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Optical and Mass-Spectral Characterization of Mixed-Gas Flowing Atmospheric-Pressure Afterglow Sources

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Abstract

Plasma-based ambient desorption/ionization (ADI) sources for mass spectrometry (MS) often use helium as the primary discharge gas due to the large reaction cross section of excited helium species with atmospheric gases, which ultimately leads to efficient reagent-ion formation. However, some studies have shown mixed-gas plasmas provide unique advantages. For instance, our group showed that a helium-oxygen flowing atmospheric-pressure afterglow (He:O₂-FAPA) source yielded enhanced ion signals for small polar analytes, but compounds with aromatic rings underwent chemical modification to produce pyrylium species. Here, it is shown that the addition of H₂ to the helium FAPA gas significantly decreased the reagent-ion signals, but analyte-ion signal was not affected to the same degree as reagent ions. In addition, mass spectra obtained with He:H₂-FAPA were chemically cleaner with fewer ions stemming from analyte

species and produced less oxidation of analytes. Addition of nitrogen increased the abundance of negative reagent ions (e.g., NO_2^- and NO_3^-) which led to the enhanced ion signal for RDX. To better understand these unique advantages of a mixed-gas FAPA, the impact of molecular-gas (O_2 , N_2 , or H_2) addition on the optical-emission spectra from the discharge was also measured. Spatially resolved emission was obtained from the anode- and negative-glow regions. In general, addition of small fractions ($\sim 0.1\%$) of molecular gases decreased helium and OH emission intensities. Atomic oxygen and hydrogen emission increased with the addition of O_2 and H_2 , respectively. Furthermore, emission characteristics of N_2 , N_2^+ , and NO with respect to molecular gas composition on He-FAPA were also measured. Fundamental plasma parameters, such as OH rotational temperature (T_{rot}), were also calculated for these mixed-gas systems.

1. Introduction

Ambient desorption/ionization-mass spectrometry (ADI-MS) provides the capabilities to directly desorb/ionize analytes from sample surface in the open air with little or no sample pretreatment, which significantly increases the sample throughput [1]. Since its introduction in 2004 by Takats *et al.* [2], ADI-MS has found many applications ranging from rapid screening of pharmaceutical products [3], explosives [4], and drugs-of-abuse [5], to quantitative analysis [6] and mass-spectral imaging [7-9]. A variety of different ADI-MS sources have been reported with the most extensively used being desorption electrospray ionization (DESI) [2] and direct analysis in real time (DART) [10]. Out of more than 40 ADI-MS sources, at least one third of the techniques are plasma-based [11, 12], which means they rely on electrical discharges for the desorption and/or ionization process. The most widely used plasma-based sources include DART [4, 10, 13, 14], dielectric-barrier discharge ionization (DBDI) [15], low-temperature plasma (LTP) probe [16], flowing atmospheric-pressure afterglow (FAPA) [17-21], atmospheric-

1 pressure solid analysis probe [22-26], and plasma-assisted desorption/ionization (PADI) [27].
2 Although, these plasma-based sources have different designs and powering schemes, which leads
3 to very different plasma processes, it has been frequently noted they produce similar reagent and
4 analyte ions in molecular MS.

5 Plasma-based ADI sources for MS generally use helium as the discharge gas due to the
6 large reaction cross section of excited helium species with atmospheric gases such as N₂, O₂,
7 H₂O, *etc.*, which ultimately leads to greater reagent-ion densities. However, some mixed-gas
8 plasmas were found to provide improved sensitivity compared to only-helium discharges. For
9 instance, Brewer *et al.* [28] showed that the addition of a small percentage of O₂ to a He or Ar
10 radiofrequency atmospheric-pressure glow discharge (rf-APGD) enhanced ion signal for some
11 pharmaceutical compounds up to nine times. In addition, mass spectra obtained with this mixed-
12 gas plasma contained fragmentation patterns that were similar to electron-ionization (EI) mass
13 spectra that are database searchable. In another case, Wright *et al.* [29] examined the addition of
14 hydrogen to a helium dielectric barrier discharge (DBD), which led to enhanced ion signals of up
15 to 68 times for several analytes. Further, these signal enhancements were noted for gaseous
16 analytes and analytes coated on glass slides with addition of H₂ to an argon plasma.

17 Here, we explore the effects of molecular gases on the performance and characteristics of
18 the discharge of a helium FAPA source. The FAPA utilizes a direct-current atmospheric-
19 pressure glow discharge (APGD), which is in contrast to the previously reported mixed-gas
20 experiments that used alternating-current (AC) discharges. Molecular gases such as O₂, N₂, and
21 H₂ were added to the He plasma of the FAPA source, while reagent- and analyte-ion signals
22 were measured with mass spectrometry. To better understand the plasma processes and

ionization chemistry, optical emission spectra of mixed-gas plasma of the FAPA source were also recorded.

