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Observations on the Interpretation and Analysis of Sulfuric Acid Hydrate Infrared Spectra

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New infrared spectra of pure bulk molecular sulfuric acid and its mono- and tetrahydrates under equilibrium water partial pressure conditions have been obtained using an internal reflection geometry. For each of the species present (H_2SO_4, HSO_4^- and SO_4^{2-}), a well-defined set of core SO_4 vibrations has been identified and assigned to individual vibrational modes. Using these data, earlier literature data has been reexamined. Existing methods for the quantification of composition and ion speciation in H_2SO_4/H_2O mixtures are examined and the need for a more sophisticated method for the determination of sulfate aerosol composition is proposed.

Introduction

The motivation behind this work is to gain a more detailed understanding of the form, composition, and ion speciation in sulfuric acid hydrates used as mimics of atmospheric particulate material. There have been a number of studies in recent years[1−9] which have attempted to simulate this important component of atmospheric particles in the laboratory. These studies have mainly used infrared spectroscopy (and to a lesser extent, Raman spectroscopy) to identify the concentration of sulfuric acid in both thin films and aerosols through the spectral characteristics of the appropriate H_2O, H_3O^+, HSO_4^-, and SO_4^{2-} species on the basis of historical literature.[10−16] As a result of variation of experimental conditions and methods of synthesis, there is a great degree of complexity apparent in both the historical and the more recent spectra which has attracted a number of alternative assignments: this has hindered our understanding of these systems and current opinion is still far from consensus. In this letter, new measurements of the infrared absorption spectra of relatively pure one-component thin solid sulfuric acid hydrate films *obtained under equilibrium conditions* are used in the reanalysis of the spectra presented in two of the most frequently cited reference works. Furthermore, we demonstrate that the widely accepted methods currently in use for the measurement of H_2SO_4% by weight composition from IR spectra are not intrinsically reliable, one of which leads to a consistent overestimation of sulfuric acid concentration.

Experimental and Analysis

The apparatus used to form and characterize sulfuric hydrate films consists of a stainless steel vacuum reaction chamber coupled to an FTIR spectrometer and gas handling line.[17−19] A germanium internal reflection element (IRE) is suspended at the center of the sample chamber. The temperature of the substrate is controlled by coil heating vs. liquid nitrogen cooling of a Ni foil substrate carrier, and is measured using a chromel−alumel thermocouple in contact with the front surface of the IRE. Temperature calibrations are performed using the ice-frost-point method described by Middlebrook *et al.*[20] Gaseous samples are admitted to the vacuum chamber via three separate internal Pyrex nozzles connected to high-precision leak valves. Ultrapure deionized water was degassed prior to use via freeze−pump−thaw cycling. Anhydrous sulfur trioxide, water, deuterated water, and hydrogen chloride (Aldrich, UK, 99%) were used without further purification.

Infrared spectra are obtained in an attenuated total internal reflection (ATR) geometry, which permits a clear identification of bulk composition for films in the 300ñ500 nm thickness range. The IR beam is internally incident upon the IRE surface at an angle of **55**° to the surface normal, leading to an effective depth of penetration of ca. 200 nm at 1500 cm^{-1}. Spectra are produced from the co-addition of 64 interferograms at 4 cm^{-1} resolution, ratioed against the clean IRE background, and presented in absorbance units. The lower wavenumber for transmission through Ge is ca. 700 cm^{-1}. Thin sulfuric acid and sulfuric acid hydrate films of appropriate composition are formed from the co-deposition of gaseous $H_2O(D_2O)$ and SO_3 at temperatures from 180 to 250 K. Plots of the integrated OH region versus time during deposition yield typical film thicknesses of 450 ± 20 nm.[18] Since the vapor pressure of sulfuric acid is extremely low below 220 K, the equilibrium film composition is determined by the partial pressure of water. Changes in water partial pressure or film temperature result in immediate and reversible changes in composition. Under the temperature and water vapor pressure conditions used in this study, there is no evidence for the formation of molecular hydrates and clusters which can be observed in cryogenic matrixes.[21]

