

Experimental Study on the Interference of Water Vapor on the Chemical Ionization of OH by Sulfur Hexafluoride Ion

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Abstract: The interference of water vapor on the chemical ionization (CI) of hydroxyl radicals (OH) by sulfur hexafluoride ion (SF_6^-) was investigated using a flow tube system coupled to a high-pressure CI mass spectrometer. Water vapor, which is required to study heterogeneous reactions of OH under real tropospheric conditions, transforms the reagent ion SF_6^- into SF_4O^- and $\text{F}(\text{HF})_n^-$, resulting in a substantial loss in CI sensitivity. Therefore, under humid conditions, peaks corresponding to OH are drastically diminished, while those corresponding to OH-water complex ions ($[\text{OH}(\text{H}_2\text{O})_n]^-$) are enhanced. $[\text{OH}(\text{H}_2\text{O})_3]^-$ was observed as the major OH species. The observation of $[\text{OH}(\text{H}_2\text{O})_n]^-$ by isolating humid conditions to the CI region and preliminary *ab initio* calculations suggested that $[\text{OH}(\text{H}_2\text{O})_n]^-$ ions were produced from reactions between OH ions (OH^-) and water molecules. An additional helium buffer flow introduced into the CI region reduced loss of the reagent ion and resulted in a partial recovery of OH peak intensities under humid conditions.

Keywords: Chemical Ionization, OH, Sulfur Hexafluoride Ion, Water Complex

Introduction

The heterogeneous reactions of hydroxyl radicals (OH) occur on the surface of various atmospheric aerosols and have been studied to explain discrepancies between field measurements and theoretical values based on atmospheric modeling. Knowledge of such reactions also increases our understanding of the chemical reactions occurring in Earth's atmosphere.¹⁻⁴ However, little is known of the OH heterogeneous reactions that occur under real tropospheric conditions when water vapor may be present at up to 4% by volume. Due to its relatively large dipole moment (1.83×10^{-18} esu·cm) and its ability to form strong hydrogen bonds, water vapor is easily adsorbed onto atmospheric aerosol surfaces, where it can facilitate various heterogeneous reactions. For example, the heterogeneous reactions of OH with certain inorganic aerosols, such as MgCl_2 , sea salt, and SiO_2 , are enhanced under wet conditions. In contrast, the

reactivity of OH with adsorbed water remains unaffected or slightly decreases on other organic or inorganic aerosols.^{5,6}

Chemical ionization mass spectrometry (CIMS) is widely used in experimental atmospheric studies because it is less destructive than other ionization methods and results in a lesser degree of fragmentation and relatively simple mass spectra.⁷⁻⁹ In CIMS detection, a reagent ion, or "parent ion," such as SF_6^- , F^- , O_2^- , and NO_2^- , collides with a gas-phase molecule of interest, whereby electron transfer occurs via the following reaction:



where X^- is the reagent ion and A is the gas-phase molecule of interest.

However, technical problems arise in CI experiments at high water-vapor pressures. Providing a sufficient amount of water vapor for CI requires a considerable flow of carrier gas that builds up relatively high pressures of 100-200 Torr inside a flow tube reactor. Such high-pressure conditions slow the diffusion of radicals into the reactor surface significantly.^{11,12} Increasing the surface area of the reactor by employing a miniature tube array or glass bead packing inside the flow tube simultaneously maximizes the rate of heterogeneous reactions and minimizes diffusion limits by shortening the distance between reactants and the surface.

The sensitivity of CIMS is also affected by high water-vapor pressure. Water vapor readily interacts with SF_6^- , the reagent ion, to form SF_4O^- and $\text{F}(\text{HF})_n^-$.^{13,14} The resulting loss of the reagent ion significantly lowers CIMS sensitivity

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for many analytes, including OH. Water vapor also forms clusters such as $[\text{OH}(\text{H}_2\text{O})_n]^-$ with OH in the CI region, resulting in a further reduction in OH sensitivity. Although humid conditions significantly reduce CIMS sensitivity, few studies have addressed the dependence of water-parent ions or water-OH complexes on the relative humidity (RH).