The use of optical emission spectroscopy (OES) has been used by a number of groups to monitor and understand plasma-based ADI processes. For instance, Chan et al. [30] used spatially resolved OES from the AC dielectric-barrier discharge of a helium LTP to determine the origin of contaminant species, such as O₂, N₂, and H₂O. Franzke et al. [31-34] have measured OES from helium DBDI to better understand plasma processes in the homogeneous and filamentary modes. Shelley et al. [35] applied a combination of OES and MS to characterize differences between the corona-to-glow discharge and the APGD of the DART and FAPA sources, respectively. Similarly, Kratzer et al.[36] compared AC DBD, RF APGD, and the DC DART sources with MS and OES for the direct determination of acetaminophen.

The use of OES also allows determination of fundamental plasma parameters, such as rotational temperature (T_{rot}) from OH and N₂ emission bands and electron number density (n_e) from Stark broadening of the H $_{\beta}$ line. Chan et al. [37] used spatially resolved rotational temperatures calculated from OH and N₂ to elucidate that He₂⁺ serves as an important energy carrier from the AC LTP discharge to the open air. A similar behavior was observed in the afterglow of a DC helium FAPA source [38]. In that same work, both T_{rot} and n_e were determined at multiple locations within the discharge with maxima in the negative-glow region of 1,170 K and *ca.* 10¹³ cm⁻³, respectively.

There have been far fewer optical studies of mixed-gas ADI plasma sources. Schütz et al. [39] presented a survey emission spectrum from an argon-propane DBDI source that, ultimately, was shown to produce similar analyte ions and analytical performance to a helium

DBD. Farnsworth et al. [29, 40, 41] has used a combination of emission, fluorescence, and absorption spectroscopies to monitor changes in helium species, particularly helium metastable atoms (He^m), in helium and $\text{He}:\text{H}_2$ DBD source. We draw on these earlier works to better understand plasma processes occurring in the mixed-gas FAPA sources tested here.

2. Experimental

2.1. Reagents

All reagents used were analytical grade. Ultra-high purity (UHP) helium (99.999%) and nitrogen (99.999%) were purchased from Airgas (Radnor, PA, USA). This grade of helium has maximum impurity levels of 1 ppm_v O_2 , 1 ppm_v H_2O , 0.5 ppm_v total hydrocarbons, and 5 ppm_v N_2 . All gas lines were purged for at least an hour before use to minimize impurities beyond those from the main supply. It is important to note that the level of impurities in the gas supply (<5 ppm_v) is negligible compared to the amounts of molecular gases added in these studies (>1,000 ppm_v); for the sake of simplicity, we ignore molecular gas contributions from impurities in the main helium supply for the comparisons presented below.

Helium/oxygen (80%/20%) and helium/hydrogen (60%/40%) mixtures were also obtained from Airgas (Radnor, PA, USA). Naphthalene, anthracene, benzene, aniline, and RDX (as 1000 $\mu\text{g/mL}$ standard in methanol) were purchased from Sigma-Aldrich (St. Louis, MO, USA). These target compounds were selected for this study to cover a diverse range of analyte properties known to be important in desorption and ionization pathways with plasma-based ADI sources. For instance, aniline was chosen as a species that typically undergoes proton-transfer ionization with protonated water clusters ($[(\text{H}_2\text{O})_n\text{H}]^+$) to form MH^+ . Meanwhile, the non-polar character of naphthalene leads to ionization via either charge transfer (with *e.g.*, O_2^+ , N_2^+ , or NO^+) or photoionization, which yields M^+ ions. While anthracene is also non-polar, it has a

1 sufficiently high proton affinity (877 kJ/mol)[42] to be ionized through proton transfer in
2 addition to charge-transfer or photo ionization. While the aforementioned test species readily
3 form positive ions, RDX typically produces negative ions formed through anion attachment with
4 *e.g.*, NO_2^- , NO_3^- , or Cl^- (if a source of chloride is present) [10, 16]. Subjecting these species to
5 mixed-gas FAPA conditions allowed for monitoring any changes in ionization pathways.

6 **2.2. FAPA Source**

7 A pin-to-plate FAPA source used for these experiments has been described elsewhere
8 [43, 44]. Briefly, a DC atmospheric-pressure glow discharge (APGD) was sustained between a
9 stainless-steel pin cathode (1 mm diameter) and brass plate anode, which were held in place
10 inside a quartz discharge chamber with flowing helium. Discharge species (*e.g.* excited species,
11 ions, and electrons) exited a 1.6-mm hole in the plate where they interact with atmospheric gases
12 and analytes. A high DC potential (*ca.* -500 V) was applied to the pin cathode from a custom
13 built high-voltage power supply (Prosolia Inc., Indianapolis, IN, USA) while the plate anode was
14 connected to ground potential. The FAPA source was powered in current-controlled mode at
15 20 mA. Helium flow to the source was controlled by a mass flow controller (model C50L-AL-
16 DD-2-PV2-V0-SCR; Sierra Instruments Inc., Monterey, Ca, USA) that can provide a maximum
17 of 5 L min^{-1} . Another mass flow controller (model C50L-AL-DD-2-PV2-V0-SCR; Sierra
18 Instruments Inc., Monterey, Ca, USA) that can provide up to 25 mL/min was used to control
19 He/O_2 , He/H_2 , or nitrogen flow, which was mixed with the main helium flow in a T-junction just
20 before the discharge chamber. These mass flow controllers have a repeatability of $\pm 0.25\%$ of full
21 the scale, which equates to $\pm 13 \text{ mL/min}$ and $\pm 0.063 \text{ mL/min}$ for the main helium flow and the
22 supplemental molecular-gas flow, respectively. In this setup, these two flow controllers and the

1 aforementioned mixed-gas supplies result in maximum molecular gas compositions of 0.5% O₂,
2 1.0% H₂, or 2.5% N₂.

