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In Situ Analysis of Ash Deposits from Black Liquor CombustionP. Bernath¹, Scott A. Siquefield², Larry L. Baxter, Gian Sclipa, C. Rohlfig, M. Barfield³

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Abstract

Aerosols formed during combustion of black liquor cause a significant fire-side fouling problem in pulp mill recovery boilers. The ash deposits reduce heat transfer effectiveness, plug gas passages, and contribute to corrosion. Both vapors and condensation aerosols lead to the formation of such deposits. The high ash content of the fuel and the low dew point of the condensate salts lead to a high aerosol and vapor concentration in most boilers. In situ measurements of the chemical composition of these deposits is an important step in gaining a fundamental understanding of the deposition process. Infrared emission spectroscopy is used to characterize the composition of thin film deposits resulting from the combustion of black liquor and the deposition of submicron aerosols and vapors. New reference spectra of Na_2SO_4 , K_2SO_4 , Na_2CO_3 and K_2CO_3 pure component films were recorded and compared with the spectra of the black liquor deposit. All of the black liquor emission bands were identified using a combination of literature data and ab initio calculations. Ab initio calculations also predict the locations and intensities of bands for the alkali vapors of interest.

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Abstract

Aerosols formed during combustion of black liquor cause a significant fire-side fouling problem in pulp mill recovery boilers. The ash deposits reduce heat transfer effectiveness, plug gas passages, and contribute to corrosion. Both vapors and condensation aerosols lead to the formation of such deposits. The high ash content of the fuel and the low dew point of the condensate salts lead to a high aerosol and vapor concentration in most boilers. In situ measurements of the chemical composition of these deposits is an important step in gaining a fundamental understanding of the deposition process. Infrared emission spectroscopy is used to characterize the composition of thin film deposits resulting from the combustion of black liquor and the deposition of submicron aerosols and vapors. New reference spectra of Na_2SO_4 , K_2SO_4 , Na_2CO_3 and K_2CO_3 pure component films were recorded and compared with the spectra of the black liquor deposit. All of the black liquor emission bands were identified using a combination of literature data and ab initio calculations. Ab initio calculations also predict the locations and intensities of bands for the alkali vapors of interest.

Introduction

Infrared emission spectroscopy of solids is well known, but the technique has not been widely used primarily because bulk and powdered solids tend to give poor spectra due to multiple absorption, emission, and scattering of the radiation before it has a chance to escape the sample [1-3]. However, high quality spectra are obtainable from thin films and small particles with dimensions less than about 100 microns.

Infrared emission spectroscopy is an excellent tool for the characterization of the surface of catalysts and the deposits formed in combustion processes. The use of the technique for characterization of coal and biomass deposits was previously illustrated [4, 5]. We illustrate the potential of the technique with the deposits formed during the combustion of black liquor. These deposits are almost entirely Na_2CO_3 and Na_2SO_4 .

Black liquor is a recycled byproduct formed during the pulping of wood in the papermaking industry [6]. Na_2S and NaOH are used to break down the complex organic glue, known as 'lignin', that binds wood fibers. In this process large amounts of carbonate are formed from oxidation of the organics, and the sulfide is oxidized to sulfate. After the fibers are removed from the caustic solution the solution is burned in boilers to recover and reuse the inorganic chemicals and generate process steam and electricity, usually for on-site use. Such boilers are called recovery boilers, with the dominant process and boiler design being that developed by Kraft – hence the term Kraft recovery boilers. As fired, black liquor is approximately one third organics (mostly from the wood), one third inorganics (mostly from the process), and one third water. The liquor used in this work was diluted to approximately 80% water. In the combustion environment of the recovery boiler, a fraction of the inorganics vaporize and recondense to form submicron aerosols which deposit and foul heat transfer surfaces. The resulting decrease in boiler efficiency motivates the study of these salt film deposits.

