remain essentially unchanged in intensity when experimental conditions (deposition rate, deposition temperature, matrix:guest ratios) were varied. They are, therefore, assigned to the ν_1 symmetric ν(O−H) stretch and ν_9 antisymmetric ν(OH) stretch, respectively. Both their relative intensities and their calculated wavenumber values[2] are in agreement with this wavenumber ordering of the symmetric and antisymmetric ν(O−H) stretching modes, respectively.

In contrast, the lower wavenumber band at 3516.6 cm^{-1} demonstrates marked changes in its relative intensity with experimental parameters, some of which are reproduced in Figure 2. Along with the intensity increase of this band, one can observe the growing in of a new feature into the 3572 cm^{-1} band, causing its width to grow and its peak intensity to slightly shift. In our previous study,[3] where the matrix layers contained varying amounts of trapped water vapor species, the 3516.6 cm^{-1} band was assigned to the $(H_2O)_3$ trimer. Because we now succeeded in producing matrix layers which show only sulfuric acid related bands, this assignment must be corrected. The presently suggested assignment of the simultaneously growing bands at 3516.6 and 3571.7 cm^{-1} is to the acid dimer, $(H_2SO_4)_2$.

“Wet” Sulfuric Acid Matrices. The spectral region most relevant to the study of intermolecular interactions between sulfuric acid and water molecules is, naturally, the wavenumber range of 3800−2000 cm^{-1} in which the ν(O−H) stretches are

TABLE 1: Bands of H_2SO_4 and Its H/D Isotopic Derivatives in Ar Matrices[a]

ν(OH)/ν(OD) range						skeletal mode range		
H_2SO_4	H_2SO_4/H_2O	$H_2SO^{18}{}_4/H_2O^{18}$	15% $D_2SO_4/H_2SO_4/H_2O/HDO$	$D_2SO_4/HDO/D_2O$	assignment	H_2SO_4 anhydrous	H_2SO_4/H_2O	assignment
	3776.2w, 3755.9w, 3710.9w	3741.9w	3775.7vw, 3755.7vw, 3711.1vw,		ν_3 mode of rotating H_2O monomer	1452.1s		$\nu(S{=}O)_{2\ as}$
	3707.0w				free $\nu(OH)_{donor}$ in $(H_2{}^{16}O)_2$	1215.9s		$\nu(S{=}O)_{2\ sym}$
	3696.9w				**free ν(OH) of H_2O in $H_2O\cdot H_2SO_4$**	1156.8w		SOH as. bend
				3682.2 w, 3671.3vw	ν(OH) of HDO	1135.9w		SOH sym. bend
	3581.9m	**3571.8w**		**3581.4m**	**bound ν(OH) of H_2O in $H_2O\cdot H_2SO_4$**			
	(3573.2s)				bound $\nu(OH)_{donor}$ of H_2O in $(H_2{}^{16}O)_2$	881.6s	**929.0**	$S(OH)_2$ as. Stretch
3572.0m	*3571.8m*	*3560.9w*	3571.8s		*$\nu(OH)_{as}$ in H_2SO_4*	887.1*w		
3571.7sh					$\nu(OH)_{accept.}$ in $(H_2SO_4)_2$			
			3569.5vw	*3569.1s*	*ν(OH) $HDSO_4$*	831.2w	**838.6**	$\nu(S{-}(OH)_2)_{sym}$
3566.6s	*3566.5s*	*3557.5, 3555.9s*	3566.6s		*$\nu(OH)_{sym}$ in H_2SO_4*	834.1*w		
3516.6w	*3516.6m*	*3505.7w*	*3516.6s*	*3516.8w*	*$\nu(OH)_{donor}$in $(H_2SO_4)_2$*	558.1w		O−S=O rock
			2723vw, 2656vw	2793vw, 2782w, 2772vw, 2758vw, 2745vw, 2724vw, 2648vw, 2643w	DOH/D_2O	547.9w		$S{=}O_2$ bend
	2936.6vw				*$(H_2SO_4)_n$*	505.5vw		$S{=}O_2$ wag
	2722.0, 2593.3vw				**bound $\nu(OH)_{donor}$ H_2SO_4 in $H_2O\cdot H_2SO_4$**			
				2643w	**bound $\nu(OD)_{donor}$ of D_2O in $D_2O\cdot D_2SO_4$**			
				2634.5s	*$\nu(OD)_{as}$ in D_2SO_4*			
			2634.5s, 2631.9vw sh		ν(OD) of $HDSO_4$			
				2631.6s	*$\nu(OD)_s$ in D_2SO_4*			
			2594.5m	*2594.5m*	*$\nu(OD)_{donor}$ $(D_2SO_4)_2$*			
				2226.2vw	*$(D_2SO_4)_n$*			
				2117.0, 1986.5 vw	**bound $\nu(OD)_{donor}$ in $D_2SO_4\cdot D_2O$**			

[a] s, strong; m, medium; w, weak; vw, very weak; sym, symmetric; as, asymmetric. Fonts: regular font, H_2O bands; italic font, H_2SO_4 bands; bold font, H_2O in $H_2SO_4\cdot H_2O$ complex bands. *Acid dimer band.

