Monitoring Reaction Intermediates in Plasma-Driven SO₂, NO, and NO₂ Remediation Chemistry Using In Situ SERS Spectroscopy

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ABSTRACT: In situ surface-enhanced Raman scattering (SERS) spectroscopy is used to identify the key reaction intermediates during the plasma-based removal of NO and SO₂ under dry and wet conditions on Ag nanoparticles. Density functional theory (DFT) calculations are used to confirm the experimental observations by calculating the vibrational modes of the surface-bound intermediate species. Here, we provide spectroscopic evidence that the wet plasma increases the SO₂ and the NO₂ removal through the formation of highly reactive OH radicals, driving the reactions to H₂SO₄ and HNO₃, respectively. We observed the formation of SO₃ and SO₄ species in the SO₂ wet-plasma-driven remediation, while in the dry plasma, we only identified SO₃ adsorbed on the Ag surface. During the removal of NO in the dry and wet plasma, both NO₂ and NO₃ species were observed on the Ag surface; however, the concentration of NO₃ species was enhanced under wet-plasma conditions. By closing the loop between the experimental and DFT-calculated spectra, we identified not only the adsorbed species associated with each peak in the SERS spectra but also their orientation and adsorption site, providing a detailed atomistic picture of the chemical reaction pathway and surface interaction chemistry.

Nitrogen oxide (NO), nitrogen dioxide (NO₂), and sulfur dioxide (SO₂) are toxic by-products of burning fossil fuels. These NOₓ emissions are one of the key factors responsible for acid rain and atmospheric photochemical smog. In addition to NOₓ regulations, starting January 1, 2020, the International Marine Organization (IMO) has limited the sulfur content in fuel oil used on board ships from 3.5% (i.e., heavy fuel oil) to 0.50% m/m. At this time, heavy fuel oil ("Bunker Fuel") comprises 4% of every barrel of crude oil, which corresponds to 10 000 tons/day of global sulfur emissions. The new 0.5% limit corresponds to a 90% reduction in SO₂ emissions, which can potentially be achieved using a plasma-generated OH radical-based approach. Although technologies for removing NOₓ efficiently currently exist (e.g., selective catalytic reduction (SCR)), effective methods for SO₂ treatment are still lacking. For example, the efficiency of SO₂ wet scrubber technologies is limited by the low SO₂ solubility in water, which is some orders of magnitude lower than the H₂SO₄ solubility. As such, one attractive solution is to first convert SO₂ to H₂SO₃ (i.e., SO₂ → HSO₃ → H₂SO₄) via the plasma generation of OH radicals and then capture the products by means of a "wet scrubber" with nearly unity capture.

In recent years, plasma-based processes have been successfully proven for highly effective NO remediation by many research groups (including our own). However, the plasma-based treatment of SO₂ remains challenging. This problem is intensified in diesel exhaust due to the rapid consumption of the vast majority of the oxygen radicals in the plasma by the oxidation of NO to NO₂. In other words, the NO remediation reaction is a competing reaction pathway for the plasma-generated radicals. Yamamoto’s group used a single-stage wet-type plasma reactor for the removal of particulates, NOₓ, and SO₂ simultaneously. More recently, we reported a substantial enhancement in SO₂ removal by discharging a transient nanosecond pulsed plasma in a water vapor-saturated gas mixture. However, the detailed reaction mechanism with the plasma-based process is complex and not fully understood. Figures S1 and S2 of the Supporting Information illustrate the multitude of possible chemical pathways in these plasma-based processes. Here, the major products and intermediates are NO₂, N₂O, N₂O₅, N₂, HNO₂, and HNO₃ for the NO₂ removal, while SO₂, SO₃, HSO₃, and H₂SO₄ are present during the SO₂ removal. Nevertheless, identifying the surface intermediate species involved in the
chemical reaction is very difficult using conventional methods for product analysis.