The strong bands at 880 cm^{-1} and 1140 cm^{-1} found in the black liquor deposit could be easily assigned to Na_2CO_3 and Na_2SO_4 , respectively, but the weaker bands were more difficult to

assign. The spectra of Na_2SO_4 and K_2SO_4 solids available in the literature [7-10] were not of sufficient quality, therefore new reference spectra of solid Na_2SO_4 , K_2SO_4 , Na_2CO_3 and K_2CO_3 were recorded. The comparison of the emission spectra of these salt films with the spectra of the black liquor deposit allowed the identification of all of the unknown bands.

Black liquor combustion generates alkali vapors, predominantly sodium salts (Na_2SO_4 and Na_2CO_3). As gas composition and temperature in a boiler change, a portion of these vapors form condensation aerosols with a mean diameter of about 0.7 microns [11, 12]. The aerosols and vapors are carried into the upper furnace, where they accumulate on relatively cool heat transfer surfaces. This paper details in situ, time-resolved detection of the accumulation of these materials on surfaces and provides ab initio calculations for the vibrational spectra of the vapors. Some infrared spectra of matrix-isolated sulfates [13-17] and carbonates [18] are published.

Experimental

The Multifuel Combustor (MFC) at the Combustion Research Facility, Sandia National Labs., California [19] was used to make thin films of the black liquor deposit constituents, Na_2SO_4 , K_2SO_4 , Na_2CO_3 , and K_2CO_3 . The MFC is a down-fired, turbulent flow reactor of small pilot-scale size that allows for particle and gas temperature histories to be adjusted over a wide range of conditions. Total fuel residence time can vary from milliseconds to 5 s in the facility. In these experiments, black liquor and pure alkali salts were fired separately in the combustor. Spectroscopic analyses of thin films collected on simulated boiler tubes in the MFC provided reference spectra and sample spectra, respectively. For the salts, aqueous solutions with concentrations of nominally 100 g/L were aspirated into the top of the combustor and carried through the furnace by a flow of nominally 30 L/s of air. The combustor's gas-fired preheater was not lit, but the silicon carbide (SiC) walls of the combustor were held at a temperature of 1000-1100°C by electrical SiC heating elements. The deposits were collected at the bottom of the combustor on a hollow rotating stainless steel rod 1.7 cm in diameter. The air flow through the combustor maintained the temperature of the rod at about 400°C. The salt deposits on the rod had a thickness of about 100-200 microns at the end of the experiments.

In situ emission spectra of the salt films were recorded at the resolution of 2 cm^{-1} with a Biorad Model FTS 40/60 Fourier transform infrared spectrometer (FT-IR) equipped with a KBr backed beamsplitter and a DTGS detector. Spectra of the original rod surface were recorded prior to salt accumulation and subtracted from the salt spectra. Scans were collected over 10 minutes (256 scans) and were co-added for each of the original surface and the salt spectra. The resulting spectra (Figs. 1-4) exhibited high signal-to-noise ratios and good peak definition in the mid-infrared ($350\text{-}3000\text{ cm}^{-1}$) region.

The deposit from the black liquor was prepared in a similar manner as the reference salt films. In this case the temperature of the walls of the furnace was about 900°C while the rotating stainless steel rod was at 300°C. The black liquor contained about 10% organic material, mainly lignin and its degradation products, that burned before the residual deposit formed. A time series of emission spectra (Fig. 5) of the deposit on the rod was recorded with the spectrometer. For each spectrum, 16 scans were co-added in 0.5 minutes of integration. After 52 minutes the black liquor flow was stopped and a final spectrum (Fig. 6) was measured.

Results and Discussion

The deposit from the black liquor has an infrared spectrum (Figure 6) with numerous vibrational bands. The major bands and their assignments, compared with the reference spectra, are listed in Table 1. The sharp, strong band at 880 cm^{-1} is the characteristic out of plane bending mode $\nu_2(a'')$ of the CO_3^{2-} ion [20-24]. The CO_3^{2-} ion has D_{3h} symmetry with modes $\nu_4(e')$ 681 cm^{-1} , $\nu_2(a'')$ 880 cm^{-1} , $\nu_1(a_1')$ 1067 cm^{-1} and $\nu_3(e')$ 1380 and 1440 cm^{-1} in dilute solution. The doubly degenerate $\nu_3(e')$ mode experiences reduced symmetry in solution and appears as two bands [20]. Only the a_2'' and e' modes are infrared active for the D_{3h} point group but in condensed phases the effective symmetry is lower and other modes can appear [20].