This paper describes the use of a flow tube system coupled to a CIMS to explore the interactions among water molecules, reagent ions (SF_6^-), and/or OH radicals that reduce CIMS sensitivity. Preliminary *ab initio* calculations supported experimental observations and identified the specific locations where various complex-forming reactions occur. In addition, the recovery of experimental sensitivity by introducing a buffer flow of helium (He) is briefly discussed.

Experimental

Experiments were performed under flow conditions using a modified version of a previously developed apparatus.^{5,6,15} The modified flow tube system is shown in Figure 1. In the modified system, the reactor tubes in which OH heterogeneous reactions occur were removed because the OH reactions were not of interest. Instead, a mixing tube was connected directly to the CIMS system. Another modification is the use of a switchable water-vapor introduction line.

Hydroxyl radicals were generated by two sequential reactions.



Hydrogen radicals (H) were produced by a 30-W microwave discharge and subsequent reaction with O_2 (99.5%; Matheson Tri-Gas) to generate hydroperoxyl radicals (HO_2), which were then stabilized by He gas (M). HO_2 reacted promptly with excess hydrogen radicals to generate OH. Since Rxn. (3) is relatively fast, the production of HO_2 was negligible ($\text{HO}_2/\text{OH} \sim 1 \times 10^{-2}$). To

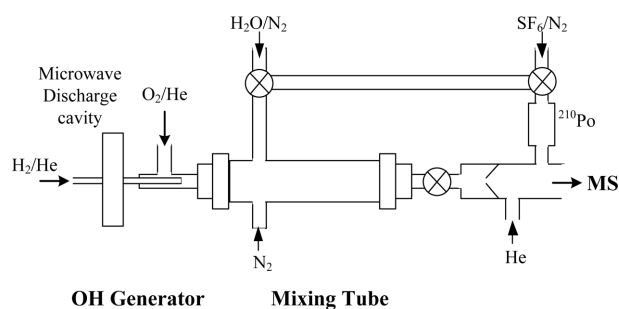


Figure 1. A schematic diagram shows the flow tube system coupled to a chemical ionization mass spectrometry (CIMS) system.

prevent OH loss via self-recombination, the flow containing OH was expanded in a mixing tube and diluted with N_2 (99.5%; Praxair, Jefferson City, MO, USA), the primary carrier gas. The detection sensitivity of OH was 4.2×10^7 molecules cm^{-3} cps^{-1} .

Conditions of up to 50% RH were established using a water bubbler. Humid gas was selectively injected into the flow tube system or into the CI region using the switchable water-vapor introduction line shown in Figure 1.

A small flow of sulfur hexafluoride (SF_6 , 99.99%; Matheson Tri-Gas) was initially diluted with N_2 to 0.1% by volume and exposed to a radioactive polonium source (^{210}Po ; NRD) to produce SF_6^- reagent ions in the CI region. A mass spectrometer equipped with a quadrupole mass analyzer (Extrel) and a continuous-dynode electron multiplier (Channeltron 4870E; Burle Electro-Optics) were used for quantitative measurements.

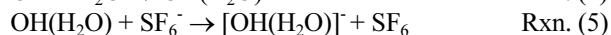
Preliminary *ab initio* calculations were performed to characterize the complex-forming reactions. Hybrid density functional theory at the B3LYP level with a 6-31(d,p) basis set was used for geometry optimization and energy calculations. All calculations were carried out in Gaussian 03.¹⁶

Results and Discussion

Changes in the peak intensities of SF_6^- and its products from reactions with water are shown in Figure 2 (a). The SF_6^- peak in the CI region was drastically diminished under wet conditions. The peak intensities of SF_4O^- , $\text{F}(\text{HF})_2^-$, and $\text{F}(\text{HF})_3^-$ reached the same level as that of SF_6^- at 16% RH. At 50% RH, $\text{F}(\text{HF})_3^-$ was the major fluorine compound, while peaks associated with SF_6^- were negligible. Although SF_4O^- can act as a reagent ion, the degree of CI was lowered through significant losses of both SF_6^- and SF_4O^- .