TABLE 2: Comparison of Experimental and Calculated Vibrational Frequencies (cm^{-1}) of the H_2SO_4 Molecule and Its Monohydrate $H_2SO_4\cdot H_2O$

	Ar matrix (this work)		harmonic MP2-TZP[a]		harmonic DFT/PW91-TZP[b]		CC-VSCF/MP2-TZP[a]		MP2/6-311+G (2d, 2p)[c]	MP2/6-311+G (2d, 2p)[d]
assignment	H_2SO_4“dry”	$H_2SO_4\cdot H_2O$	H_2SO_4	$H_2SO_4\cdot H_2O$	H_2SO_4	$H_2SO_4\cdot H_2O$	H_2SO_4	$H_2SO_4\cdot H_2O$	H_2SO_4	H_2SO_4
H_2O asymmetric stretch (free)		3696.6		3985.76		3730		3737.83		
H_2O symmetric stretch (bonded)		3581.9		3840.92		3508		3593.20		
OH symmetric stretch	3572.0		3819.96		3632		3589.54		3610. 0	3596
H_2SO_4 OH free				3822.33		3638		3627.80		
OH asymmetric stretch	3566.6		3815.49		3627		3499.51		3605.2	3592
H_2SO_4 OH bound		2722.0		3302.88		2771		2972.83		
		2593.3								
HOH bend of H_2O				1618.92		1607		1573.00		
$S{=}O_2$ asymmetric stretch	1452.1		1456.17	1468.32	1426	1464	1434.33	1436.40	1462.1	1458
				1368.04		1343		1336.23		
$S{=}O_2$ symmetric stretch	1215.9		1196.95	1186.77	1160	1140	1182.67	1171.86	1211.5	1212
				1157.92		1131		1152.78		
SOH asymmetric bend	1156.8		1160.69		1153		1127.55		1161.2	1155
SOH symmetric bend	1135.9		1149.91		1138		1118.16		1142.5	1139
$S(OH)_2$ asymmetric stretch	881. 6	929.0	839.80	884.40	801	917	821.13	867.52	850.1	888
$S(OH)_2$ symmetric stretch	831.2	838.6	791.77	820.39	743	856	779.15	834.05	796.4	832
O−S=O rock	558.1		529.93	538.25	513	635	524.62	536.05	536.9	558
intermolec. mode				527.29		527		540.42		
$S{=}O_2$ bend	547.9		511.7	504.17	499	509	518.78	514.14	535.6	548
intermolec. mode				461.97		491		599.82		
$S{=}O_2$ wag	505.5		476.46	382.92	463	389	480.32	476.21	483.8	499

[a] Reference 1. [b] Reference 9. [c] Reference 23. [d] Reference 2.

vibrationally active. Traces A−D of Figure 3 reproduce the spectra recorded from layers with a successively increasing water content in the range of 3800−3500 cm^{-1}. One notes again the total absence of water bands in trace A as compared to the wide spectral features of ice clusters in trace D. In trace E, a spectrum of matrix-isolated water vapors (no acid) is included for comparison.

The spectral traces show two well-separated groups of bands originating in the vibrations of the H_2O and H_2SO_4 species, respectively. In the water band region of the spectra of the matrix layers containing both sulfuric acid and water, five spectral features, not recorded in the spectrum of the “dry” acid layer but apparent in the pure water matrix layer, are assigned[13−15] to water monomers and dimers as listed in Table 1.

The “sulfuric acid ν(OH) region” between 3600 and 3500 cm^{-1} is, unfortunately, also the region where the ν(OH) of donor water in the $(H_2O)_2$ dimer is active. The availability of the spectrum of “dry” sulfuric acid and the better control of the

TABLE 3: H-Bond Energies (kJ/mol) in $H_2O \cdot H_2SO_4$ and $(H_2SO_4)_2$ from Empirical Correlations and Computational Methods

	empirical correlations				computational methods		
complex	$\Delta\nu^a$	I	r (H···O)^b	II	III^c	IV^d	V^e
$H_2O \cdots HOSO_2OH$	911	39.0	0.1645	33.0	38		
$HOH \cdots OSO(OH)_2$	125	14.0	0.205	17.0			
total stabilization		53		50		52.1	56.0
$(H_2SO_4)_2$	57	10.0					50−60

[a] $\Delta\nu$, cm^{-1} experimental shift from free acid (this work). [b] r(H···O), nm, microwave data.[4] **I** $-\Delta H = 1.3(\Delta\nu)^{1/2}$.[20] **II** $-\Delta H = 0.134r^{-3.05}$.[22] [c] Reference 5. $H_2O \cdots HOSO_2OH$ bond only. [d] Reference 6. Sum for major $H_2O \cdots HOSO_2OH$ and minor $HOH \cdots OSO(OH)_2$ bonds. [e] Reference 8.

