CLIMATE MISSING LINKS: AQUEOUS GREENHOUSE
SPECIES IN CLOUDS, FOGS, AND AEROSOLS

J. S. Gaffney, N.A. Marley, and M.M. Cunningham

Bldg. 203
Environmental Research Division
Argonne National Laboratory
Argonne, Illinois 60439

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Heading

Recently, there has been considerable interest regarding possible greenhouse effects due to combustion and energy-related pollution. This concern has been due to the release and secondary production of greenhouse gases such as carbon dioxide, freons, methane, nitrous oxide, and ozone. These gases can absorb infrared radiation as it comes back from the heated ground and therefore effectively trap the infrared radiation in the troposphere, leading to climatic change.

Beyond these gases, clouds, aerosols, and fogs may also play important roles in affecting the radiation balance by scattering incoming radiation.

This work describes the measurement of water soluble infrared absorbers that are known to be derived from pollution. Polluted precipitation is likely to be an important contributor to radiation balance that is currently being neglected. Pollutants characterized include sulfate, nitrate, formate, acetate, oxalate, phenol, p-nitrophenol, ammonium, carbonate, bicarbonate, formaldehyde (dihydroxy methane), methanol, and ethanol. Band positions and band strengths have been determined. These species show measurable infrared absorption bands in the atmospheric window regions (i.e., 900-1600 cm^{-1}). These data are discussed with regard to the reported discrepancies in the radiatively important water infrared absorption region commonly referred to as the "foreign broadened continuum".

Key word index: Greenhouse effects, Water continuum, Infrared absorption, Atmospheric chemistry.

There has been considerable interest regarding the potential changes in our global and regional climate due to man's release of greenhouse gases into the atmosphere. A major concern has arisen due to the release of carbon dioxide into the troposphere from increased combustion of fossil fuels accompanying the industrial revolution¹. Other trace gases have also been identified as potentially important greenhouse gas species including the chlorofluorocarbons, nitrous oxide, and methane, as they have strong infrared absorptions in the atmospheric windows where water and carbon dioxide do not absorb^{2,3}. Other gases, such as ozone, organic nitrates, and peroxyacyl nitrates have also been identified as important greenhouse species.

However, the greenhouse gases are not the only pollutants that are controlling our regional and global climatic conditions. Recently, it has become increasingly apparent that clouds can play a major role in the climate equation⁴⁻⁶. This is due to the fact that cloud droplets can act as effective scatterers of incoming radiation. Since the incoming light is scattered into the atmosphere and does not reach the ground this can lead to a net cooling effect. To understand the potential of cloud moderation of climate, a better understanding of the formation of clouds and their radiative and light scattering properties will be needed for modeling climate change.

Cloud condensation nuclei from both natural and anthropogenic sulfur sources have been identified as potentially significant in their possible effects on cloud formation⁴⁻⁶. As well, aerosols and dust can cause effects on climate leading to cooling or heating depending upon the material's optical properties and its spatial positioning within the troposphere.⁶ Indeed, the optical absorption in the visible and ultraviolet, as well as the infrared characteristics need to be understood if we are to model pollution effects on climate change on regional and global scales.

In the past it has been very difficult to accurately determine the infrared absorption strengths of dissolved aqueous species due to the strong water background. However, with the development of internal reflectance techniques, it is now feasible to determine the infrared band positions and band strengths of dissolved inorganic and organic species in water. By using cylindrical internal reflectance techniques, it has been shown recently that infrared band

strengths and band positions in aqueous solutions can be accurately determined using these methods^{7,8}.

In this work, we have determined the infrared band positions and bandstrengths in aqueous solution for sulfate, nitrate, bicarbonate, ammonium, acetate, oxalate, formate, formaldehyde (dihydroxy methane), ethanol, methanol, phenol, and p-nitrophenol, as a representative cross section of important water soluble air pollutants. The spectra were obtained using Fourier transform infrared techniques and the band strengths were determined by varying the concentrations of the solutions and obtaining effective Beer-Lambert plots⁷.

Cylindrical internal reflectance spectra for aqueous solutions are presented in Fig. 1 for the addition of oxalate, formate, and acetate. This figure demonstrates the apparent shifts in the aqueous continuum spectrum when these species are in solution. Considerable attention has been given to the "foreign broadened continuum" in water. It is clear from these data that dissolved pollutant species in water will affect the apparent water absorption spectrum and apparently broaden it.