3 As can be seen in Figure S4, the FAPA discharge power increased monotonically with O₂
4 and N₂ composition. Oxygen addition led to a greater change in discharge power with an
5 increase of 25% when 0.5% O₂ was added to the discharge, compared to an 18% power increase
6 for the same amount of N₂ in the discharge. Interestingly, addition of H₂ to the helium FAPA
7 required lower voltages and powers to sustain the discharge. As H₂ composition was elevated
8 above 0.3%, the discharge voltage and power began to rise. The biggest change in discharge
9 power for H₂ addition, compared to only helium, was -10% at an H₂ composition of 0.3%.

10 A manual translational stage (PT3; Thorlabs Inc., Newton, NJ, USA) was used to
11 precisely align the FAPA source with the mass spectrometer inlet. Volatile analytes were
12 introduced to the FAPA afterglow through a fused-silica capillary with helium as the carrier gas
13 at 10 mL/min flow rate. Solid analytes were introduced to the FAPA afterglow with a glass
14 probe fixed on a one-dimensional translational stage (PT1; Thorlabs Inc., Newton, NJ, USA),
15 similar to the methods described before [18, 19].

16 Higher resolution optical emission spectra of mixed-gas FAPA sources, which were
17 performed at Brigham Young University, used a different flow mixing setup. For the He:H₂ and
18 He:O₂ mixtures, the flows from two sources, UHP He (99.999% purity) and 1% H₂ or O₂ in He,
19 were combined using two matched mass flow controllers (MKS model 1170A, Andover, MA).
20 The flows from the two sources were varied to give a final support gas ranging from UHP He
21 (containing a maximum of 0.0005% v/v molecular gas impurity) to 1% of the dopant gas in He,
22 at a total flow rate of 1 L min⁻¹. For the He-N₂ mixture, low flows of pure N₂ gas were metered

1 into a flow of UHP He to give the desired N₂ percentages. The N₂ flows were delivered by a
2 mass flow controller (Teledyne Model HFC-302, Thousand Oaks, CA) that had been calibrated
3 with a primary calibrator (Definer 220, Mesalabs, Butler, NJ) to ensure accurate final
4 concentrations of added N₂ to be between 0% and 1%, though it should be noted that the UHP
5 He supply contained N₂ at a maximum impurity level of 5 ppm_v.

6 **2.3. Mass Spectrometry**

7 Mass spectra were acquired with a Thermo LTQ XL linear ion trap mass spectrometer
8 (Thermo Scientific, San Jose, CA, USA). The LTQ-XL mass spectra were collected with a
9 maximum injection time of 100 ms, three microscans per spectrum, and a capillary temperature
10 of 275 °C. Capillary and tube-lens voltages of 15 and 65 V, respectively, were used to detect
11 larger-mass analyte ions. To acquire reagent-ion mass spectra in the positive-ionization mode,
12 the instrument was operated in the low mass range mode, which allows detection of ions down to
13 m/z 15. In this mode, the capillary and tube lens voltages were decreased to 2 and 31 V,
14 respectively.

15 Any changes in reagent- or analyte-ion signals from a He-FAPA to a mixed-gas FAPA
16 are reported as relative signal differences. Additionally, it is well known that the background
17 level and structure (i.e. background ions formed/detected) in ADI-MS varies across instrument
18 type, local environment, sample probe/substrate used, etc. Therefore, any reported changes in
19 analyte-ion signal were background subtracted prior to taking the ratio. These studies were
20 conducted to broadly characterize shifts in molecular ionization and plasma processes with
21 different mixed-gas FAPA systems; a more detailed examination of S/N or S/B changes with
22 mixed-gas FAPA should be carried out for a particular application where analytes and required
23 limits-of-detection are well defined.

2.4. Emission Spectroscopy

Optical emission spectra were recorded in two locations with two different spectrometers. In one case, a fiber-coupled Avantes six channel spectrometer (Model: AVS-RACKMOUNT-USB2, Avantes Inc., Apeldoorn, Netherlands) capable of simultaneously measuring emission from 175 to 1100 nm was used to measure low-spectral resolution (*ca.* 0.1 nm) emission profiles from the FAPA source. Using this setup for inspecting the mixed-gas FAPA sources allowed emission to be collected from a spot of only *ca.* 50 μm in diameter. Translation of the FAPA under the collection optics enabled collection of spatially resolved emission. Emission spectra from the negative glow and the anode glow of the FAPA operated with helium, He:O₂, He:H₂, and He:N₂ can be found in Figures S1-S3 of the Supplemental Information.