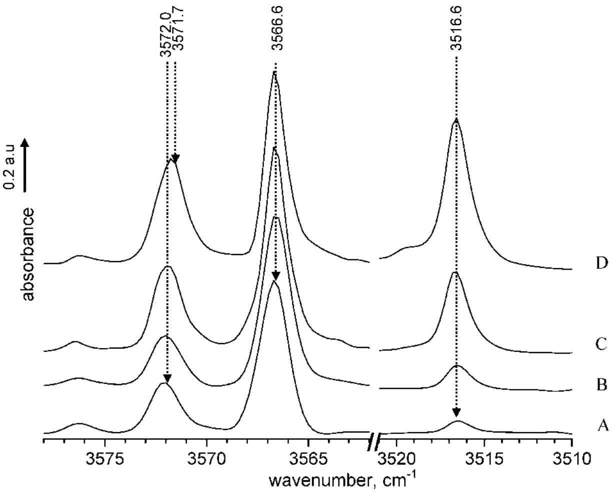

Figure 2. Spectra of sulfuric acid in a "dry" Ar matrix: The synchronous increase of the 3572 and 3516.6 cm^{-1}dimer band.

water content of the matrices necessarily lead us to conclude that the changes observed in the 3571.8 cm^{-1} band result from overlaps of the 3572 cm^{-1} H_2SO_4 monomer band (with possibly some dimer contribution, see above) with the 3573.4 cm^{-1} water dimer band and are not the sought after ν(OH) band of the $H_2SO_4 \cdot H_2O$ complex, as suggested previously.[3] One notes that the spectrum of pure matrix-isolated acid, trace Figure 3A shows the H_2SO_4 band at 3572 cm^{-1}, and Figure 3E shows the $(H_2O)_2$ dimer in the pure water matrix spectrum.

On the other hand, the two bands at 3696.9 and 3581.9 cm^{-1} are not recorded in either of the layers containing water species or acid species only. They appear only in "wet" matrix layers of H_2SO_4 and show a good correlation between both relative intensities. Assuming that the interaction between H_2SO_4 and H_2O molecules is by hydrogen bonding, with a resulting red shift in the ν(OH) frequency of the relevant hydroxyl bond, the reasonable assignment of these bands is to the *water moiety* in an $H_2SO_4 \cdot H_2O$ complex. This conclusion relies both on the reasonably sized red shifts of these bands from those observed bands for trapped H_2O species and on the fact that these bands are observed only in acid-containing layers but are positioned at wavenumber values higher than those of the ν(OH) bands of trapped H_2SO_4.

Finally, after the careful comparison of the "dry" and "wet" matrix layers, we discerned three bands below 3000 cm^{-1} at 2936.6, 2722, and 2593.3 cm^{-1}. They are of low peak intensity but very broad relative to the other bands recorded for the matrix layers ($\Delta\nu_{1/2} = 30$ cm^{-1}) and were not discerned in previous experiments.[3] These bands recorded in the spectrum of a "wet" matrix are seen in Figure 4B. They are absent in the spectrum of the "dry" matrix shown in Figure 4A. Figure 4C shows the analogs of these bands in the spectrum of deuterated acid on a frequency scale shifted by a factor of 1.30, the approximate isotope shift expected for deuteration.

The band at 2929.2 cm^{-1}, the intensity of which changes with deposition duration and rate, may be related to sulfuric acid polymers. Its frequency coincides with the peak position of the ν(OH) band in the spectra of crystalline H_2SO_4.[16] The relative intensity of the other two bands, at 2727.0 and 2593.3 cm^{-1}, remains constant in all spectra, and we can now assign them to the monohydrate complex of acid. We shall relate in more detail to this assignment in the Discussion section. Here we note that the effects of both the major and minor hydrogen bonding in both the H_2O and H_2SO_4 moieties of the $H_2SO_4 \cdot H_2O$ complex have thus been spectoscpically observed. To confirm our assignments, particularly for the bands in the hydroxyl stretch region, we recorded spectra of matrix-isolated isotopically enriched acid/water species. These included both deuterated and ^{18}O-enriched samples.

Deuterated Sulfuric Acid Matrices. Figure 5 compares the spectra "dry" matrix-isolated H_2SO_4, shown in trace A with the spectra of matrix-isolated D_2SO_4 in trace C. The two regions, 3500−3600 and 2580−2680 cm^{-1} correspond to the wavenumber range of the ν(OH) and ν(OD) stretching modes, respectively. In between them, Figure 5B shows the spectrum of an istopic solution of 15% D_2SO_4 in H_2SO_4.

Overall, the spectral features in the ν(OH) region have their counterparts in the ν(OD) wavenumber range. Thus, the prominent acid monomer bands at 3565−3672 cm^{-1} have their analogs in the 2630−2645 cm^{-1} region, the 3516.6 cm^{-1} dimer band is shifted to the 2594−2597.5 cm^{-1} range, and, finally, the 3581.6 cm^{-1} band, now assigned to the H_2O moiety in the $H_2SO_4 \cdot H_2O$ complex, is mirrored in the 2643.0 cm^{-1} band in the ν(OD) range (the isotopic frequency ratio is 1.355 for all three). For the monomeric D-isotopomers, all ν(OD) stretches ($\nu(OD)_{sym}$ and $\nu(OD)_{asym}$ of D_2SO_4 and ν(OD) of $HDSO_4$) have very similar wavenumber values. The band showing the largest intensity gain in the mixed isotope spectrum is at 2634.5 cm^{-1}, and this line is, therefore, assigned to the ν(OD) stretch in the mixed $HDSO_4$ isotopomer.

As noticed above, the newly observed bands of the hydrogen-bonded H_2SO_4 hydoxyls have their counterparts in the spectra of "wet" deuterated acid matrices as three weak and broad bands at 2226.2 cm^{-1} for the deuterated acid polymer and 2117.0 and 1986.5 cm^{-1} for the bonded ν(OD) of the acid moiety in $D_2SO_4 \cdot D_2O$ complex, respectively.