Since its discovery, more than four decades ago, surface-enhanced Raman scattering (SERS) has shown significant promise for sensing individual molecules adsorbed onto metal nanostructures or substrates with nanoscale roughness.\textsuperscript{20–24} SERS is a highly sensitive vibrational spectroscopic technique that allows the detection of low concentrations of molecules through the amplification of electromagnetic fields generated by the excitation of surface plasmons. In short, SERS significantly increases the signal from the weak yet structurally rich technique of Raman scattering. Thus, SERS presents a promising technique for the identification of surface active species during the NO\textsubscript{x} and SO\textsubscript{2} removal processes. However, the SERS spectral signatures are mainly determined by the interactions between molecules and surfaces. Therefore, a correct interpretation of the chemical mechanism in SERS is required to extract the vibrational information contained in these spectra.\textsuperscript{25} First-principles calculations enable a consistent treatment of the enhancement mechanisms and thus provide a means for interpreting the SERS spectra.\textsuperscript{25,26}

In this work, we provide spectroscopic evidence of the intermediates formed during the NO and SO\textsubscript{2} plasma-based removal on Ag nanoparticles by in situ SERS. Moreover, we verify the identification of surface species using density functional theory (DFT) calculations. To our knowledge, this is the first time that experimentally measured SERS vibrational modes of NO\textsubscript{2}, NO\textsubscript{3}, SO\textsubscript{3}, and SO\textsubscript{4} adsorbed on Ag nanoparticles have been confirmed by atomistic simulations, thus, providing peak assignment (e.g., SO\textsubscript{3} vs SO\textsubscript{4}) molecular orientation, and adsorption site.

Here, we utilize a transient pulsed plasma discharge in a glass-slide plasma-based reactor, which consists of two parallel copper electrodes separated by an approximately 5 mm gap (see Figure 1).\textsuperscript{27–29} Further details are given in the Supporting Information.

Figure 2a shows SERS spectra collected during plasma discharge (13 kV pulses at 200 Hz) in a flowing SO\textsubscript{2} gas environment (5 sccm, 500 PPM) both with and without water vapor. Under these conditions, we have shown that the SO\textsubscript{2} removal is 6X more effective in wet plasma than in dry plasma (see Figure S3).\textsuperscript{1} The SERS spectra shown in Figure 2a exhibit similar features to those reported by Hirokawa et al.\textsuperscript{30} and Maeda et al.\textsuperscript{31} for SO\textsubscript{3} and SO\textsubscript{4} adsorbed on Ag nanoparticles. Here, we find that the SERS spectra are quite different in the dry plasma (i.e., without water vapor) than in the wet plasma (i.e., with water vapor). In the wet-plasma discharge, prominent sharp peaks are observed at 618 and 928 cm\textsuperscript{−1} corresponding to SO\textsubscript{3} species and at 958 and 1044 cm\textsuperscript{−1} corresponding to SO\textsubscript{4} species.\textsuperscript{30,31} Additionally, small peaks are detected at 249, 470, and 821 cm\textsuperscript{−1}. In the dry plasma, small peaks at 190, 971, and 1090 cm\textsuperscript{−1} corresponding to SO\textsubscript{3} are observed.\textsuperscript{30,31} The main SO\textsubscript{3} peak around 600 cm\textsuperscript{−1} has a somewhat lower relative intensity than that calculated by DFT, and it is broadened and red shifted to 559 cm\textsuperscript{−1}. Additionally, during the dry-plasma discharge, no SO\textsubscript{4} peaks are observed experimentally. As a control experiment, we also flowed H\textsubscript{2}SO\textsubscript{4} vapor across the Ag nanoparticles (without plasma discharge), which exhibited prominent peaks at 243, 624, 967, and 1171 cm\textsuperscript{−1}, as shown in Figure S4 of the Supplementary Information. To properly assign and correlate the measured signals, Table 1 lists the vibrational frequencies observed during the experiments together with the calculations performed by DFT.