Higher-resolution optical spectra were obtained to determine rotational temperatures within the plasmas. For these measurements, the plasma was imaged onto the entrance slit of a monochromator (model 2061, McPherson, Chelmsford, MA) with unit magnification. Matched achromats were used for collection of the N₂⁺ spectra, and matched plano-convex fused-silica lenses were used to collect the N₂ and OH spectra. In the latter case, the positions of the lenses were adjusted to compensate for chromatic aberration at the UV wavelengths. The entrance slit of the monochromator was 2 mm high and 20 μm wide. Because the negative glow was a thin layer very near the tip of the stainless-steel pin cathode, the discharge was positioned such that the upper 2 mm of the cathode was in the viewing region during collection from the negative glow. For collection of emission from the anode glow, the discharge was lowered by 7 mm, resulting in collection of radiation from the region immediately below the brass cap that served as the anode.

High-resolution spectra were obtained with a 1200 groove/mm grating installed on the 1-meter monochromator, which, combined with the 20- μ m entrance and exit slits, produced a nominal instrumental linewidth of 17 pm. Given the stigmatic optics of the monochromator and the relatively small slit height, the actual instrumental width is close to the nominal value. Radiation emerging from the exit slit of the monochromator impinged on a photomultiplier tube (R928, Hamamatsu, Hamamatsu City, Japan), and the resulting photocurrent was converted to a voltage with a commercial amplifier (Keithley, model 428, Beaverton, OR). Voltages were then digitized and stored for further analysis.

2.5. OH rotational temperature determination

The method used here to calculate rotational temperature is same as explained by Chan *et al.* [45] and Shelley *et al.* [43] Briefly, four emission lines in the Q₁ branch were used to construct a plot of $\ln(I\lambda/gA)$ versus E_{exc} , where λ , I, A, g, and E_{exc} are the emission wavelength, intensity of the line, the transition probability, the degeneracy of the excited energy level, and the energy of the excited state in eV, respectively [43, 45]. The slope of the linear plot obtained was equal to $(-1/kT_{rot})$, where k is the Boltzmann constant in eV K⁻¹ and T_{rot} is the rotational temperature in K [43, 45]. The relative slope error was used to calculate the relative standard deviation of calculated temperatures [43].

3. Result and discussion

3.1. He:O₂-FAPA source for mass spectrometry

Significant presence of molecular gases in the atomic plasmas (e.g., He, Ar, etc.) often quench reagent-ion formation, which results in little or no analyte signals. Therefore, most plasma-based ADI sources are operated with ultra-high purity gases; even then, ultra-high purity

helium (99.999%) contains small amounts of water (< 0.5 ppm) and other impurities. In addition, water molecules adsorbed on the inner wall of transfer lines gets swept into the discharge. It has been shown that these impurities can be effectively removed before the discharge chamber, but only with rather cumbersome approaches[46].

In this study, small fractions of molecular gases were controllably added to the helium glow discharge of a FAPA source to study the effects on plasma processes and ionization chemistries. Previously, our group has shown that the addition of a small fraction (0.1%, v/v) of O_2 enhances the protonated water cluster signal with corresponding enhancement in ion signals for small, polar analytes like acetone and methanol [44]. In contrast, compounds with aromatic rings undergo chemical modification in the He: O_2 -FAPA to produce pyrylium ions (*e.g.*, $[M-3H+O]^+$). Formation of pyrylium was confirmed with the help of exact mass measurement, tandem mass spectrometry, measurement of isotopically labelled species, and reaction of pyrylium ions formed in the FAPA afterglow with ammonia.

3.2. He:H₂-FAPA source for mass spectrometry

The effect of addition of molecular hydrogen gas (H_2) to He-FAPA was also studied. It was found that the addition of even a small amount of H_2 (0.17%, v/v) significantly quenched reagent-ion formation in the FAPA afterglow (*cf.* Figure 1). Specifically, signal for protonated water dimer (*i.e.* $[(H_2O)_2H]^+$) at m/z 37 decreased by more than three orders of magnitude. This decline in reagent ions is likely due to the quenching of excited helium atoms by collision with hydrogen molecules, effectively inhibiting the most common reagent-ion formation pathways in helium plasma sources [17, 29, 41]. Similar results were also observed by Heywood *et al.* [41] where collisionally assisted laser-induced fluorescence (LIF) was used to map helium metastable densities in the afterglow of a helium DBD. In the presence of 1% H_2 , helium metastable atoms

could not be detected in the afterglow plasma of the DBD. In spite of the disappearance of helium metastable atoms and reagent ions, enhanced ion signal was observed for a range of organic analytes [29].

Figure 1. Reagent-ion mass spectra obtained with A) He-FAPA and B) He:H₂-FAPA with 0.17% v/v H₂ (inset shows the zoomed in view of y-axis). Protonated acetone ion signal was due to the presence of acetone in ambient laboratory air.

In the case of the DC FAPA, though, introduction of H₂ to the helium discharge of FAPA led to a decrease in analyte-ion signal. Interestingly, though, analyte signal did not decrease to the same degree as that of the reagent ions. As can be seen in the Figure 1B, reagent-ion signal dropped by about two order of magnitude with H₂ addition, while aniline, naphthalene and anthracene ion signals decreased only by 3.1, 6.4, and 12.0 times, respectively (*cf.* Figure 2, Figure 3, Figure 4). This disproportionate change indicates that the He:H₂ system likely yielded a reagent species that could not be detected via mass spectrometry (e.g., below the low-mass cut-off of the instrument).