The relevant bands and their assignments are summareized in Table 1.

Matrix-Isolated $H_2S^{18}O_4$. Figure 6 shows the effects of ^{18}O enrichment on the matrix isolation spectrum of sulfuric acid. With the corresponding spectrum of "dry" normal H_2SO_4 as reference in Figure 6A, the spectrum of the acid ν(OH) region of an ^{18}O-enriched sample is shown in Figure 6B. The wavenumber values of the new bands produced by the isotopic enrichment are listed in Table 1. The bands of matrix-isolated "normal" H_2SO_4 also appear in the isotopically mixed layer

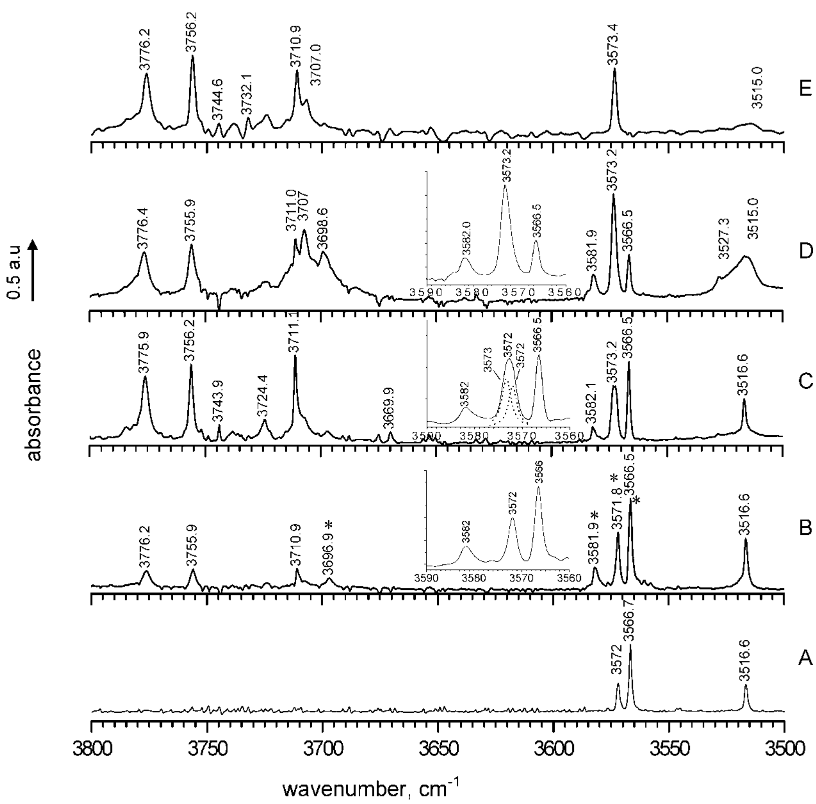

Figure 3. Variations in the stretching bands of sulfuric acid in Ar matrices with the increase of water content of the matrix layer: (A) "dry" matrix and (B, C, and D) increasingly "wet" matrices. (Insets) Expanded range of the acid band at 3572 cm^{-1} and water dimer band at 3573.4 cm^{-1}. (B) Bands of the $H_2SO_4 \cdot H_2O$ complex are denoted by an asterisk. (E) Pure H_2O in an Ar matrix (1:1000).

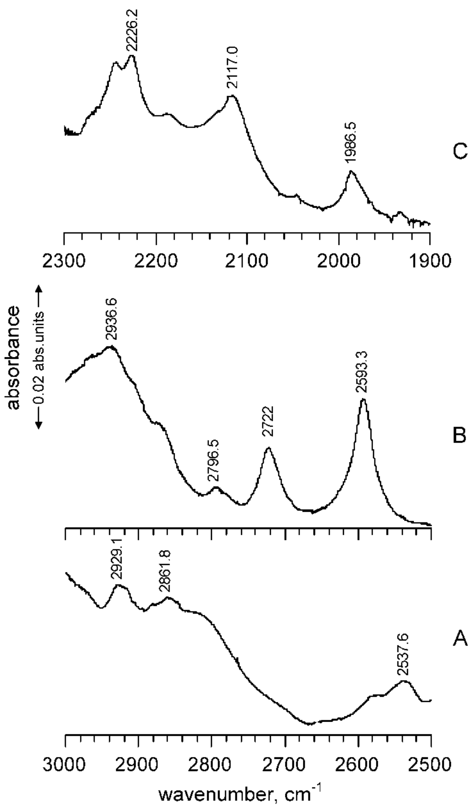

Figure 4. Spectra of sulfuric acid in Ar matrices below 3000 cm^{-1}: (A) H_2SO_4 in a "dry" matrix layer, (B) H_2SO_4 in a "wet" matrix layer, (C) D_2SO_4 in an argon matrix.

along with new bands, shifted from their original postion by about 10 cm^{-1}, due to the substitution. This is very clear in the 3516.6 cm^{-1} weak and wide band of dimeric $(H_2SO_4)_2$ shifted to 3505.7 cm^{-1} in the isotopically mixed sample. The band structure in the region of the symmetric and antisymmetric monomer stretches is somewhat more complicated due to the spectral activity of mixed $^{16}O-^{18}O$ istopomers. The calculated spectrum[17] shown in Figure 6C shows that the observed spectrum is indeed of a sample with about 50% isotopic enrichment and that, except for the additional band at 3571.8 cm^{-1} (on the high wavenumber side of the monomeric ν(OH) bands), the observed bands in both A and B are due to "pure" H_2SO_4 species in the matrix layer.