We calculated the adsorption of SO\textsubscript{3} and SO\textsubscript{4} on the Ag nanoparticles by DFT at the Ag atop site and on the (111)Ag surface (see Figures S5 and S6). We found that the SO\textsubscript{3} is adsorbed via the sulfur atom with a binding energy of −5.34 eV for the SO\textsubscript{3} adsorbed to the atop Ag site and −5.33 eV for the SO\textsubscript{3} adsorbed to the (111)Ag surface. SO\textsubscript{4} is bidentate coordinated through two oxygen atoms with an interaction energy of −4.42 eV for the SO\textsubscript{4} adsorbed to the atop Ag site and −4.35 eV for the SO\textsubscript{4} adsorbed to the (111)Ag surface.

Figure 2b,c shows the calculated Raman spectra for SO\textsubscript{3} and SO\textsubscript{4} adsorbed on the Ag clusters. Interestingly, the vibration modes vary significantly for the two Ag surfaces (i.e., atop and (111)). In addition, the dominant features for SO\textsubscript{3}, adsorbed to the atop Ag surface are predicted at 181, 535, and 890 cm\textsuperscript{−1}, corresponding to the S−Ag stretching, O−S bending, and symmetric O−S stretching of sulfite, respectively. For SO\textsubscript{4} adsorbed to (111)Ag surfaces, the main peaks are calculated at 422 cm\textsuperscript{−1} (O−S bending), 449 cm\textsuperscript{−1} (O−S wagging), 551 cm\textsuperscript{−1} (S−Ag stretching + O−S bending), 804 cm\textsuperscript{−1} (symmetric O−S stretching), 864 cm\textsuperscript{−1} (asymmetric O−S stretching), and 1079 cm\textsuperscript{−1} (O−S stretching).
The dominant features for SO₄ adsorbed to the atop Ag surface site are calculated at 221, 446, 556, 799, and 1030 cm⁻¹, corresponding to the S−Ag stretching, O−S bending, S−Ag stretching + O−S bending, symmetric O−S stretching, and symmetric O−S stretching vibrational modes of sulfate, respectively. For SO₄ adsorbed to (111)Ag surfaces, the main Raman signals are predicted at 219 cm⁻¹ (relative motion between SO₄ and Ag₂0), 393 cm⁻¹ (O−S waggling), 542 cm⁻¹ (O−S bending), 840 cm⁻¹ (symmetric O−S stretching), 904 cm⁻¹ (asymmetric O−S stretching), and 1141 cm⁻¹ (O−S stretching). Detailed drawings of the vibrational modes and frequencies of SO₃ and SO₄ adsorbed on the Ag nanoparticles can be found in Figures S5 and S6 of the Supplementary Information.

During the removal of SO₂ in dry plasma, the small peak observed at 189 cm⁻¹ can be assigned to SO₃ adsorbed on a defect site (atop), while the broad peak around 1099 cm⁻¹ can be correlated with SO₃ adsorbed on (111)Ag. Additionally, the absence of the peaks around 220, 960, and 1044 cm⁻¹ indicates that SO₄ is not present and only SO₃ species are formed. The SO₃ species are present on defect sites during the SO₂ removal reaction in dry-plasma discharge. The spectrum collected during the SO₂ removal with wet plasma shows Raman signals corresponding to SO₃ species adsorbed on the (111)Ag surface at 470 and 821 cm⁻¹. The peak at 1044 cm⁻¹ can be assigned to SO₄ adsorbed to the Ag atop site. The peaks at 249, 618, 821, 890, 928/958/1044, and 1088/1171 cm⁻¹ can be assigned to SO₃ adsorbed on the (111)Ag surface.