Another notable observation with the addition of H₂ to FAPA was that there was a noticeable shift in the ionization pathway of analytes with He:H₂-FAPA compared to He-FAPA. For aniline, the protonated molecular ion (MH⁺) was the only species detected with a He:H₂-FAPA, while He-FAPA yielded a molecular ion (M⁺) at 30% of the abundance of MH⁺ (*cf.* Figure 2). In another case, the molecular cation of naphthalene dominated the mass spectrum

1 when a He:H₂-FAPA was used, while MH⁺ was the base peak (with M⁺ at 50% abundance) with
2 He-FAPA (*cf.* Figure 3). Mass spectra of anthracene obtained with He:H₂-FAPA was dominated
3 by MH⁺ with a small amount of M⁺; these detected species also differ from the mass spectra
4 obtained with He-FAPA (*cf.* Figure 4). In all cases, oxidation of aromatic analytes, a common
5 occurrence in FAPA-MS [19, 20, 47], was significantly lower for a He:H₂-FAPA. Overall, a
6 He:H₂-FAPA produced chemically cleaner mass spectra albeit with lower total ion signal and
7 fewer analyte ion types.

8 The shift in ionization pathways and resulting analyte ions combined with the drastic
9 decrease in measured reagent-ion signals indicates formation of alternative reagents or reactive
10 species that cannot be detected with mass spectrometry. As was proposed by Wright *et al.* [29],
11 some examples of possible reagent species could include HeH⁺, H₃⁺, or even high-energy
12 photons [29, 41]. Both HeH⁺ and H₃⁺, at *m/z* 5 and 3, respectively, are too low of mass to be
13 detected by the MS instruments used here or by Farnsworth *et al.* [29, 40, 41]. Meanwhile, the
14 role and contribution of vacuum-ultraviolet photoionization with mixed-gas FAPA will be the
15 focus of a future publication. However, preliminary photoionization studies indicate that high-
16 energy photons are not responsible for the shift in ionization pathway [48].

17 Not surprisingly, naphthalene has a lower proton affinity than anthracene and aniline
18 (803 kJ/mol vs. 877 kJ/mol and 883 kJ/mol, respectively).[42] That would indicate that the
19 reagent responsible for protonating aniline and anthracene (but not naphthalene) has a proton
20 affinity between that of naphthalene and anthracene. The reagent-ion spectra of He:H₂-FAPA
21 (*cf.* Figure 1B) did not reveal any protonating reagents of abundance within the mass range that
22 could be recorded. Additionally, the HeH⁺ and H₃⁺ reagent ions proposed by Wright *et al.*[29]
23 might not be the cause of this disparity because both have proton affinities lower than all the

1 tested analytes by at least 380 kJ/mol.[42] They could not be ruled out entirely, though, because
2 that large of a proton-affinity difference between reagent and analyte can lead to significant
3 fragmentation of analyte ions beyond the mass range recorded in these studies.[49, 50]

4 Interestingly, acetone, which was detected only in the He-FAPA reagent-ion spectrum (as
5 MH^+), has a proton affinity of 812 kJ/mol,[42] so it could protonate aniline and anthracene, but
6 not naphthalene. The lack of protonated acetone signal in the He:H₂-FAPA reagent-ion
7 spectrum, though, raises questions about the likelihood of ambient acetone serving as the
8 protonating reagent. In any case, the shift in ionization pathways observed with He:H₂-FAPA is
9 unique enough to delve deeper into this in a follow-up study.

Figure 2. Mass spectra of aniline (C₆H₅NH₂, M = 93 u) obtained with A) He-FAPA and B) He:H₂-FAPA with 0.17% v/v H₂.

Figure 3. Mass spectra of naphthalene ($C_{10}H_{10}$, $M = 128$ u) obtained with A) He-FAPA and B) He: H_2 -FAPA (0.17% H_2).

Figure 4. Mass spectra of anthracene ($C_{14}H_{10}$, $M = 178$ u) obtained with A) He-FAPA and B) He: H_2 -FAPA (0.17% H_2).

3.3. He: N_2 -FAPA source for mass spectrometry

For plasma-based ADI-MS sources, N_2 plays an important role in afterglow chemistry and reagent-ion formation [17, 51]. To monitor the effect of N_2 gas on plasma processes and ionization chemistry within the FAPA source, small fractions of N_2 were precisely introduced to the He plasma. In the positive-ionization mode, presence of N_2 in the He-FAPA quenched reagent-ion signal, which led to lower analyte signals, similar to H_2 addition. In negative-ionization mode, however, reagent-ion signals for NO_2^- and NO_3^- increased with the addition of

1 0.2% N₂ (*cf.* Figure 5). Furthermore, the ratio of NO₃⁻ to NO₂⁻ increased from 2.3 to 177.2 with
2 0.2% N₂ in a He-FAPA.

