Comment on "Investigations on HONO formation from photolysis of adsorbed HNO$_3$ on quartz glass surfaces" by S. Laufs and J. Kleffmann, Phys. Chem. Chem. Phys., 2016, 18, 9616

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COMMENT

Comment on "Investigations on HONO formation from photolysis of adsorbed HNO₃ on quartz glass surfaces" by S. Laufs and J. Kleffmann, *Phys. Chem. Chem. Phys.*, 2016, **18**, 9616

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Laufs and Kleffmann observed HNO₃ surface photolysis rates resemble that of HNO₃ in the gas phase after depositing HNO₃ in air at ~50% relative humidity onto quartz glass surfaces. They questioned the dry HNO₃ coverage (1.1×10^{14} molecules/cm² after depositing ~15 mTorr HNO₃ on silica at 0% humidity) used to derive our previously published HNO₃ near-UV surface absorption cross sections. We directly determined the HNO₃ coverage on a quartz surface using a quartz crystal microbalance (QCM). A similar HNO₃ monolayer coverage obtained by QCM confirms that our estimated HNO₃ coverage is reasonable. We also obtained an NO₂ quantum yield from the 308 nm HNO₃ photolysis on fused silica. In this Comment, we provide an explanation of the variance in HNO₃ surface photolysis rates by clarifying the effects arising from important differences in the HNO₃ coverage on quartz/silica in the presence of humidity versus those in the absence of humidity.

In an article published in *Physical Chemistry Chemical Physics*[1], Laufs and Kleffmann reported photolysis rates of nitric acid (HNO₃) films following deposition of HNO₃ (10 ppbv) in humidified air onto the interior surfaces of a cylindrical quartz reactor and then irradiated the films with UV-Vis lamps. At 50% relative humidity, their observed HNO₃ surface photolysis rates resemble that of HNO₃ in the gas phase. They reported achieving monolayer HNO₃ coverage on quartz. Their results led them to question the HNO₃ coverage used to derive the HNO₃ near-UV surface absorption cross sections published previously by Zhu et al.[2] and Du and Zhu.[3] In our Comment, we provide an explanation of the variance in findings by clarifying the effects arising from important differences in HNO₃ coverages on quartz/silica in the presence of humidity, as studied by Laufs and Kleffmann, versus those in the absence of humidity, as observed in our previous studies.

In our studies, we monitored HNO₃ surface absorption on silica as a function of the HNO₃ pressure using Brewster angle cavity ring-down spectroscopy. Our measurements were performed by depositing mTorr levels of HNO₃ on fused silica surfaces with an exposure time about minutes in the absence of humidity. We reported near UV absorption cross sections of HNO₃ on fused silica surfaces to be two to three orders of magnitude larger than those in the gas phase. We observed that the HNO₃ surface adsorption reached a plateau at a HNO₃ pressure of about 14−18 mTorr, suggesting monolayer adsorption of HNO₃ on silica, with estimated coverage of 1.1×10^{14} molecules/cm² using the van der Waals radius[4] of HNO₃. Since our previous studies assumed that the HNO₃ surface adsorption achieved monolayer coverage, we have elected to directly determine the HNO₃ coverage on a quartz surface by adapting a quartz crystal microbalance (QCM) (Inficon SQM-160 Deposition Monitor and 6 MHz quartz crystal) to our surface-study chamber. We assumed similar coverage of HNO₃ on quartz and on silica. Once HNO₃ is deposited onto the quartz crystal resonator, the frequency shift of the resonator is

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related to the mass deposited onto the crystal surface according to the Sauerbrey Equation[5,6],

$$\Delta f = \left[\frac{-2f_0{}^2}{A\sqrt{p_q\mu_q}}\right]\Delta m \qquad 1)$$

where f_0 is the resonant frequency of the crystal, A is the area of the crystal surface, p_q is the density of quartz (2.648 g/cm^3), μ_q is the shear modulus of quartz for an AT-cut crystal (2.947 x 10^{11} g/cm·s^2), Δf is the frequency shift of the crystal, and Δm is the mass deposited onto the crystal surface.

High purity HNO_3 was prepared by repeated vacuum distillations, as previously reported[2,3]. Frequency shifts following deposition of HNO_3 on the quartz crystal surface were measured in the 0−20 mTorr range with 2 mTorr increments at a typical exposure time of about 2 mins. Ring-down measurements for the evacuated cavity were made simultaneously to ensure HNO_3 was completely removed from the quartz crystal surface before each deposition experiment. Each set of measurements was repeated daily over a four-day period to ensure they were obtained under conditions of repeatability. The averaged results from these measurements can be seen in Figure 1 below.
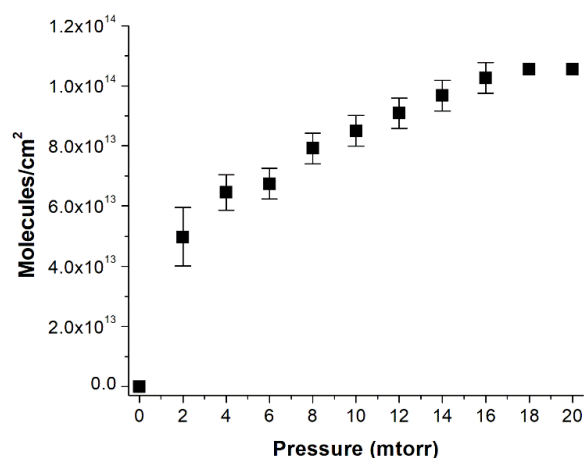

Figure 1. Coverage of HNO_3 on QCM as a function

of the HNO_3 pressure at room temperature. Error bars are listed as 1σ.