Molecular Sulfuric Acid. H_2SO_4 is formed by co-deposition *in vacuo* of H_2O and SO_3 at partial pressures of $5 \cdot 10^{-6}$ and $1 \cdot 10^{-6}$ mbar respectively, directly onto the IRE at 250K. Neither reactant sticks to form a substantial single-component film under these conditions, so the only material retained by the substrate is the reaction product(s). Figure 1a shows the IR spectrum of the film formed after 60 min of deposition and 30 min standing *in vacuo*. This film is stable indefinitely at 250 K under UHV conditions as a result of the extremely low vapor pressure of H_2SO_4. The low wavenumber region of the spectrum is dominated by a number of strong peaks characteristic of the molecular acid which correlate well with transmission IR data for concentrated liquids[10−16] and molecular species[21] reported in the literature. Cooling slowly to 180 K results in further spectral changes as the sulfuric acid apparently crystallizes: the antisymmetric stretching modes of the sulfate core, split (Figure 1b), most probably a result of the interaction of more than one

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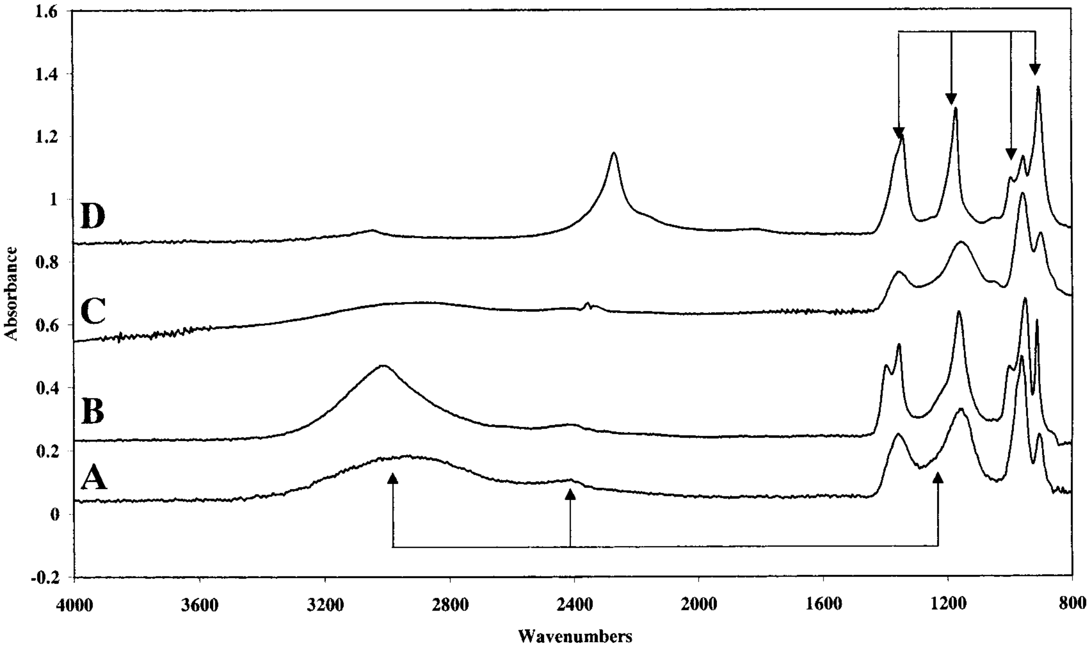

Figure 1. Molecular sulfuric acid spectra. (a) after deposition from H_2O and SO_3 *in vacuo* at 250 K. (b) after cooling to 180 K. (c) 18 M liquid H_2SO_4 at 293 K. (d) as (b), but using D_2O. Arrowed features show the approximate band locations for the OH (bottom) and S−O (top) motifs.