By using Fourier transform infrared (FTIR) digital subtraction techniques to remove the water background, the aqueous absorption spectra for selected inorganic and organic pollutant species have been obtained and are given in Fig. 2 and 3. It is clear from these data, that both dissolved inorganic and organic pollutants have substantial infrared absorption bands in the water window regions and must be considered in radiative balance calculations regarding climate change on regional and global scales.

In Table 1 we have tabulated the location of the peak infrared absorptions for the inorganic and organic species studied. The band-widths and half-widths are also given in this Table 1. In Table 2, the infrared absorptivities at the peak maxima are presented, while in Table 3, the integrated band absorptivities are given for these species. It should be noted that these absorption bands are quite broad and are therefore quite effective in absorbing infrared radiation. In particular, it is interesting to note that sulfate and nitrate, which are known to be major pollutants in acid rain, have strong absorptions in the infrared. As well, formaldehyde (dihydroxy

methane in solution) and a number of the organics are also reasonably strong absorbers and cannot be neglected when calculating infrared absorbance cross sections in the troposphere.

In this work it has been determined that the effective path length in our cylindrical internal reflectance measurements was approximately 0.01 mm at the wavelengths of interest⁷. Thus, if one assumes a liquid water content through the troposphere of a few millimeters and uses available data for the concentrations of these species found in cloudwater and precipitation,⁹ we have determined that these dissolved materials may be important with regard to the radiative properties of our troposphere considering the abundances of clouds, fogs, and aerosols.

However, it is important to recognize the concentrations of these species are known to have a high variability when compared to a greenhouse gas such as carbon dioxide. Sulfate and nitrate levels due to the combustion of fossil fuels are well known to be much higher in the northern hemisphere than in the southern hemisphere. Indeed, on regional levels it is likely that the contribution of these aqueous greenhouse species will vary. In Fig. 4, to illustrate this concept, we have taken mean relative values for both an eastern United States and a western United States urban pollution situation for comparison. As one can readily see from these two hypothetical scenarios, the infrared absorption of these dissolved greenhouse species will depend strongly upon the relative concentrations of the pollutants and the distributions of their sources. As well, the chemical conversion in the troposphere to aerosols and soluble species must be taken into account to evaluate their radiative properties.

Therefore, any consideration of the global climatic consequences of dissolved greenhouse species must consider their spatial and temporal distributions. These data as well as other meteorological considerations support the fact that global climate change must be evaluated with the inclusion of all the important species and should be examined on a regional scale where microclimatic changes could be the dominant effects of real social and political concern. Thus, the inclusion of dissolved greenhouse species in cloudwater, fogs, and aerosols must be considered if we are to adequately evaluate the radiative balance in our troposphere.

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FIGURE CAPTIONS

1. Cylindrical internal reflection Fourier transform infrared spectrum of aqueous solutions. (A) 0.1 M oxalate, (B) 0.1 M formate, (C) 0.1 M acetate, and (D) distilled water.
2. Water background subtracted infrared spectra of 0.1 M solutions for the inorganics, (A) sulfate, (B) nitrate, (C) bicarbonate, and (D) ammonium.
3. Water background subtracted infrared spectra of 0.1 M solutions of the organics, (A) oxalate, (B) formate, (C) acetate, (D) p-nitrophenol, (E) phenol, (F) formaldehyde (dihydroxy methane), (G) ethanol, and (H) methanol.
4. Estimated contributions to the apparent water continuum in the infrared for two different urban scenarios. (A) a western United States (e.g. Los Angeles) pollution situation where organics and nitrate would predominate, and (B) an eastern United States site (e.g., New York) where sulfate would likely be the principal pollutant. The values for estimated pollutant contributions are given in reference 10.

A

B

WAVENUMBER

TABLE 1. Infrared absorption bands for species in aqueous solutions determined in this study. Peak maximum (location), peak width, and peak half-width are all reported in cm^{-1} . Multiple bands in this region are as indicated.