The latter band is best assigned as the isotopically shifted counterpart of the band at 3581.6 cm^{-1} band in the normal acid sample, presently assigned by us to the H_2O moiety in the binary $H_2SO_4 \cdot H_2O$ complex.

Skeletal Mode Region (1500−800 cm^{-1}). Figure 7 extends the range of the spectra shown in Figure 3 to the skeletal mode region, down to 800 cm^{-1}, with wavenumber values listed in Table 1.

The spectral features affected by the H_2SO_4 and water ratios in the matrix are seen in the range below 1000 cm^{-1}, where the modes involving the antisymmetric and symmetric S−O bond stretches are active. For the pure sulfuric acid molecule isolated in a dry matrix, the bands at 881.6 (m) and 831.2 (w) cm^{-1} are, respectively, assigned to these modes. Increasing the H_2SO_4 concentration in the matrix layer causes the appearance and gradual growth of spectral bands at 887.1 and 834.1 cm^{-1} to the high wavenumber sides of the respective monomer bands. These bands, clearly observed in all "dry" matrices (Figure 7A−C), may, therefore, be associated with the modes of the $(H_2SO_4)_2$ dimer. Such assignment is well supported by the fact that the intensity increase of these bands closely follows the increase of the intensity of the dimer band at 3516.6 cm^{-1} in

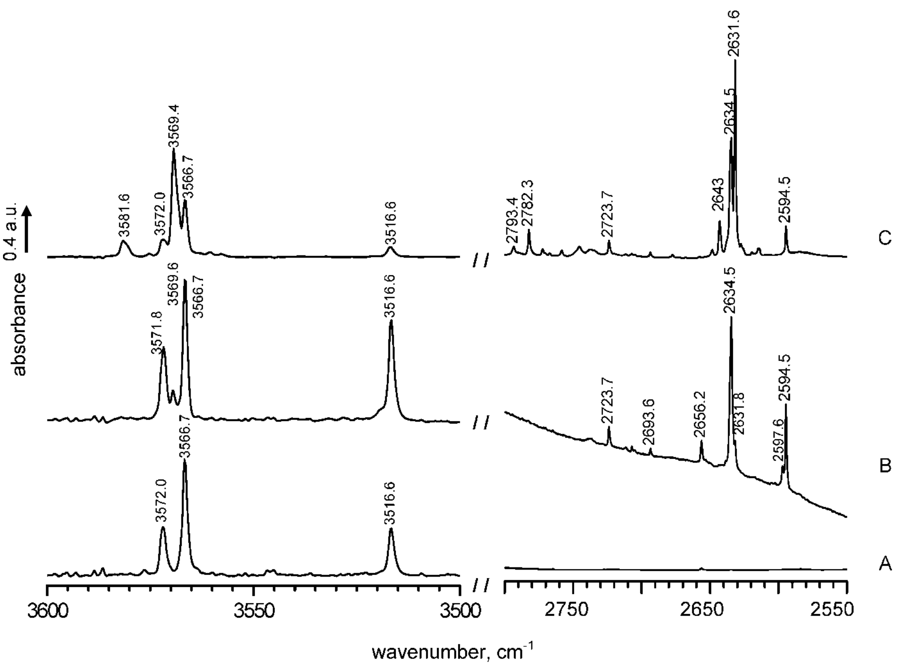

Figure 5. Spectra of sulfuric acid H_2SO_4/D_2SO_4 in Ar matrices: (A) H_2SO_4, (B) 15% H_2SO_4 in D_2SO_4, (C) D_2SO_4.

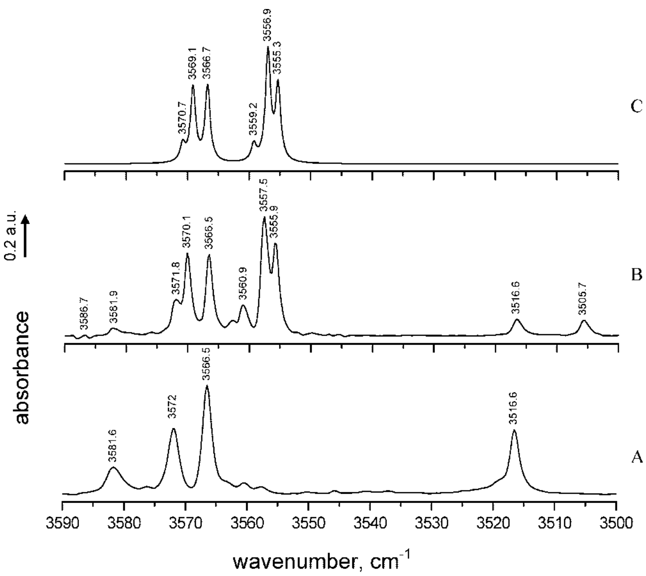

Figure 6. Effects of ^{18}O enrichment on the spectra of sulfuric acid: (A) $H_2S^{16}O_4$ in an argon matrix, (B) $H_2S^{18}O_4$ in an argon matrix (approximate enrichment 50%), (C) $H_2S^{18}O_4$ calculated (scaled harmonic) spectrum for 50 atom % ^{18}O.

the ν(O−H) wavenumber region. In the spectrum of the most concentrated matrix layer an additional very weak band is recorded at 891 cm^{-1} and assigned to higher acid molecule aggregates.