Figure 2(b) shows that the intensity of the OH peak decreased with the addition of water into the flow tube system, which was due to not only the loss of CIMS sensitivity as described above, but also to the conversion of OH into OH-water complexes.¹⁷⁻²⁰ In particular, the peak intensity of $[\text{OH}(\text{H}_2\text{O})_3]^-$ exceeded that of OH^- at greater than 10% RH and reached a maximum at 18% RH. The observation that $[\text{OH}(\text{H}_2\text{O})_3]^-$ becomes the major OH-containing species under high RH is supported by an infrared spectrometric study with quantum chemical calculation²¹ and our preliminary *ab initio* calculation, which predicted the cyclic complex of $[\text{OH}(\text{H}_2\text{O})_3]^-$ to be the most stable.

The observed OH-water complexes ($[\text{OH}(\text{H}_2\text{O})_n]^-$) originate from the complexation of OH radicals and water molecules in the flow tube and subsequent ionization in the CI region (Rxn. (4) to (5)) followed by the formation of clusters of OH^- ions with water molecules (Rxn. (6) to (7)).



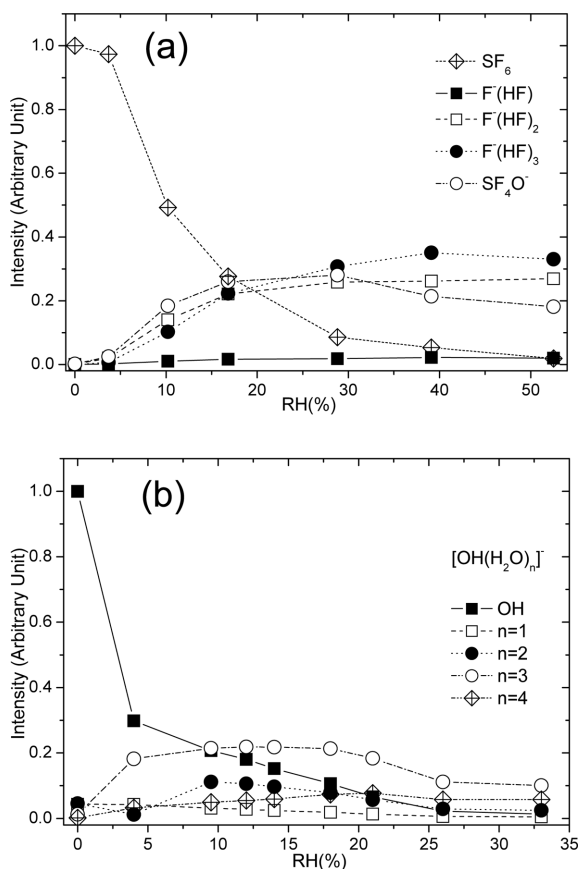


Figure 2. Intensity changes in peaks attributed to (a) SF_4O^- and $\text{F}(\text{HF})_n$ and (b) $\text{OH}(\text{H}_2\text{O})_n$ are shown as a function of the relative humidity (RH). No correlation exists in the arbitrary units between (a) and (b).

or,



According to preliminary *ab initio* calculations on Rxn (4), $\text{OH}(\text{H}_2\text{O})$ dissociates into an OH radical and a water molecule immediately after production, resulting in an extremely small equilibrium constant of $2.1 \times 10^{-26} \text{ cm}^3 \text{ molecule}^{-1}$. This implies that the amount of the OH-water complex is negligible in the CI region. Conversely, Rxn. (7) and further clusterization with water were favorable in terms of enthalpy. Thus, $[\text{OH}(\text{H}_2\text{O})_n]^-$ in CIMS likely results from Rxns. (6) and (7), with subsequent clusterization in the CI region. High humidity conditions were created in the CI region using the water-vapor introduction line to examine the origin of $[\text{OH}(\text{H}_2\text{O})_n]^-$. The resulting distribution of $[\text{OH}(\text{H}_2\text{O})_n]^-$ under humid conditions was similar to that shown in Figure 2 (b),