Figure 1 shows that a monolayer HNO_3 coverage of ~1×10^{14} molecules/cm^2 is reached at a HNO_3 pressure of approximately 16 mTorr and an exposure time of about 2 minutes. The dependence of HNO_3 adsorption on HNO_3 pressure determined by QCM is in excellent agreement with our previous determination of the dependence of the HNO_3 near-UV surface absorption on HNO_3 pressure observed on a silica surface. This is anticipated because the adsorption of HNO_3 on quartz is similar to that on silica. The similar HNO_3 monolayer coverage obtained through QCM measurements further confirms that our previously estimated HNO_3 monolayer coverage of 1.1×10^{14} molecules/cm^2 is reasonable.

Based upon our wavelength-dependent HNO_3 near-UV surface absorption cross sections and using a HNO_3 near UV surface photolysis quantum yield of 1, we conclude that the HNO_3 surface photolysis rate is 2−3 orders of magnitude faster than that of HNO_3 in the gas phase. This conclusion is valid for HNO_3 deposition on a silica surface with coverage ~10^{14} molecules/cm^2 in the absence of humidity. However, Laufs and Kleffmann's experiments were conducted in the presence of humidity. Both HNO_3 and H_2O can be deposited on quartz surfaces, and can compete for surface adsorption sites. We have studied the competitive co-adsorption[7] of HNO_3 and H_2O on silica surfaces, and provided an empirical formula to calculate the HNO_3 fractional coverage on silica in the presence of humidity. At 50% relative humidity (RH), there are about 4 layers of H_2O on silica surfaces at room temperature.[8-9] It is anticipated that when HNO_3 and H_2O molecules are co-deposited onto silica surfaces, HNO_3 molecules are incorporated into the H_2O layers. This is because water vapor is in great excess as we learned from a separate experiment.[10] While the 2nd-4th H_2O layers may hold more HNO_3 due to the hydrogen-bonding interactions between HNO_3 and H_2O, like the solvation of HNO_3 by the surrounding H_2O molecules, the 1st H_2O layer (i.e.,

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the H_2O layer in direct contact with the quartz/silica surface) is expected to be occupied by both HNO_3 and H_2O molecules. Based on our analysis,[7] we expect that the fractional HNO_3 coverage at the H_2O layer that directly contacts with quartz/silica at 50% RH is approximately two orders of magnitude lower than that on quartz/silica surfaces under no-humidity conditions. Therefore, we conclude that differences in the HNO_3 photolysis rates between our study and that by Laufs and Kleffmann were primarily caused by the difference in the HNO_3 coverage on quartz/silica in the absence versus presence of humidity.

Although the HNO_3 near UV surface absorption cross sections are 2−3 orders of magnitude larger than those of the HNO_3 vapor, its coverage is decreased by at least two orders of magnitude compared to those in the absence of humidity. This results in a similar HNO_3 photolysis rate on quartz/silica at 50% RH to that in the gas or liquid phase. Laufs and Kleffmann deposited 10 ppbv of HNO_3 in humidified air (~50% humidity) on the inner surfaces of the quartz flow-reactor. Nitric acid was washed off the quartz surfaces and the HNO_3 concentration was determined using ion chromatography. Using the geometrical surface area of the flow-reactor, they derived an HNO_3 surface concentration of 1×10^{14} molecule/cm^2, which led them to conclude that HNO_3 had saturated the monolayer surface adsorption sites on quartz. However, this method of HNO_3 coverage determination failed to account for the large number of H_2O molecules that were multilayer-adsorbed to the quartz surface (which excluded HNO_3 molecules from occupying the same physical space). The actual HNO_3 fractional surface coverage on the quartz surface at 50% RH is much lower than their claimed coverage of 1.0×10^{14} molecules/cm^2.

We also determined the NO_2 quantum yield from the 308-nm excimer laser photolysis of HNO_3 adsorbed on fused silica using Brewster angle cavity ring-down spectroscopy. The NO_2 surface absorption was found to depend linearly on photolysis fluence, confirming that NO_2 is a product formed from single photon photolysis of adsorbed HNO_3. The NO_2 quantum yield was 0.62 ± 0.17, where error quoted represents 1σ standard deviation.

Through this open response to Laufs and Kleffmann's paper, we show that seemingly contradictory results related to HNO_3 surface photolysis in the absence versus presence of humidity can be explained using fundamental concepts of HNO_3/H_2O competitive co-adsorption and multilayer adsorption. In this example, a key parameter that changes dramatically following deposition of HNO_3 vapor in the absence versus in the presence of 50% RH is the HNO_3 coverage on quartz/silica. Rather than being viewed as conflicting results, once clarified, each set of findings provides valuable information. In the real atmosphere, many pollutants on the surfaces of the ground, buildings, and aerosols can modify the HNO_3 surface coverage. It is important to determine the HNO_3 surface coverage under different atmospheric conditions so that oxidant formation contribution from adsorbed HNO_3 photolysis corresponding to such coverage can be obtained.

Conflicts of interest

The authors declare no competing financial interest.

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