The strong band (Figure 6) at 1148 cm^{-1} in the black liquor deposit is characteristic of the antisymmetric stretch vibration of the tetrahedral SO_4^{2-} ion. In dilute solution, the SO_4^{2-} ion (T_d point group) has modes $\nu_2(e)$ 450 cm^{-1} , $\nu_4(t_2)$ 611 cm^{-1} , $\nu_1(a_1)$ 983 cm^{-1} and $\nu_3(t_2)$ 1105 cm^{-1} [24, 25]. Only the t_2 modes are infrared active but the other modes can appear in condensed phases [26, 27].

In condensed phases, it is common to observe a shift in the functional group frequencies, and the center band positions depend more strongly on temperature than in gas-phase spectra. In addition, agreement between literature reference spectra and observed feature locations is complicated by several factors. Literature references are predominately derived from pure, room-temperature samples of micronized mineral pressed in a KBr wafer and examined in transmission using an FTIR or other suitable spectroscopic instrument. By contrast, these *in situ* emission spectra of the ash deposits containing many inorganic phases are collected at combustion temperatures on deposition probes. The sample mixture, morphology, and temperature may alter the spectral signatures. Mixtures of samples may cause weak or broad features to become indistinguishable from either the background or features from other species. Temperature changes in a material can change the location of a room temperature feature by a few wavenumbers (usually less than 10 cm^{-1}) at $400\text{ }^\circ\text{C}$ [28] and as much as 40 cm^{-1} at $1700\text{ }^\circ\text{C}$ for halide and oxide crystal [29]. The changes can either increase or decrease the wavenumber, although decreases in wavenumber are most common. Changes are also more pronounced for crystalline material than for amorphous material [30] and are more significant at low wavenumbers than at high wavenumbers. Deposit thickness variations for pure, thin films have been reported for materials of interest to ash deposition [31] and in the literature for liquids [32]. Deposit thickness can also have a pronounced effect on feature shapes and apparent position. The combination of *ab initio* calculation and literature reference spectra combined provide definitive assignment of the observed features of our spectra.

While the 880 cm^{-1} CO_3^{2-} and 1048 cm^{-1} SO_4^{2-} peaks are readily assigned, the interpretation of the smaller peaks is much less certain. In addition the cations associated with the SO_4^{2-} and CO_3^{2-} anions are not certain. The elemental composition of the black liquor was found to be C (34.8%), H (3.0%), O (35.0%), Na (22.6%), K (0.62%), S (2.9%), Cl (0.67%) and N (0.08%) on a dry basis. The remainder consists of inert material such as Fe_2O_3 and SiO_2 (i.e. dirt, sand, etc.) that enter the process with the wood. The potassium also enters the process as a constituent of the wood. Thus the deposit could contain K_2SO_4 and K_2CO_3 as well as Na_2SO_4 and Na_2CO_3 . Reference spectra of pure Na_2SO_4 (Figure 1), K_2SO_4 (Figure 2), Na_2CO_3 (Figure 3), and K_2CO_3

(Figure 4) were therefore recorded for comparison purposes and the bands measured (Tables 1 and 2).

The observed sulfate bands were readily assigned on the basis of previous work [24-27]. The forbidden $V_2(e)$ mode near 450 cm^{-1} was too weak to identify but the symmetric stretching vibration $V_1(a_1)$ appeared as a shoulder. Two weak bands appeared near 2100 cm^{-1} and are assigned in the literature [26] as the $V_1 + V_3$ combination band and the $2V_3$ overtone. The $V_1 + V_3$ assignment is plausible since the predicted band position is 2132 cm^{-1} , but the $2V_3$ assignment for the 2153 cm^{-1} band (Na_2SO_4) is less certain since $2 \times V_3 = 2274\text{ cm}^{-1}$.