In the "wet" matrix layers (Figure 7D−F), two additional bands become apparent and grow in intensity with the increasing water content of the matrix. One of these is recorded on the high wavenumber side of the symmetric ν(S−O) stretch at 838.6 cm^{-1} and is of very weak intensity. The other, of somewhat higher intensity, at 929.0 cm^{-1} is much more blue shifted from the corresponding symmetric ν(S−O) stretch. Both have to be attributed to be the products of the interaction of H_2SO_4 and H_2O molecules: they appear only in "wet" matrices, and their intensity increase is well correlated with the growth of the spectral features of H_2O species in the matrix. We note that the growth of these $H_2SO_4 \cdot H_2O$ bands is at the expense of the adjacent $(H_2SO_4)_2$ dimer bands.

The observed unequal blue shifts in both the ν(S−O) mode frequencies fit well the calculated[5] asymmetric S−O bond shortening upon complexation. However, a comparison of our experimental frequencies results with the theoretically obtained values (Table 2) shows a good fit between the observed and calculated shifts due to complexation of the asymmetric $S(OH)_2$ stretch. This is not the case for the symmetric $S(OH)_2$, where the calculations predict that the $H_2SO_4 \cdots H_2O$ interaction will bring about much larger shifts than actually observed.

Discussion

The present study was motivated by our failure to observe the red-shifted ν(OH) stretching mode band of the bonded hydroxyl in the monohydrate complex $H_2SO_4 \cdot H_2O$ predicted by the original calculations of Arstila et al.,[5] confirmed by Beichert et al.[6] and then by more recent calculations.[1] The work of Beichert et al.[6] suggested the possibility of a less stable "back-bonded" structure for the complex. To examine this possibility, similarities between the $H_2SO_4 \cdot H_2O$ spectrum[3] and the complex formed by dimethyl sulfone, $(CH_3)_2SO_4$ (with no hydroxyl bonds of it own), and water have been investigated.[18]

The experimental difficulty in discerning the relevant spectral bands arises from the inherent vapor-phase equilibrium over the liquid acid. This equilibrium dictates the presence not only of acid molecular species but also of a large variety of water-related and mixed acid water species, as is evident from the size of Table 1 in ref 3 which lists the then observed spectral bands. As our present experiments indicate, the intrinsic width of these bands presented one more experimental difficulty by lowering the peak intensity of the relevant bands and causing them to go unobserved. The possibility of a dissociative trajectory of the $H_2SO_4 \cdot H_2O$ complex into SO_3 and H_2O has been considered and found as not plausible.[19]

The present experiments which afforded us with spectra of matrix layers ranging from "dry" to "wet" allow us to not only reliably identify the "missing bands" but also observe the effects of hydrogen bonding on the H_2O moiety in the monohydrate