Aqueous Species	Location	Width	Half-Width
Sulfate (SO_4^{-2})	1100	240	75
Nitrate (NO_3^-)	1355	245	100
Bicarbonate (HCO_3^-)	1360	250	70
Ammonium (NH_4^+)	1455	195	75
Acetate (CH_3COO^-)	1522	225	50
	1413	195	50
Oxalate ($\text{C}_2\text{O}_4^{-2}$)	1575	250	60
	1310	100	25
Formate (HCOO^-)	1580	270	50
Formaldehyde (Methylene glyoxal)	1026	185	60
Ethanol	1045	135	35
Methanol	1020	90	25
Phenol	1243	185	46
p-Nitrophenol	1281	195	60
	1340	170	35
	1513	230	60

TABLE 2. Infrared absorptivities at peak maxima for some important pollutant species in aqueous solutions. The Beer-Lambert law was found to apply in all cases, i.e., $A = \epsilon lc$, where A is the measured absorbance, ϵ is the absorptivity ($M^{-1} \text{ cm}^{-1}$), l is the pathlength (0.01 mm), and c is the concentration (M). Reported are the band locations (cm^{-1}), the absorptivities (ϵ , $M^{-1} \text{ cm}^{-1} \times 10^2$), and the linear regression data (slope, intercept, and R^2 values).

Aqueous species	Location	$\epsilon \times 10^2$	Slope	Intercept	R^2
Sulfate (SO_4^{-2})	1100	9.5	1.246	0.001	0.999
Nitrate (NO_3^-)	1355	4.3	0.459	0.000	0.999
Bicarbonate (HCO_3^-)	1360	12.0	1.274	0.002	0.995
Ammonium (NH_4^+)	1455	1.8	0.160	0.005	0.994
Acetate (CH_3COO^-)	1522	4.0	0.378	0.014	0.987
	1413	2.7	0.275	0.004	0.996
Oxalate ($\text{C}_2\text{O}_4^{-2}$)	1575	9.2	0.839	0.008	0.999
	1310	5.3	0.586	-0.001	0.999
Formate (HCOO^-)	1580	5.4	0.489	0.004	0.999
Formaldehyde (Methylene glyoxal)	1026	3.0	0.316	0.001	0.998
Ethanol	1045	0.92	0.127	0.000	0.999
Methanol	1020	1.1	0.152	0.000	0.990
Phenol	1243	1.6	0.166	0.000	0.960
p-Nitrophenol	1281	3.2	0.328	0.001	0.997
	1340	5.3	0.516	-0.002	0.997
	1513	4.7	0.402	0.006	0.992

TABLE 3. Infrared absorptivities of integrated band strengths for some important pollutant species in aqueous solutions. The Beer-Lambert law was found to apply in all cases, i.e., $A = \epsilon lc$, where A is the measured absorbance, ϵ is the integrated absorptivity ($M^{-1} \text{ cm}^{-2}$), l is the pathlength (0.01 mm), and c is the concentration (M). Reported are the band locations (cm^{-1}), the absorptivities (ϵ , $M^{-1} \text{ cm}^{-2} \times 10^4$), and the linear regression data (slope, intercept, and R^2 values).

Aqueous species	Location	$\epsilon \times 10^4$	slope	intercept	R^2
Sulfate (SO_4^{-2})	1100	7.26	95.15	0.019	0.999
Nitrate (NO_3^-)	1355	4.64	49.13	-0.089	0.997
Bicarbonate (HCO_3^-)	1360	9.18	97.35	-0.193	0.995
Ammonium (NH_4^+)	1455	1.19	11.76	0.635	0.959
Acetate (CH_3COO^-)	1522	2.62	24.87	1.015	0.983
	1413	1.21	12.38	0.355	0.989
Oxalate ($\text{C}_2\text{O}_4^{-2}$)	1575	5.73	52.13	1.608	0.996
	1310	1.47	16.15	-0.054	0.999
Formate (HCOO^-)	1580	2.93	26.70	0.910	0.999
Formaldehyde (Methylene glyoxal)	1026	1.97	20.45	-0.075	0.995
Ethanol	1045	0.35	4.89	-0.017	0.991
Methanol	1020	0.26	3.68	0.030	0.996
Phenol	1243	0.74	7.68	-0.002	0.952
p-Nitrophenol	1281	2.20	22.19	-0.131	0.996
	1340	2.32	22.51	-0.184	0.988
	1513	3.00	29.08	0.546	0.990

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