TABLE 1: Summary of IR Band Assignments for normal and Deuterated Sulfuric Acid[18−19a]

18 M liquid 293 K	co-dep. 250 K	solid, 180 K	co-dep. deuterated	Assignment
2960 (br)	2950 (br)	3010 (s)	2274(s)	$\nu_{as}S(O-H)_2,\nu_{s}S(O-H)_2$
2410 (w)	2420 (w)	2420 (w)	1819(w)	
1359 (s)	1361 (s)	1358 (s)	1343(s)	$\nu_{as}(O=S=O)$
1240 (sh)	1240 (sh)	1240 (sh)	-	$\delta_{as}S(O-H)_2$
1158 (s)	1159 (s)	1165 (s)	1172 (s)	$\nu_{s}(O=S=O)$
-	-	-	-	$\delta_{sS}(O-H)_2$
957 (vs)	965 (s)	951 (s)	955 (m)	$\nu_{as}(S-(OH)_2)$
902 (s)	905 (m)	913 (s)	904 (s)	$\nu_{s}(S-(OH)_2)$

[a] vs = very strong, s = strong, m = medium, w = weak, br = broad, sh = shoulder.

H_2SO_4 molecule in the unit cell. A suitable reference for the ATR−IR spectrum of liquid sulfuric acid can be obtained from concentrated 18 M acid dropped on the face of an ex vacuo ATR accessory at room temperature, as shown in Figure 1c. Finally, Figure 1d shows the spectrum of D_2SO_4 obtained from the reaction between D_2O and SO_3 under the same deposition conditions. Band positions and assignments are given in Table 1. Note that in this case, the splitting of the antisymmetric stretching modes is less than for the undeuterated material, which can be attributed to the presence of some slight disorder in the crystalline material. The vacuum-deposited film at 250 K is clearly either a liquid or a highly amorphous solid. The arrows in the figure identify the OH-modes (bottom) and sulfate core modes (top).

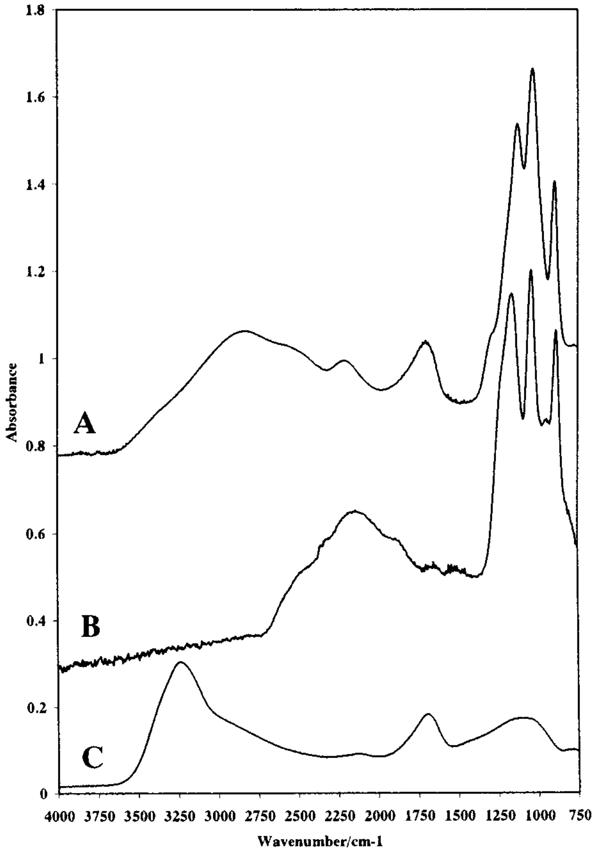

Figure 2. Sulfuric acid monohydrate spectra. (a) SAM deposited from H_2O and SO_3 at 180 K. (b) as above, formed from D_2O and SO_3. (c) amorphous 1:1 HCl:H_2O hydrate for H_3O^+ ion comparison.