3 Interestingly, ion signal for the high-explosive RDX significantly increased with He:N₂-
4 FAPA compared to He-FAPA. In plasma-based ADI, RDX and other nitrated compounds are
5 typically ionized via anion attachment with NO₂⁻ and NO₃⁻ [16, 19]. The [RDX+NO₃]⁻ signal
6 increased by more than seven times with addition of 0.2% N₂, while [RDX+NO₂]⁻ signal
7 remained nearly the same in the presence of He:N₂-FAPA (*cf.* Figure 6). Overall, He:N₂-FAPA
8 mass spectra for RDX produced better ion signal and were simpler.

9 This relative change in analyte-ion abundance was not as drastic as the shift in the ratio of
10 NO₃⁻ to NO₂⁻ from the reagent-ion spectra. A number of factors could possibly contribute to this
11 effect including the thermodynamics of the respective anion-attachment reactions (which has not
12 been well characterized) and concentration of NO₃⁻, NO₂⁻, and neutral RDX in the ionization
13 region. Further complicating matters, RDX is known to partially dissociate at elevated
14 temperatures to produce NO_x [52], which can be converted to NO₂⁻ and NO₃⁻ in plasmas.
15 However, Harper *et al.* [16] reported mass spectra for RDX with an LTP source using helium or
16 air as the discharge gas. They showed that mass spectra obtained with a helium LTP contained
17 [RDX+NO₂]⁻ at 40% of [RDX+NO₃]⁻, whereas an air-based LTP yielded [RDX+NO₂]⁻ that was
18 only 5% of the [RDX+NO₃]⁻ signal. Though LTP is a different plasma source entirely, their
19 results closely align with the findings of this study and indicate that this phenomenon is common
20 amongst many, or perhaps all, plasma-based ADI-MS sources. From these reports it is clear that
21 N₂-doped plasma sources enhance sensitivity and signal-to-noise (S/N), while producing simpler
22 spectra, for the detection of explosives, especially those that ionize via anion attachment (e.g.,
23 RDX and HMX).

Figure 5. Reagent ion mass spectra in negative-ionization mode obtained with A) He-FAPA and B) He: N_2 -FAPA with 0.2% N_2 .

Figure 6. Mass spectra of RDX ($\text{C}_3\text{H}_6\text{N}_6\text{O}_6$, $M = 222$ u) in negative-ionization mode obtained with A) He-FAPA and B) He: N_2 -FAPA with 0.2% N_2 .

3.4. Optical characterization of He: O_2 -FAPA

Mass-spectral data provides limited information on plasma processes and ionization chemistry and lacks the information on neutral, excited atoms and molecules that might play significant roles in desorption/ionization chemistry. To better understand the ionization

chemistry and plasma processes with mixed-gas FAPA, optical emission from excited species within the discharge was measured. Emission spectra obtained from a He:O₂-FAPA discharge showed that addition of O₂ decreases emission for most species, including He, N₂⁺, N₂, and OH, whereas atomic oxygen emission (at 777.3 nm) at the anode glow increased with O₂ addition up to 0.3% O₂ and decreased upon further O₂ addition. The decrease in He emission could be explained by quenching of excited He atoms by molecular oxygen.

At the negative glow (i.e. near the cathode), emission from every species except atomic oxygen dramatically decreased with the addition of only 0.1% O₂ (*cf.* Figure 7b). Interestingly, though, both He and N₂ emission intensity increased monotonically from that point with addition of more O₂ to the discharge. The increased intensity of these emission lines with more oxygen could be due to energy transfer with excited molecular oxygen species or higher gas temperatures in the plasma. No molecular oxygen emission bands were observed in the spectra, which indicates O₂* species were not abundant in the discharge and, as a result, are unlikely to be the cause of enhanced He and N₂ emission. In contrast, it is well known that gas temperatures of plasmas are higher when a molecular discharge gas is introduced, due to the introduction of vibrational energy levels. In fact, above 0.3% O₂ in the FAPA plasma, the cathode became red hot and the discharge appeared to transition towards an arc. Visually, the positive column contracted radially and went from a purple/pink glow to a white filament; all indications of a glow-to-arc transitional discharge. In addition, a plot of the FAPA discharge power as a function of O₂ composition (*cf.* Figure S4a) shows a notable change in slope starting at *ca.* 0.15% O₂. Transition from a glow to an arc discharge is commonly characterized by a strong negative dynamic resistance. Because the FAPA discharge current was held constant in this case, the negative dynamic resistance of an arc-like discharge is manifested as a decline in the positive

slope of the discharge power (i.e. the derivative of power with respect to gas composition) as is observed in Figure S4a. Therefore, it is likely that the increase in emission intensity for He, O, and N₂ at larger O₂ fractions is due to a significant shift in the electric field distribution and possibly also the overall increased discharge power (*cf.* Figure S4) as it transitioned from a stable glow discharge to an arc.