### Table 1. Some Important Vibrational Frequencies of Reactants and Potential Products during SO₂ Plasma Discharge

<table>
<thead>
<tr>
<th>Component</th>
<th>SO₃ dry-plasma</th>
<th>SO₃ wet-plasma</th>
<th>H₂SO₄</th>
<th>SO₄ dry-plasma</th>
<th>SO₄ on Ag atop</th>
<th>SO₄ on (111)Ag</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO₃ dry-plasma</td>
<td>181 (SO₃)</td>
<td>249 (SO₃)</td>
<td>243 (SO₃)</td>
<td>211</td>
<td>N/A</td>
<td>219</td>
</tr>
<tr>
<td>SO₃ wet-plasma</td>
<td>470</td>
<td>468</td>
<td>448 (small)</td>
<td>442/49</td>
<td>393</td>
<td></td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>470</td>
<td>468</td>
<td>448 (small)</td>
<td>442/49</td>
<td>393</td>
<td></td>
</tr>
<tr>
<td>SO₄ dry-plasma</td>
<td>559</td>
<td>618</td>
<td>624</td>
<td>535</td>
<td>556</td>
<td>551</td>
</tr>
<tr>
<td>SO₄ on Ag atop</td>
<td>592</td>
<td>632</td>
<td>624</td>
<td>535</td>
<td>556</td>
<td>551</td>
</tr>
<tr>
<td>SO₄ on (111)Ag</td>
<td>592</td>
<td>632</td>
<td>624</td>
<td>535</td>
<td>556</td>
<td>551</td>
</tr>
</tbody>
</table>

*Values obtained from DFT calculations.*

The vibrational frequencies of SO₃ and SO₄ adsorbed on Ag nanoparticles can be found in Figures S5 and S6 of the Supplementary Information.
and 958 cm$^{-1}$ are assigned to SO$_4$ species. However, for these peaks, it is not possible to discriminate between SO$_4$ adsorbed on atop or (111)Ag, and probably species on both sites coexist.

The results presented here indicate that SO$_2$ is partially converted to SO$_3$ in the dry plasma, with a low SO$_2$ removal rate. The further oxidation of SO$_3$ via (HSO$_3$) is limited, and no SO$_4$ via H$_2$SO$_4$ is detected in the Raman spectra due to low amount of OH radicals. In the wet plasma, the formation of highly reactive OH radicals drives the SO$_2$ conversion to H$_2$SO$_4$ in a two-step process: SO$_2$ $\rightarrow$ HSO$_3$ $\rightarrow$ H$_2$SO$_4$ achieving high SO$_2$ removal rates. In our previous work, we demonstrated that the wet plasma is 6 times more effective than the dry plasma at removing SO$_2$. In that previous work, we provided spectroscopic evidence of the short-lived, highly reactive OH radical generation in the presence of vapor water through plasma emission spectroscopy. In the present work, we provide spectroscopic evidence of the SO$_4$ formation during the removal of SO$_2$ in the wet plasma. The absence of Raman signals corresponding to adsorbed atop SO$_3$ in the wet plasma may indicate that this species is rapidly oxidized to SO$_4$ and, as such, SO$_3$ and SO$_4$ species accumulate on the highly coordinated Ag sites.

Figure 3a shows the SERS spectra collected during plasma discharge (13 kV pulses at 200 Hz) in a flowing NO gas environment (5 sccm, 500 ppm) with and without water vapor.

![SERS spectra](image)

**Figure 3.** (a) SERS spectra measured during NO removal with dry and wet plasma. SERS spectra of (b) NO$_2$ and (c) NO$_3$ species calculated by DFT.

Using a coaxial plasma-based reactor (see Figure S7), we observed NO and NO$_2$ removals of 40 and 4% with dry plasma, respectively, while the wet-plasma discharge produced a removal of 100% for NO and 98% for NO$_2$. When discharging the dry plasma in NO gas, peaks at 243 and 818 cm$^{-1}$ are observed and assigned to NO$_2$ species$^{32-34}$ while the peak at 1046 cm$^{-1}$ corresponds to NO$_3$ species$^{33,34}$. In the wet-plasma discharge, Raman signals are measured at 237, 819, 963, 1041, and 1297/1444 cm$^{-1}$, showing the formation of NO$_2$ and NO$_3$ species$^{32-34}$. The Raman spectra observed during the wet- and dry-plasma discharge cannot be correlated with NO molecules or ions, indicating that NO is adsorbed on the surface as NO$_2$/NO$_3$. As a control experiment, we also flowed HNO$_3$ vapor across Ag nanoparticles (without plasma discharge) (see Figure S8), which showed prominent peaks at 258, 855, 933, 1052, and 1396 cm$^{-1}$. To further confirm the species observed during the experiments, the spectra are compared with those predicted by DFT calculations. Table 2 lists the vibrational frequencies observed during the experiments together with those predicted by simulations.