Sulfuric Acid Monohydrate, $H_3O^+HSO_4^-$. Sulfuric acid monohydrate is readily formed either from the dilution of a molecular H_2SO_4 film at 180−190 K by exposure to water vapor (ca. $5 \cdot 10^{-7}$ mbar) or directly from gaseous SO_3 and H_2O (D_2O) at 180 K. The resulting IR spectra are identical.[18,19] Figure 2a shows a typical 450 ± 20 nm co-deposition film at 180 K. This remains stable in vacuo at this temperature indefinitely (> 8 h). By comparison to literature spectra,10−16,18,19 this film shows the characteristic features of the H_3O^+ and HSO_4^- ions alone. To identify bisulfate core vibrations, the deuterated analogue was also formed as shown in Figure 2b, clearly identifying the features at 1130, 1034, and 902 cm^{-1} in h_4−SAM and 1165, 1043, and 887 cm^{-1} in d_4−SAM We have previously assigned these bands to the asymmetric and symmetric SO_3 stretch and the S−O stretch of the pseudo-C_{3v} SO_4 core of the bisulfate ion, respectively.[18] Deuteration also removes the weak feature seen at 1290 cm^{-1} in h_4−SAM, confirming its assignment to the δ(OH) of the bisulfate ion. The remaining features result from the vibrational modes of the H_3O^+ (D_3O^+) ion and the

TABLE 2: Summary of IR Band Assignments for normal and Deuterated SAM[18] [a]

SAM	d_4–SAM	Assignment
2830 (s, br)	2200 (s, br)	ν_s, ν_{as} (H_3O^+), bisulfate ν(OH)
2220 (w, br)	-	H_3O^+ overtone/combination
1715 (m)	1250 (w, sh)	$\delta_{as}(H_3O^+)$, $\delta_{as}(D_3O^+)$
1290 (w, sh)	-	bisulfate δ(OH)
1133 (s)	1165 (s)	$\nu_{as}(HOSO_3)$
1035 (s)	1043	$\nu_s(HOSO_3)$
899 (s)	887	ν(S−OH)

[a] s = strong, m = medium, w = weak, sh = shoulder, br = broad.

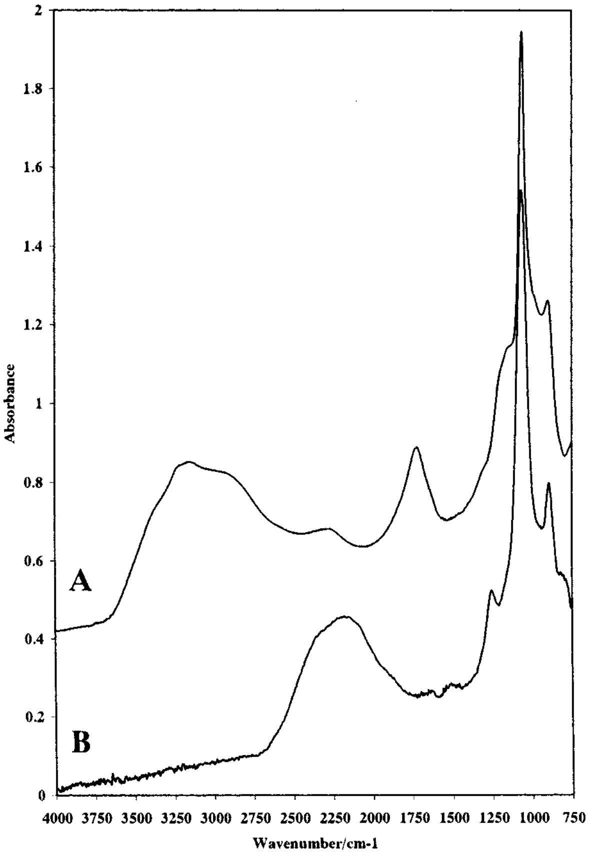

Figure 3. Sulfuric acid tetrahydrate spectra. (a) formed from hydration of SAM at 180 K. (b) as (a) but fully deuterated.