It might seem perhaps surprising that N₂⁺ emission did not exhibit the same trend as other emitting species at higher O₂ compositions. However, ionization and excitation in a He FAPA discharge is very non-thermal, particularly for N₂ and N₂⁺, [37, 53] due to the large contributions of charge transfer and Penning ionization. Addition of oxygen gas to this system disrupts some of the non-thermal ionization pathways, which would lower ion densities, including excited N₂⁺. In addition, N₂ emission did not decrease to the same level as N₂⁺, OH, and H_α emission. Although the FAPA consists of a non-equilibrium plasma, decrement in N₂⁺ emission might have shifted the steady state towards N₂.

Figure 7. Relative emission intensity of NO, OH, N₂, N₂⁺, O, and He from anode and negative glow with respect to O₂ composition on He discharge of FAPA source.

Overall, the optical emission results from He:O₂ FAPA showed an abrupt change in emission characteristics with 0.1% oxygen and relatively small change with further O₂ addition.

1 These findings corroborate the mass-spectral characterization where the biggest impact on
2 reagent-ion signal was also observed with 0.1% O₂ [44].

3 Gas-kinetic temperature is an important parameter for plasma-based ADI sources
4 as gas temperature plays vital role in desorption of analytes. Approximate gas-kinetic
5 temperature can be obtained by calculating rotational temperatures (T_{rot}) from the rovibronic
6 emission of excited OH. Here, the OH rotational temperature was calculated for both the anode
7 and negative glow as a function of O₂ composition (*cf.* Figure 8A). It should be noted that the
8 error bars presented in Figure 8 are the associated errors in fitting the slope of the Boltzmann
9 plots. The error bars are results of non-linearity of the data points which could be caused by
10 imperfect transition probability or slight dis-equilibrium in the distribution of the OH rotational
11 levels. Although at first glance, one could conclude that the OH rotational temperatures with gas
12 composition (shown in Figure 8) are statistically insignificant based on the presented errors (only
13 He vs. 1% N₂ is statistically significant for $p < 0.05$). The observed trends are clear and
14 consistent, particularly for the anode glow, because the changes in temperature appear to be
15 systematic and not random. In the negative glow, the rotational temperature remained
16 approximately constant over the range examined. At the anode glow, the OH rotational
17 temperature increased monotonically with O₂ composition. Thiagarajan *et al.* [54] and Motret *et*
18 *al.* [55] also observed a rise in rotational temperature with molecular gas composition in helium
19 and argon plasmas. Because of the presence of ro-vibrational levels in a molecule, heat capacities
20 of molecular gases are higher than those of monoatomic gases. The addition of a molecular gas
21 to a glow discharge typically changes the distribution of the electric field (e.g., increasing the
22 field near the cathode) [56, 57]. As such, the measured rotational temperature increases.

Figure 8. OH rotational temperatures estimated from rotational emission band from anode and negative glow with respect to A) O_2 composition, B) H_2 composition, and C) N_2 composition. As a reminder, error bars represent one standard deviation in the temperature determination based on the error in the slope of the fit from the Boltzmann plots.

3.5. Optical characterization of He: H_2 -FAPA

With He: H_2 -FAPA, a monotonic decrease in He emission intensity was observed in both the negative glow and the anode glow with increasing H_2 composition (*cf.* Figure 9). Emission from O and OH decreased by more than 70% when 0.17% H_2 was added and declined further with more H_2 at both the anode and cathode. In the anode glow, emission from N_2^+ decreased by more than ~40% upon H_2 addition and declined further with more H_2 in the discharge, while it decreased by ~35% on 0.17% and remains approximately same even with further H_2 addition.

Hydrogen alpha and beta emission lines both increased by about five-fold in the anode glow when any H_2 was added to the discharge. However, the opposite trend for hydrogen atom emission was observed in the negative glow (i.e. a decreased of *ca.* 40%). Currently, the reason for H-emission decrement in the negative glow is not known. With H_2 addition, most emission intensity changed significantly with respect to the He-FAPA on 0.17% addition for almost all species and effect was little to none on further addition. The emission data show that addition of H_2 quenched excited helium atoms and N_2^+ . Both of those species are known to be important reactants in the production of protonated water cluster reagent ions. These findings correlate well

1 with the mass-spectrometric observation of decreased reagent ion signals in the presence of
2 hydrogen (*cf.* Figure 1).

3 Interestingly, N₂ emission increased with H₂ composition at both the anode and cathode.
4 The added molecular gas serves as an energy sink for Penning and charge-transfer ionization, a
5 major contributor to the formation and excitation of N₂⁺ due to the large collision cross sections
6 with excited/ionized helium species.[37, 53] The molecular gas depletes excited helium species
7 and limits direct production of N₂^{+*} from them. Meanwhile, excited N₂ production was enhanced
8 relative to N₂^{+*} due to interactions with vibronically excited or ionized H₂. These
9 excited/ionized H₂-related species would be intermediates in the excitation of N₂. In contrast,
10 from an energetic point of view, ionization of N₂ from H₂⁺ is thermodynamically unfavorable.

11 In fact, this process is at least partially confirmed in the reagent-ion mass spectra where
12 protonated water cluster signal declined by more than three orders of magnitude. In helium
13 plasma ionization sources, N₂⁺ is a primary reagent in the formation of [(H₂O)_nH]⁺. So, such a
14 dramatic decline in these reagent ions indicates a major loss in N₂⁺ formation.