The assignments for the Na_2CO_3 and K_2CO_3 spectra were also straightforward (Table 2). All of the four CO_3^{2-} modes were found as well as several overtones and combination bands. Interestingly the overtones and combination bands which contain V_3 are all split into two bands. This splitting of the V_3 fundamental is well-known in solutions and melts [20] but is not obvious (Figures 3 and 4) in the spectra of the solids. The V_3 fundamental is badly chopped up by water vapor in our spectra.

The direct comparison of Figs 1-4 with Fig. 6 allows all of the bands in the black liquor deposit to be assigned (Table 1). There is no clear evidence for K_2SO_4 and K_2CO_3 in the deposit, but they cannot be ruled out because most of their band positions are nearly co-incident with the corresponding Na_2SO_4 and Na_2CO_3 bands. They would, in any case, be a fairly minor constituent of the deposit based on the black liquor composition.

Surprisingly the high temperature behavior of Na_2SO_4 and Na_2CO_3 is not well established. The decomposition reactions:

certainly occur, but a substantial fraction of the high temperature vapors are Na_2SO_4 [33, 34] and Na_2CO_3 [35] molecules. The extent of decomposition is typically measured by mass spectrometry. Since the parent ions of molecules such as Na_2SO_4 and Na_2CO_3 tend to fragment, mass spectrometry often underestimates the concentration of inorganic species. Molten Na_2SO_4 and Na_2CO_3 are also very corrosive, so the container material may influence the decomposition. Thus, the extent of decomposition is not reliably known for Na_2SO_4 and Na_2CO_3 at high temperatures.

The existence of molecular Na_2SO_4 and K_2SO_4 in the gas phase is supported by the infrared and Raman spectra recorded for isolated molecules trapped in inert matrices at low temperatures [15, 16]. Infrared absorption spectra of K_2CO_3 (but not Na_2CO_3) have also been published [18].

These results all suggest that molecular Na_2SO_4 and Na_2CO_3 will be important species in the fume produced in Kraft black liquor recovery boilers. As a prelude to the gas phase study of these molecules, we completed ab initio calculations of the infrared spectra. The Gaussian 92 program [36] was used with the standard 6-31G* basis set and electron correlation at the MP2 level. Geometries were optimized at the MP2 / 6-31G* level of theory and the vibrational frequencies and intensities were calculated.

For the Na_2SO_4 molecule the lowest energy structure has D_{2d} symmetry (Figure 7). This structure is consistent with the matrix-isolation spectra [15] as well as the electron diffraction [37] and molecular beam deflection data [38] on the isovalent Cs_2SO_4 molecule. The optimized

geometry has a S-O bond length of 1.517 Å and a Na-O bond length of 2.205 Å. The S-O bond lengths are typically 1.47 Å for the SO_4^{2-} anion in crystals [13], 1.471 Å derived from the electron diffraction results on Cs_2SO_4 [38], and 1.48 Å calculated for Li_2SO_4 [13]. The O-S-O bond angles are calculated to be 107.3° facing a Na atom and 110.6° facing away from Na.

The predicted vibrational frequencies and intensities of Na_2SO_4 are reported in Table 4. The only experimental values available for comparison are the N_2 matrix values [15] of 1131 cm^{-1} $\nu_5(\text{b}_2)$, 1103 cm^{-1} and 1097 cm^{-1} $\nu_8(\text{e})$, 961 cm^{-1} $\nu_1(\text{a}_1)$, 640 cm^{-1} $\nu_6(\text{b}_2)$ and 610 cm^{-1} $\nu_9(\text{e})$.