OH(OD) stretch of bisulfate. The assignment of the H_3O^+ vibrations are supported by reference to the spectrum of an amorphous 1:1 HCl:H_2O hydrate film (Figure 2c), which shows similar features to h_4–SAM in the 4000−1500 cm^{-1} region. The obvious H_3O^+ modes are identifiable as the broad features at ca. 3200 cm^{-1} (symmetric and asymmetric OH stretches) and 1700 cm^{-1} ($\delta_{as}(H_3O^+)$): less obvious in the SAM spectra is the very broad $\delta_s(H_3O^+)$ mode which underlies the sulfate core modes in the 1500−800 cm^{-1} range. On deuteration, the OD stretching features shift down in wavenumber to ca. 2400 cm^{-1} and the $\delta_{as}(D_3O^+)$ mode appears as a shoulder to the bisulfate core modes at ca. 1260 cm^{-1}. The last remaining feature to be assigned in the SAM spectrum is the broad band at ca. 2820 cm^{-1}, which results from the OH stretching mode of the bisulfate ion. Band assignments for SAM are summarized in Table 2.

Sulfuric Acid Tetrahydrate, $(H_5O_2{}^+)_2SO_4{}^{2-}$. The result of exposing SAM to $1 \cdot 10^{-4}$ mbar H_2O is shown in Figure 3a. Most notably, the bisulfate features are lost to be replaced with a strong, sharp feature at **ca.** 1064 cm^{-1}, which is accompanied by subtle but distinct changes to the OH-related bands. The phase present at these higher water pressures is sulfuric acid tetrahydrate (SAT). A free sulfate ion in solution has T_d symmetry with an IR-active fundamental at 1104 cm^{-1} (ν_3, the T_2 asymmetric SO_4 stretch[22]) and a Raman active fundamental at 981 cm^{-1} (ν_1, the A_1 totally symmetric SO_4 stretch). Given that when IR active, sulfate core vibrations are strongly absorbing (i.e. they are accompanied by large dipole moment changes), the intense, sharp band can readily be assigned to ν_3. This is confirmed by deuteration, as shown in Figure 3b, which shows the spectrum of hydrated d_4–SAM to produce d_{10}–SAT: the sharp feature remains in place. Deuteration also shows that the weak feature at 900 cm^{-1} (893 cm^{-1} in d_{10}–SAT) is related to the sulfate ion core. A potential assignment of this mode is to the totally symmetric SO_4 stretch (formally forbidden in T_d) given its proximity to the Raman-active ν_1 mode of the free ion (975 cm^{-1}) and the closely related $\nu_s(OSO_3)$ mode of the bisulfate ion. This suggests that the ion is somewhat distorted from a pure tetrahedral shape, in agreement with the known crystal structure. However, it is also possible that this feature arises from overtones or combinations of lower frequency modes (of which there are many), possibly increased in intensity by resonance with neighboring fundamentals. Nevertheless, this band is a characteristic of the $SO_4{}^{2-}$ species in SAT. Band assignments for SAT are given in Table 3.

Discussion

These spectra, obtained under equilibrium conditions (since the film is readily able to exchange material with the ambient gases) clearly show the distinctive features of the hydronium, bisulfate, and sulfate ions in crystalline systems. In the atmospheric chemistry literature, the most frequently cited papers presenting assignments of these species are those of Middlebrook et al.[20] and Zhang et al.[23] The spectra and assignments given above are in excellent agreement with the latter for the tetrahydrate species: however, the assignment of the mono- to tri- hydrates and the molecular acid is contentious. For example, the spectra given by Zhang et al. for the lowest three hydrates are clearly complicated mixtures of components. The 1:1 mixture does not show the simplicity expected from the monohydrate, which the spectra presented above reveal as relatively simple, comprising a set of H_3O^+ features and $HSO_4{}^-$ features. This is also true for films with intermediate composition, which are unlikely to be the pure 1:2 and 1:3 hydrates on the basis of their metastability. During the conversion of SAM to SAT, we have previously observed spectral features similar to those given by Zhang et al. which we have attributed to intermediate species which are effectively distorted $HSO_4{}^-$ or $SO_4{}^{2-}$ ions in constricted environments.[19] It is likely therefore that the low temperatures utilized have stabilized, disordered, or distorted intermediate forms which, although they contain the relevant stoichiometric ratio of H_2O and H_2SO_4, do not represent the pure crystalline hydrates. The point of contact between the Zhang et al. hydrates and this work is the tetrahydrate (recognized as the most stable under these condition), which shows comparable features. As a result of the high water vapor pressures required for their formation in our apparatus, no data is available in our study for the higher hydrates for comparison.