Figure 9. Relative emission intensity of NO, OH, N₂, N₂⁺, O, He, and H from anode and negative glow with respect to H₂ composition on He discharge of FAPA source.

Addition of H₂ to He-FAPA led to a slight increase in the rotational temperature at both the negative and anode glows (*cf.* Figure 8). The monotonic patterns for rotational temperatures in both the anode glow and the negative glow on H₂ addition were more consistent compared to O₂ or N₂ addition. It was also visually observed that the discharge is still quite stable with H₂ addition, in contrast to what was observed when O₂ was added at 0.3%. Again, the overall slight increment in temperature with H₂ addition might be due to availability of vibrational levels to impart energy into.

3.6. Optical characterization of He:N₂-FAPA

Mass spectrometry data showed that addition of even small fraction (0.2%) of N₂ to the He plasma of the FAPA source decreased the reagent-ion signal in the positive-ionization mode. Similar to H₂ addition, N₂ also quenched the excited helium atoms, but the effect was less dramatic compared to the addition of O₂ and H₂ (*cf.* Figure 10). Unlike He:O₂ and He:H₂-FAPA, NO emission increased with N₂ addition, which could be related to the enhancement on NO₃⁻ signal observed with mass spectrometry. To extract a more detailed relationship between these

excited atoms and molecules with the ions observed with mass spectrometer, a thorough computational study is needed [58].

Figure 10. Relative emission intensity of NO, OH, N₂, N₂⁺, O, He, and H from anode and negative glow with respect to N₂ composition on He discharge of FAPA source.

Rotational temperature of OH slightly increased at both anode and cathode also on addition of N₂ and the increment pattern seemed smooth except at negative glow with 0.75% N₂ addition. The negative glow at pin cathode is very thin and the glow changes in coverage and uniformity occasionally. The irregular rotational temperature data obtained at 0.75% N₂ addition could be due to such change in coverage of negative glow. For the anode glow, OH rotational temperature increased by approximately 190 K, 100 K, and 140 K on addition of 1.00% O₂, H₂, and N₂, respectively.

4. Conclusions

Addition of molecular gases to He-FAPA resulted unique plasma chemistries as observed with mass spectrometry. The presence of a small fraction of oxygen in a He-FAPA increased protonated water cluster signal and also produced an enhancement in analyte-ion signal small polar analytes such as acetone and methanol, but, compounds with aromatic rings underwent significant chemical modification to produce pyrylium ions.[44] Addition of hydrogen produced

chemically cleaner mass spectra of the analytes tested albeit at lower total signals. Nitrogen addition increased the NO_3^- ion signal and, correspondingly, $[\text{RDX}+\text{NO}_3]^-$ was also enhanced in negative-ionization mode. Optical characterization of mixed-gas FAPA suggested that addition of molecular gas to He-FAPA significantly quenches the metastable helium atoms that are mainly responsible for the formation of reagent ions in the afterglow of FAPA. This study sheds light on how presence of molecular gasses on helium plasma of FAPA source affects the plasma processes and ionization chemistries. Addition of molecular gases to a He-FAPA can improve detection capabilities (*e.g.*, increased sensitivity, better S/N, and/or decreased spectral complexity) as well as enable selective analyte detection. However, it is clear that careful control of the gas composition is necessary to reap these benefits as well as maintain a stable glow discharge.

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Supplemental Information for
Optical and Mass-Spectral Characterization of Mixed-Gas
Flowing Atmospheric-Pressure Afterglow Sources

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Emission Spectra of Mixed-gas FAPA

Figure S1. Optical emission spectra from the negative-glow (a, b) and anode-glow (c, d) regions of the FAPA source with only helium (a, c) and 0.1% O_2 in helium (b, d). Peaks labelled with a star (*) are helium emission lines. Note the significantly different scale in D.

Figure S2. Optical emission spectra from the negative-glow (a, b) and anode-glow (c, d) regions of the FAPA source with only helium (a, c) and 0.15% H₂ in helium (b, d). Peaks labelled with a star (*) are helium emission lines.

Figure S3. Optical emission spectra from the negative-glow (a, b) and anode-glow (c, d) regions of the FAPA source with only helium (a, c) and 0.2% N₂ in helium (b, d). Peaks labelled with a star (*) are helium emission lines.

Discharge Power with Mixed-gas Conditions

Figure S4. FAPA discharge power as a function of percent composition of O₂ (A), H₂ (B), and N₂ (C) at a discharge current of 20 mA. Note that the maximum O₂ composition that could be obtained with the flow controllers used was 0.5%.

As can be seen above in Figure S2, the FAPA discharge voltage (and power) increased monotonically with O₂ and N₂ composition. Oxygen addition led to a greater change in discharge power with an increase of 25% when 0.5% O₂ was added to the discharge, compared to an 18% power increase for the same amount of N₂ in the discharge. Interestingly, addition of H₂ to the helium FAPA required lower voltages and powers to sustain the discharge. As H₂ composition was elevated above 0.3%, the discharge voltage and power began to rise. The biggest change in discharge voltage and power for H₂ addition, compared to only helium, was -10% at an H₂ composition of 0.3%.