We calculated the adsorption of NO$_2$ and NO$_3$ on the Ag nanoparticles by DFT at the Ag atop site and on the (111)Ag surface. We found that the NO$_3$ is adsorbed via the nitrogen atom with a binding energy of $-2.14$ eV for the NO$_3$ adsorbed to the atop Ag site and $-1.69$ eV for the NO$_3$ adsorbed to the (111)Ag surface. The NO$_3$ is bidentate coordinated through two oxygen atoms (see Figures S9 and S10) with an interaction energy of $-1.68$ eV for the NO$_3$ adsorbed to the atop Ag site, while no stable configuration is found for the NO$_3$ adsorbed to the (111)Ag surface.

The calculated Raman spectra of NO$_2$ and NO$_3$ adsorbed on Ag nanoparticles are plotted in Figure 3b,c. NO$_2$ adsorbed on the atop Ag surface site exhibits peaks at 207, 303, 769, and 1274 cm$^{-1}$, corresponding to the N–Ag stretching, N–Ag bending + N–O bending, N–O bending, and N–Ag stretching + N–O bending vibrational modes of nitrite, respectively. For NO$_2$ adsorbed on the (111)Ag surface, peaks are predicted at 254, 764, and 1135/1387 cm$^{-1}$ and are assigned to the N–Ag bending + N–O bending, N–O bending, and asymmetric N–O stretching of nitrite vibration modes.

The calculated spectrum of NO$_3$ adsorbed atop on the Ag surface exhibits peaks at 210, 703/781, 989, and 1206/1422 cm$^{-1}$. The signal at 210 cm$^{-1}$ is assigned to the O–Ag stretching, the signal at 703/781 to the N–O bending, 989 cm$^{-1}$ to symmetric N–O stretching, and the bands at 1206/1422 cm$^{-1}$ to the asymmetric N–O stretching vibrational modes of the surface-bound nitrate species. It is worth mentioning that the DFT calculations could not obtain any stable configuration of the nitrate molecules on the (111)Ag surface. More details of the vibrational modes and frequencies of NO$_2$ and NO$_3$ adsorbed on the Ag nanoparticles can be found in Figures S9 and S10.

The spectra observed during the NO removal in dry plasma match nicely with those obtained by DFT for NO$_2$ adsorbed on the Ag nanoparticles, indicating the formation of nitrites on the surface. Additionally, the absence of the peak around 990 cm$^{-1}$ and the small signal at 1046 cm$^{-1}$ suggests that NO$_3$ is present on the surface at low concentrations. When the plasma is discharged in a wet NO atmosphere, the Raman signals assigned to NO$_3$ atop at 963 and 1422 cm$^{-1}$ are clearly seen, together with the signal at 1041 cm$^{-1}$, which correlates with the reference HNO$_3$ spectrum. The peaks at 819 and 1297 cm$^{-1}$ match nicely with those obtained by DFT for NO$_2$ adsorbed on the Ag nanoparticle.
cm$^{-1}$ indicate the presence of NO$_2$ atop on the Ag surface. This may indicate that the NO$_2$ and NO$_3$ species are adsorbed on defect sites during the wet-plasma NO removal.

The results obtained in this work suggest that when discharging the dry plasma in NO gas, it readily converts to NO$_2$ through atomic oxygen radicals. In the gas phase (i.e., without Ag nanoparticles), the further oxidation to NO$_3$ is limited by the availability of OH radicals. In the presence of Ag nanoparticles, the surface chemistry (i.e., strongly oxidizing nature of Ag) readily converts NO and NO$_2$ species to NO$_3$ as evidenced in the Raman spectra with the peak at 1046 cm$^{-1}$. However, the still low availability of O or OH radicals limits the total conversion to NO$_3$ (or HNO$_3$). The presence of water facilitates the formation of OH radicals, enhancing the NO removal by 2.5× and the NO$_x$ removal by 25×, thus improving the HNO$_3$ (and hence NO$_3$) production as observed by the in situ SERS spectra. Additionally, the second step minimizes the backreaction of NO$_2$ to NO.