Similarly, the features assigned to pure acid (96 wt %) at both room temperature and 210 K by Middlebrook et al. are clearly inconsistent with either the room-temperature liquid or low-temperature condensed films presented here and in the historical literature. Such a concentration represents a ratio of about four H_2SO_4 molecules per H_2O: however, the spectra

TABLE 3: Summary of IR Band Assignments for normal and Deuterated SAT[19]

SAT (rapid)	D_{10}–SAT	SAT (slow)	SAT (low T)	Assignment
3370 (sh, br)	-	3370 (sh, br)	3370 (sh)	Ice stretching modes
3230 (br)	2353 (br)	3230 (s)	3229 (s)	
3150 (sh, br)	-	3150 (sh)	3149 (sh)	
2890 (br)	2142 (br)	2840 (m, br)	not clear	(H_3O^+) and $(H_5O_2^+)$ stretches
2260 (w, br)	-	2270 (w, br)	2270 (w, br)	H_3O^+ overtone/combination
1720 (m)	1253 (w, sh)	1718 (m)	1718 (m)	$\delta_{as}(H_3O^+)$, $\delta_{as}(D_3O^+)$
-	-	1631 (sh)	1631 (sh)	SAT proton hydrate mode
1320 (sh)		~ 1300 (sh)	1290 (sh)	SAT proton hydrate mode
1210 (w)	-	1238 (w)	1220 (w)	SAT proton hydrate mode
1150 (w)		~ 1150 (w)	1153 (w)	$\nu_{as}(SO_3)$ (E in C_{3v})
1064 (vs)	1064 (vs)	1074 (vs)	1074 (vs)	$\nu_{as}(SO_4)$ ($\nu_3(T_2)$ in T_d)
-	-	1039 (w)	1039 (w)	$\nu_s(SO_3)$ (A_1 in C_{3v})
980 (vw)	-	980 (vw)	989 (w, sh)	$\nu(S{-}O)$ (A_1 in C_{3v})
898 (w)	893 (m)	900 (w)	900 (sh)	Overtone?

[a] vs = very strong, s = strong, m = medium, w = weak, br = broad, sh = shoulder.