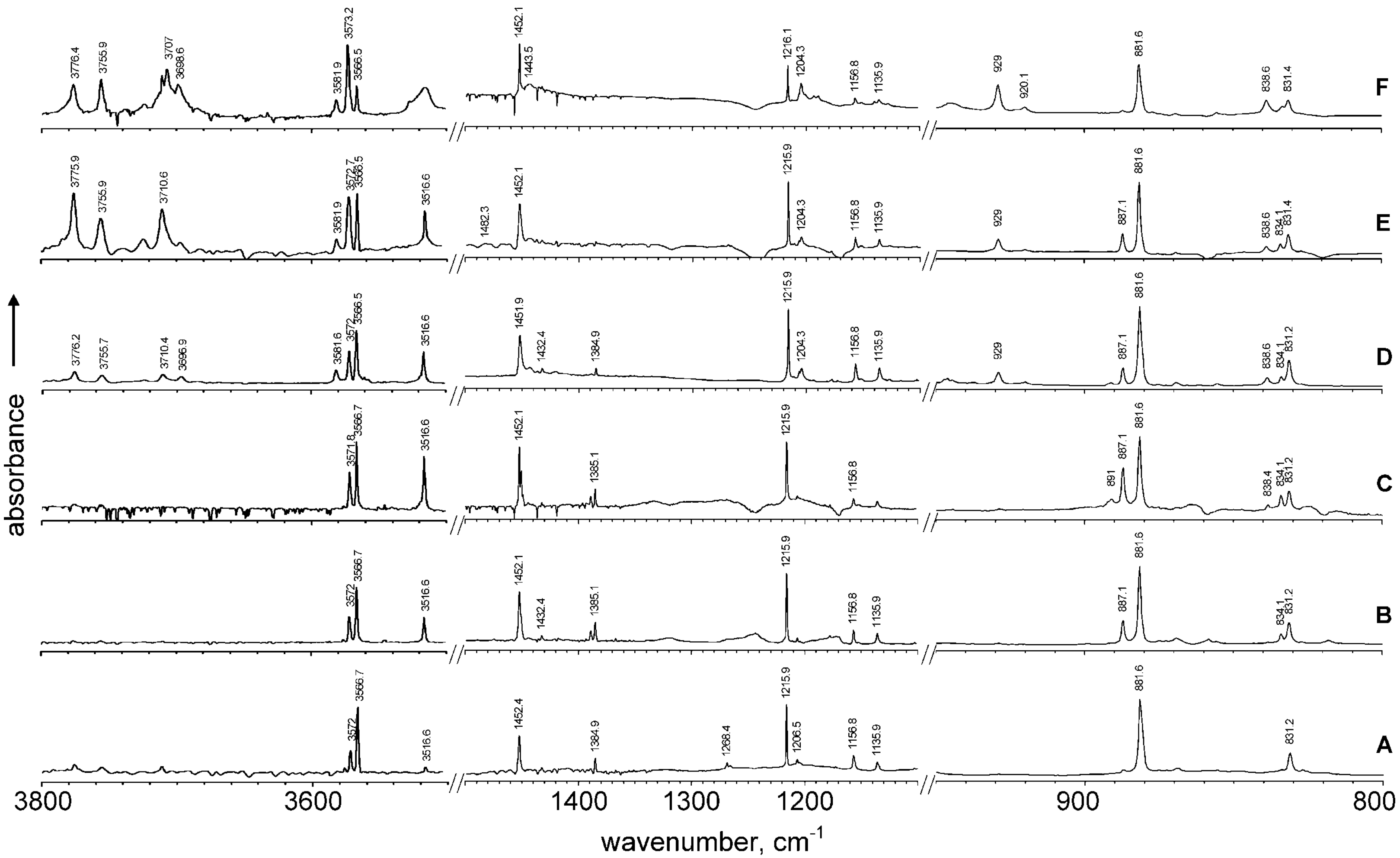

Figure 7. Variations in the spectra of H_2SO_4 with increasing concentration of acid (A−C) and water (D−F) in the argon matrix layer.

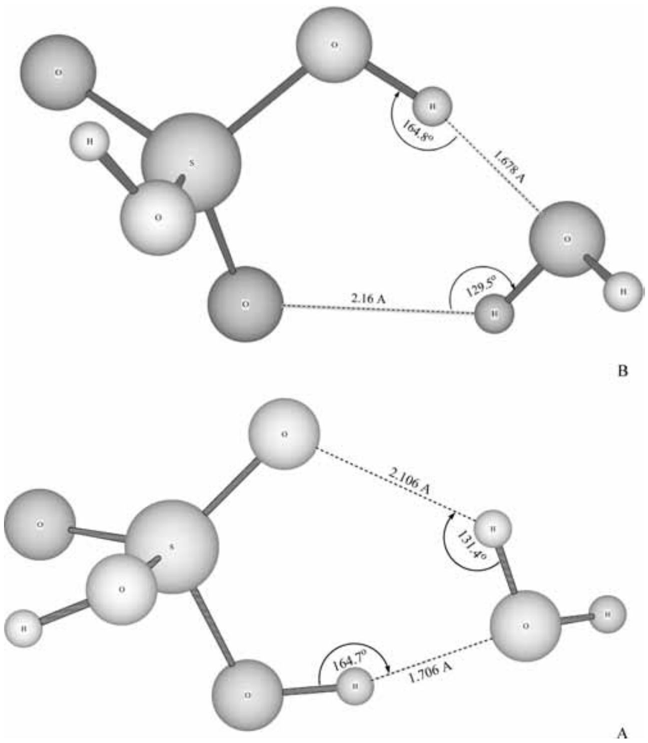

Figure 8. Calculated structures for the $H_2SO_4 \cdot H_2O$ monohydrate complex: (A) "trans" configuration of the free hydroxyl bonds of the acid, (B) "cis" configuration of the free hydroxyl bonds of the acid.

$H_2SO_4 \cdot H_2O$ complex. Thus, the current work presents assignments for the "free" and "bonded" ν(OH) in both the H_2O and H_2SO_4 moieties of the complex. The low isotopic shift factor (approximately 1.3) of the latter, along with their large red shift which (about 900 cm^{-1}), are characteristic attributes of strong hydrogen-bonded systems.[20] The spectra also show the effects of the complexation on the inner single-bonded S−O stretches in the acid moiety.

The hydrogen-bonding scheme of the acid monohydrate complex involves one major hydrogen bond between an acid hydroxyl and the water oxygen and a secondary, weaker hydrogen bond between a water hydroxyl and an oxygen of an acid S=O bond. This bonding scheme allows the free hydroxyls of the acid and of the water to be either on the same side ("cis") or on opposite sides ("trans") of the complex skeleton. These two configurations, of very similar stabilization energies (within 0.5 kJ/mol),[17] are depicted in Figure 8. It is tempting to attribute the observation of two bands for the bonded ν(OH) stretch to the existence of two different conformations of the monohydrate complex. However, this explanation is not supported by the spectral observations. First, the intensity ratio between both bands is essentially constant in all experiments in which they were observed. Second, this intensity ratio of the two bands in the "normal" $Ar/H_2SO_4/H_2O$ layers is different from that in the deuterated $Ar/D_2SO_4/D_2O$ layers (Figure 4). Third, the wavenumber difference of about 130 cm^{-1} between the two bands indicates a much larger than calculated difference in the stabilization energies.[20] We also note that we see no analogous bands of a second complex structure in the ν(OH) band of the water moiety.