The calculations for Na_2CO_3 were carried out for two molecular geometries of C_{2v} symmetry (Figures 8 and 9). The matrix isolation results are unable to distinguish between the two possibilities but calculations on Li_2CO_3 [39] indicate that the structure with two bidentate bonds to the Na atoms (Figure 9) as the ground state. For Na_2CO_3 our calculations predict that the structure in Figure 8 is a local minimum in the total energy, but it lies 20.4 kcal/mole above the structure in Figure 9. The lowest energy structure (Figure 9) has two C-O bond lengths of 1.285 Å (on the left) and one of 1.367 Å (on the right). The Na-O bond lengths are 2.170 Å (to the left) and 2.185 Å (to the right). The O-C-O angles are close to 120° with two values of 118.1° facing Na atoms and 123.9° facing away from Na atoms. The calculated vibrational frequencies and intensities are reported in Table 5. There are no suitable experimental Na_2CO_3 values for comparison.

Conclusions

Inorganic material accumulating on surfaces during black liquor combustion lends itself to analysis by emission FTIR spectroscopy. Properly instrumented laboratory reactors and diagnostics allow the determination of emission spectra from thin films ($\approx 100 \mu\text{m}$) of alkali salts and of black liquor ash deposits on simulated heat transfer surfaces. Spectral analysis indicates agreement between the assignment of bands, using ab initio calculations in all cases and literature values in some cases. Spectra with good signal-to-noise ratios and well-defined structure are obtainable from both pure materials and mixed materials generated by the combustion of industrial feedstreams.

Ab initio calculations also predict the band locations and intensities of alkali salt vapors, whose existence in practical combustion systems is suspected but has yet to be confirmed. The formation of ash deposits in the upper furnace of recovery boilers is dependent primarily on the concentrations and properties of these salt vapors, their condensation aerosols, and their reaction products. These data and calculations provide baseline information for quantitatively determining vapor concentrations and demonstrate the determination of the resulting ash deposits from such combustion systems.

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Table 1.
Vibrational Band Positions of the Black Liquor Deposit (cm⁻¹)

Position	Assignment
631	Na ₂ SO ₄ , 624
698	Na ₂ CO ₃ , 699
853	Na ₂ CO ₃ , 854
880	Na ₂ CO ₃ , 880
1000	Na ₂ SO ₄ , 995
1066	Na ₂ CO ₃ , 1069
1148	Na ₂ SO ₄ , 1137
~1400	Na ₂ CO ₃ , ~1400
1765	Na ₂ CO ₃ , 1767
2117	Na ₂ SO ₄ , 2087
2470	Na ₂ CO ₃ , 2476

Table 2
Observed Carbonate Band Positions (cm⁻¹)

Mode	CO ₃ ²⁻ Solution ^a	Na ₂ CO ₃ Film	K ₂ CO ₃ Film
V ₄ (e')	681	699 854 ^b	686 852 ^b
V ₂ (a ₂ '')	880	880 917 ⁻¹	879 903 ^b
V ₁ (a ₁ '')	1067	1069	1053
V ₃ (e')	1380;1440	~1400	~1400
2V ₂	-	1767	1738
V ₁ +V ₃	-	2476	2437
V ₁ +V ₃	-	2562 ^b	2516 ^b
2V ₃	-	2843	2788
2V ₃	-	2911 ^b	2852 ^b

^aRef., ^bShoulder

Table 3

Fundamental Vibrational Modes of Na₂CO₃ Calculated Ab Initio at MP2/6-31G* Level

Mode	Frequency ^a , cm ⁻¹	Comment
V ₈ (b ₁)	96(52)	
V ₆ (a ₂)	107(0)	
V ₅ (a ₁)	206(22)	
V ₄ (a ₁)	357(48)	Na-O ₂ vibrations
V ₁₂ (b ₂)	370(21)	
V ₁₁ (b ₂)	384(112)	
V ₃ (a ₁)	699(1)	V ₄ (e') 681 cm ⁻¹ CO ₃ ²⁻ in plane bend
V ₁₀ (b ₂)	738(12)	
V ₇ (b ₁)	842(22)	V ₂ (a ₂ ') 880 cm ⁻¹ CO ₃ ²⁻ out of plane bend
V ₂ (a ₁)	994(100)	V ₁ (a ₁) 1067 cm ⁻¹ CO ₃ ²⁻ sym. str
V ₁ (a ₁)	1347(565)	V ₃ (e') 1440; 1380 cm ⁻¹ CO ₃ ²⁻ antisym. str.
V ₉ (b ₂)	1620(748)	

^a Calculated intensities in km /mole are in parentheses.