presented can readily be identified as a mixture of H_3O^+ and bisulfate ions with no trace of molecular H_2SO_4. This places an upper limit of 84.5 wt % on the composition of this material. Furthermore, since there is very little difference between the room temperature and 210 K spectra, it is reasonable to conclude that the room temperature film consists of singly ionized species (i.e. HSO_4^-). The spectral variations observed upon dilution from "96 wt %" at room temperature are not representative of the second ionization (i.e. a shift in the $HSO_4^- \leftrightarrow SO_4^{2-}$ equilibrium), because no clear sulfate ion features are seen. However, the dilution at lower temperatures does appear to be characteristic of an aqueous sulfate system. This behavior is entirely consistent with the thermodynamics of the H_2SO_4/H_2O system (discussed in detail by Zhang et al.[23]) and the spectral variations observed upon hydration in our own studies.[18,19] A observation which can be made on the basis of the discussion above is in the quantification of sulfuric acid wt % in thin films and aerosols. There are two main methods utilized in the recent literature. Middlebrook et al.[20] suggested that an estimate of the concentration of sulfuric acid in thin films could be found from the ratio of the baseline-corrected absorbance at 3360 and 2875 cm^{-1} on the basis that this ratio relates the concentration of the dissociated acid in any hydrate film to that of the molecular acid: it has generally been recognized that this method is flawed, but the reason for this has largely been ignored. It is clear from the spectra presented here that wavenumbers selected for this calibration are dominated by hydronium and bisulfate absorptions of the monohydrate rather than the undissociated acid and so the calibration method does not conform to a 100% H_2SO_4 baseline. In fact, it actually relates the concentration to that of the monohydrate, which is 84.5 wt % H_2SO_4 (see above). A subsequent modification to this method by Anthony et al.[24] using the ratio of the integrated area of the OH bands to those of the sulfate features is more reliable, but disregards the presence of a *variety* of OH-type species at high wavenumber and the effects of ion speciation upon the total integrated intensity in the sulfate region. The method involves taking the ratio of the integrated absorbance from 3650 to 2409 cm^{-1} as being representative of the generic HO content and the 1470−820 cm^{-1} region representing the generic SO_4 content. However, the spectra presented here clearly show that OH features from both the hydrated proton species and bisulfate underlie the sulfate core modes. Furthermore, there are significant changes in the shape of the absorption profile in the sulfate region as a function of temperature (where solid hydrates and liquids are both potentially stable), and there is clearly a need for a more rigorous procedure. For example, Bertram et al. have identified flaws in the choice of limits for this procedure, while Iraci et al. have modified the method to extract compositional information from ternary $H_2SO_4/HONO_2/H_2O$ aerosols by identification of regions which are dominated by sulfate and nitrate features. For this procedure to be made more reliable, reproducible and representative individual molecular or ion spectral fingerprints from thin films are an essential complement to full spectrum measurements of optical constants (necessary for particle sizing and scattering calculations on real aerosol particles).

The major discrepancies observed both between the individual literature spectra and between the literature and those presented here, we believe, result from the nature of the experimental configuration. The film stoichiometry, given in both of the works cited above, is based upon the composition of a sample prior to cooling to appropriate temperatures which have subsequently been confined between two solid IR transparent windows. The variation of sulfate hydrate stoichiometry as a function temperature and water partial pressure is very large, and small changes in these parameters can therefore cause large changes in the structure and nature of the hydrates formed. Unless the hydrates are held in equilibrium with their appropriate water vapor pressure, they will necessarily change phase during the course of the measurement. As a result, studies which rely upon the confinement of a thin film between two plates are not operating under an ideal equilibrium situation, and may therefore give misleading results. For example, cooling a confined droplet between two plates will hinder the gas/liquid equilibrium between the hydrate and gaseous water. To provide consistent data for the interpretation of aerosol spectra (which are in intimate contact with their ambient gases), the sample needs to be able to readily exchange material with the ambient medium (i.e. a constant water partial pressure). This is readily achieved from condensed ultrathin films ($<1\ \mu m$), and such films that can be probed using transmission, internal, or external reflection optical geometries (although the latter is prone to substantial spectroscopic perturbation as a result of both orientational and reflectance effects, and interpretation of spectra becomes more difficult).[7] For example, ATR−IR − based observations of water uptake as a function of water partial pressure and temperature from our lab reported elsewhere[19] are in excellent agreement with the spectra presented by Middlebrook et al. for an open equilibrium system in a transmission geometry. This dependence of spectra upon experimental method has obvious implications in the analysis and comparison of thin film and aerosol spectra generally.

Conclusion

The spectra presented here demonstrate that there are clear spectral motifs for the ions present in sulfate hydrate films. We suggest that much of the existing literature data (both historic and recent) is perturbed by the experimental conditions under which it was obtained, particularly for those studies in which the maintenance of equilibrium was hindered. Furthermore, the presence of clear motifs potentially leads the way to a more rigorous method of composition determination through the quantification of the ratio of the individual ions rather than their total integrated intensity. If similar observations can be made on liquid systems and on systems with mixed composition, then a reliable method for spectroscopic determination of composition on aerosols could be developed using curve fitting to the individual ion fingerprints or chemometric methods to extract their relative concentration.

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