Finally, the HNO$_3$ can be captured using water and subsequently titrated, with near-unity efficiency in a wet scrubber.

This work demonstrates that the joint SERS/DFT approach can be used to study (and identify) important reaction intermediates, thus, establishing reaction pathways in a complex reaction system. As another practical example, in CO$_2$ reduction with water, more than a dozen reaction pathways have been proposed. The identification of specific pathways (and their catalytically active sites) can enable new, more selective catalysts to be developed and optimized.

In conclusion, a substantial enhancement in the removal of gaseous NO, NO$_2$, and SO$_2$ is reported by discharging a transient nanosecond pulsed plasma in a water vapor-saturated gas mixture compared to dry conditions. We have collected in situ SERS spectra during the plasma-based treatment of toxic gases NO, NO$_2$, and SO$_2$ in both dry- and wet-plasma conditions. In addition, we have calculated SERS-enhanced Raman spectra of various intermediate species (including NO$_2$, NO$_3$, SO$_3$, and SO$_4$) bounded to Ag nanoclusters using density functional theory. The dominant peaks in the simulated spectra qualitatively agree with the experimental spectra and help us to determine the correct assignment of the vibrational modes, adsorbed species, orientation, and adsorption site on the Ag nanoparticles. Through this approach, we were able to identify the reaction intermediates produced during the plasma-driven remediation process. In particular, we observed SO$_3$ species adsorbed atop and on the (111)Ag surface during the SO$_2$ removal in dry plasma, while the SO$_4$ species could not be detected, showing the limitation of the dry-plasma approach to fully convert SO$_2$ to H$_2$SO$_4$. When discharging the wet plasma, both SO$_3$ and SO$_4$ species adsorbed on highly coordinated Ag sites were identified. During NO remediation in both dry and wet plasma, NO$_2$ and NO$_3$ were detected. However, in the wet-plasma discharge, the SERS results show that the NO$_3$ production is enhanced. Additionally, we showed that NO$_2$ and NO$_3$ species are adsorbed on defect sites during the wet-plasma NO removal. To our knowledge, this is the first time that the active species have been detected by SERS spectroscopy during NO$_x$ and SO$_x$ remediation processes and correlated with theoretical calculations.

### Table 2. Some Important Vibrational Frequencies of Reactants and Potential Products during SO$_2$ Plasma Discharge

<table>
<thead>
<tr>
<th>Component</th>
<th>N−Ag stretching</th>
<th>N−Ag bending</th>
<th>N−O stretching</th>
<th>N−O bending</th>
<th>N−O asymmetric stretching</th>
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<tr>
<td>NO dry plasma</td>
<td>245</td>
<td>1046</td>
<td>1228</td>
<td>1257/1444</td>
<td></td>
</tr>
<tr>
<td>NO wet plasma</td>
<td>235</td>
<td>1304</td>
<td>1206/1422</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HNO$_3$</td>
<td>258</td>
<td>855</td>
<td>933/1052</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO$_2$ on Ag atop</td>
<td>303</td>
<td>254</td>
<td>N/A</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO$_3$ on Ag atop</td>
<td>303</td>
<td>254</td>
<td>N/A</td>
<td></td>
<td></td>
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<tr>
<td>NO$_2$ on (111)Ag</td>
<td>303</td>
<td>254</td>
<td>N/A</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO$_3$ on (111)Ag</td>
<td>303</td>
<td>254</td>
<td>N/A</td>
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Values obtained from DFT calculations.
ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.analchem.0c05413.

Experimental details; NO and SO2 removal efficiencies; chemical pathways; reference spectra; and details of the vibrational modes and frequencies of adsorbed molecules on Ag nanoparticles (PDF)

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes
The authors declare no competing financial interest.

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