An alternative possibly better explanation suggests a Fermi resonance interaction between the ν(OH) stretching mode and the first overtone of the O···H−O deformation mode. Such interactions are typical to spectra of strong hydrogen-bonded systems.[20,21]

It may be noted that the current results place the critical ν(OH) band positions at considerably lower wavenumbers than those calculated, even when the calculations purport the inclusion of anharmonicity (Table 2). The Iogansen[20] correlation between the spectral red shift and the hydrogen-bond strength indicates a hydrogen-bond stabilization energy of −39.0 kJ/mol for the main $HOSO_4O{-}H \cdots OH_2$ interaction. The complex is further stabilized by the secondary, weaker hydrogen-bond interaction between the H_2O hydrogen and the oxygen of one O=S bond of H_2SO_4. Using the Iogansen correlation again, for this interaction also (even though here it is not a linear hydrogen-bonding scheme), one arrives at an approximate additional stabilization of about −14 kJ/mol. The various theoretically calculated stabilization energies are listed in Table 3 and compare well with the sum of the energy values derived from the Iogansen correlation.

Another correlation[22] between the H-bond lengths and energies suggests bond stabilizations of 33 and 17 kJ/mol for the major and secondary hydrogen bonds of the complex, respectively, based upon the bond length found in the microwave studies of Fiacco et al.[4] Thus, both theoretically calculated and empirically obtained values suggest a hydrogen-bond stabilization of, approximately, −50 kJ/mol for the $H_2SO_4 \cdot H_2O$ complex.

As a final remark, the relatively small red shift of less than 60 cm^{-1}, observed for the ν(OH) band of the $(H_2SO_4)_2$ dimer, does not fit the even higher stabilization energy of over 60 kJ/mol suggested for it.[8] Chemical intuition also suggests the bond between two dissimilar moieties to be stronger, and therefore, a weaker bonding is expected for the $(H_2SO_4)_2$ dimer than for the $H_2SO_4 \cdot H_2O$ complex.

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References and Notes

(1) Miller, Y.; Chaban, G. M.; Gerber, R. B. *J. Phys. Chem. A* **2005**, *109*, 6565–6574.

(2) Givan, A.; Larsen, L. A.; Loewenschuss, A.; Nielsen, C. J. *J. Mol. Struct.* **1999**, *509*, 35–47.

(3) Givan, A.; Larsen, L. A.; Loewenschuss, A.; Nielsen, C. J. *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 827–835.

(4) Fiacco, D. L.; Hunt, S. W.; Leopold, K. R. *J. Am. Chem. Soc.* **2002**, *124*, 4504–4511.

(5) Arstila, H.; Laasonen, K.; Laaksonen, A. *J. Chem. Phys.* **1998**, *108*, 1031–1039.

(6) Beichert, P.; Schrems, O. *J. Phys. Chem. A* **1998**, *102*, 10540–10544.

(7) Re, S.; Osamura, Y.; Morokuma, K. *J. Phys. Chem. A* **1999**, *103*, 3535–3547.

(8) Ding, C.-G.; Laasonen, K.; Laaksonen, A. *J. Phys. Chem. A* **2003**, *107*, 8648–8658.

(9) Vaida, V.; Kjaergaard, H. G.; Hintze, P. E.; Donaldson, D. J. *Science* **2003**, 1566–1568.

(10) Natsheh, A. A.; Nadykto, A. B.; Mikkelsen, K. V.; Yu, F.; Ruuskanen, J. *J. Phys. Chem.* **2004**, *108*, 8914–8929.

(11) Kurten, T.; Noppel, M.; Venkamaki, H.; Salonen, M.; Kulmala, M. *Boreal Environ. Res.* **2007**, *12*, 431–453.

(12) Hintze, P. E.; Kjaergaard, H. G.; Vaida, V.; Burkholder, J. B. *J. Phys. Chem. A* **2003**, *107*, 1112–1118.

(13) Michaut, X.; Vasserot, A.-M.; Abouaf-Marguin, L. *Vib. Spectrosc.* **2004**, *34*, 83–93.

(14) Hirabayashi, S.; Ohno, K.; Abe, H.; Yamada, K. M. T. *J. Chem. Phys.* **2005**, *122* (1−6), 194506.

(15) Engdahl, A.; Nelander, B. *J. Mol. Struct.* **1989**, *193*, 101–109.

(16) Goypiron, A.; De Villepin, J.; Novak, A. *Spectrochim. Acta, A* **1975**, *31*, 806–818.

(17) Nielsen, C. J. Private communication.

(18) Givan, A.; Grothe, H.; Loewenschuss, A.; Nielsen, C. J. *Phys. Chem. Chem. Phys.* **2002**, *4*, 255–263.

(19) Miller, Y.; Gerber, R. B. *J. Am. Chem. Soc.* **2006**, *128*, 9594–9595.

(20) Iogansen, A. V. *Spectrochim. Acta, A* **1999**, *55*, 1585–1612.

(21) Odinokov, S. E.; Iogansen, A. V. *Spectrochim. Acta, A* **1972**, *28*, 2343–2350.

(22) Rozenberg, M.; Loewenschuss, A.; Marcus, Y. *Phys. Chem. Chem. Phys.* **2000**, *2*, 2699–2702.

(23) Demaison, J.; Herman, M.; Lievin, J.; Rudolph, H. D. *J. Phys. Chem.* **2007**, *A111*, 2602–2609.

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