Table 4

Fundamental Vibrational Modes of Na_2SO_4 Calculated Ab Initio at MP2/6-31G* Level

Mode	Frequency, cm^{-1}	Comment
$\nu_{11}(\text{e})$	68(54) ^a	NaO_2 bend
$\nu_{10}(\text{e})$	272(4)	NaO_2 bend
$\nu_3(\text{a}_1)$	276(0)	NaO_2 sym. str.
$\nu_7(\text{b}_2)$	359(140)	NaO_2 antisym. str
$\nu_4(\text{b}_1)$	379(0)	$\nu_2(\text{e})$ 450 cm^{-1} SO_4^{-1} bend
$\nu_2(\text{a}_1)$	525(0)	
$\nu_9(\text{e})$	584(36)	$\nu_4(\text{t}_2)$ 611 cm^{-1} SO_4^{-2} bend
$\nu_6(\text{b}_2)$	642(42)	
$\nu_1(\text{a}_1)$	938(0)	$\nu_1(\text{a}_1)$ 983 cm^{-1} SO_4^{-2} sym. str.
$\nu_8(\text{e})$	1104(383)	$\nu_3(\text{t}_2)$ 1105 cm^{-1} SO_4^{-2} antisym. str.
$\nu_5(\text{b}_2)$	1146(668)	

^aCalculated intensities in km/mole are in parentheses

Table 5
Observed Sulfate Band Positions (in cm^{-1})

Mode	SO_4^{-2} solution ^a	Na_2SO_4 film ^b	Na_2SO_4 solid ^a	Na_2SO_4 melt	K_2SO_4 film ^b	K_2SO_4 solid ^a	K_2SO_4 melt
$\text{V}_2(\text{e})$	451	-	-	440	-	-	-
			612			612	
$\text{V}_4(\text{t}_2)$	613	624	638	saturated	619	619	saturated
			643 ^d		711 ^d	654 ^d	
$\text{V}_1(\text{a}_1)$	981	995 ^d	988	-	975	983	-
			1105				
$\text{V}_3(\text{t}_2)$	1104	1137	1124	saturated	1120	1101	saturated
			1175 ^d				
$\text{V}_1+\text{V}_3(\text{t}_2)$	-	2087	-	2060	2064	-	2020
$2\text{V}_3(\text{t}_2)?$	-	2153 ^d	-	2190 ^d	2113 ^d	-	2150 ^d

^a S.D Ross, Spectrochimica Acta 18, 1575 (1962).

^b This work.

^c R.E. Hester and K. Krishnan, J. Chem. Phys. 49, 4356(1968).

^d Shoulder.

Figure Captions

- Figure 1 Sodium sulfate spectrum obtained from combustion tests of pure material in the MFC. Asterisks indicate residual carbonate impurity.
- Figure 2 Potassium sulfate spectrum obtained from combustion tests of pure material in the MFC.
- Figure 3 Sodium carbonate spectrum obtained from combustion tests of pure material in the MFC.
- Figure 4 Potassium carbonate spectrum obtained from combustion tests of pure material in the MFC. Asterisks indicate residual sulfate impurity.
- Figure 5 Time-resolved spectra of black liquor deposit, with peaks identified.
- Figure 6 Black liquor deposit spectra near the end of the combustion test, illustrating fully developed peaks of sulfate (+) and carbonate (*).
- Figure 7 Structure of sodium/potassium sulfate molecule.
- Figure 8 One of two alternate structures of sodium/potassium carbonate molecule (compare Fig. 9).
- Figure 9 One of two alternate structures of sodium/potassium carbonate molecule (compare Fig. 8).