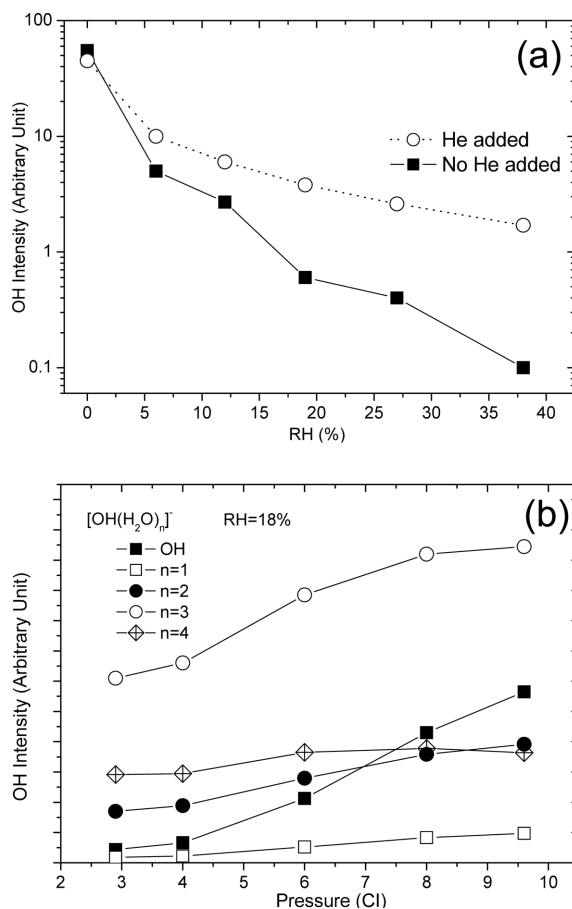


Figure 3. OH peak intensity is shown (a) as a function of the relative humidity (RH) (a) with (○) and without (■) additional helium (He) buffer flow, and (b) the dependence of $[\text{OH}(\text{H}_2\text{O})_n]^-$ peak intensity is shown as a function of chemical ionization (CI) pressure.

thereby confirming the origin of $[\text{OH}(\text{H}_2\text{O})_n]^-$ complexes.

An additional buffer flow of He into the CI region caused two opposing effects on CIMS sensitivity. The buffer flow increased the total pressure in the CI region, resulting in a dilution of OH and SF_6^- , which led to a decrease in CIMS sensitivity because lesser amounts of both species are introduced into the mass spectrometer. In contrast, the same effect dilutes water vapor in the CI region and reduces loss of the reagent ion, which increases sensitivity.

The intensity of the OH peak as a function of RH was monitored with an additional He flow of 2 SLPM (standard liters minute⁻¹) into the CI region, increasing the pressure from 1.9 Torr to 10 Torr.¹⁴ As shown in Figure 3(a), the sensitivity for OH decreased as the RH increased up to 38%. However, the sensitivity recovered significantly with additional He buffer flow, which diluted water vapor resulting in reduction of the reagent ion loss and OH-water clusterization. For example, the OH sensitivity increased by a factor of 17 with an additional He buffer flow at 38% RH.

Without the additional flow, the OH peak was barely observable.

Figure 3(b) shows intensity changes in the OH⁻ peak and its associated water complexes at 18% RH as a function of pressure in the CI region. The complexation of OH ions with water occurred even with the additional He flow, and [OH(H₂O)₃]⁻ was the major OH-containing species. However, the intensity of the OH peak increased slightly as the CI pressure increased, and eventually exceeded the peak intensities of [OH(H₂O)]⁻, [OH(H₂O)₂]⁻, and [OH(H₂O)₄]⁻ at over 8 Torr. The recovery of OH intensity through the introduction of an additional He buffer flow provides sufficient sensitivity for experimental investigations on heterogeneous reactions of OH under humid conditions.

Conclusion

A flow tube system was coupled to a CIMS instrument to investigate the interference of water vapor on OH radical detection. The sensitivity of CIMS decreased under humid conditions due to loss of the reagent ion (SF₆⁻) via reactions with water. In addition, complexes formed between OH ions and water mostly produced [OH(H₂O)₃]⁻ ions, which resulted in additional losses in OH sensitivity. The observed OH(H₂O)_n peaks in the CI region under humid conditions and preliminary *ab initio* calculations on associated reactions suggest that [OH(H₂O)_n]⁻ ions were produced from OH ions and water molecules in the CI region. OH peak intensity could be partially recovered by introducing an additional He buffer flow into the CI region. This strategy provided sufficient sensitivity for the study of OH heterogeneous reactions under humid conditions.

Acknowledgments

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