A Demonstration of Broadband Cavity-Enhanced Absorption Spectroscopy at Deep-Ultraviolet Wavelengths: Application to Sensitive Real-Time Detection of the Aromatic Pollutants Benzene, Toluene, and Xylene

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ABSTRACT: Benzene, toluene, and xylene (BTX) are serious air pollutants emitted by the chemical industry. Real-time monitoring of these air pollutants would be a valuable tool to regulate emissions of these compounds and reduce the harm they cause to human health. Here, we demonstrate the first detection of BTX using incoherent broadband cavity-enhanced absorption spectroscopy (IBBCEAS). The instrument was operated in the deep-ultraviolet spectral region between 252 and 286 nm, where aromatic compounds have intense \( \pi \to \pi^* \) absorption bands. The mirror reflectivity was calibrated by two methods and exceeded 99.63% at 266 nm. At an integration time of 60 s, the 1\( \sigma \) measurement sensitivities were estimated to be 7.2 ppbv for benzene, 21.9 ppbv for toluene, 10.2 ppbv for \(-xylene, and 4.8 ppbv for \(p\)-xylene, respectively. The absorption cross sections of BTX were measured in this work with an uncertainty of 10.0% at a resolution of 0.74 nm. The absorption cross sections reported in this work were in good agreement with those from earlier studies after accounting for differences in spectral resolution. To demonstrate the ability of the instrument to quantify complex mixtures, the concentrations of \(-xylene and \(p\)-xylene have been retrieved under five different mixing ratios. Instrumental improvements and measurements strategies for use in different applications are discussed.

1. INTRODUCTION

Benzene, toluene, and xylene (BTX) are an important class of volatile organic compounds in the atmosphere that primarily enter the atmosphere from vehicles, biomass burning, solvent use, and the petrochemical industry. Benzene is a known carcinogen and increases the risk of other illnesses. It is a notorious cause of bone marrow failure. The primary reaction pathways for monocyclic aromatics are reaction with hydroxyl radicals to form phenols or degradation to carbonyls, such as glyoxal. Oxidation of BTX also produces secondary organic aerosols and ozone, thereby aggravating air pollution and exacerbating impacts on public health.

Analytical methods for quantifying BTX in the air usually include absorption traps and subsequent separation by gas chromatography with detection by flame ionization, photoionization, or mass chromatography. Measurement time resolution is usually about 30–60 min per sample. In recent years in situ optical methods, such as long path differential optical absorption spectroscopy (LP-DOAS), have also been applied. Unlike other methods, LP-DOAS uses a long physical path (typically 500–1000 m) and measures the path-integrated concentration over this distance. However, the correlation between the two types of methods is poor because of the different spatial scales; DOAS usually reports higher values than in situ methods. Incoherent broadband cavity-enhanced absorption spectroscopy (IBBCEAS) has been applied to many gaseous molecules since it was first proposed by Fiedler et al., mostly at visible wavelengths. Optical cavity measurements in the UV range are challenging for several reasons: (1) CCD detectors have relatively low quantum efficiency in the UV, and light sources are less intense in this region. (2) Losses at optical cavity mirror surfaces by scattering and absorption are much higher than at longer wavelengths. (3) System sensitivity is limited by Rayleigh scattering at short wavelengths. (4) Increasing Mie scattering from particles, and strong ozone absorption is a...
challenge for atmospheric samples. As a result of the high inherent losses in the sample gas and the lower mirror reflectivity, the extremely long effective light pathlengths attained by optical cavity instruments at visible and near-infrared wavelengths are not feasible below 300 nm. Nevertheless, the ability to measure absorption and scattering at deep-UV wavelengths with high sensitivity would be valuable for fundamental research, monitoring of ambient air quality, and industrial emissions, and other uses.

To date, there have been few applications of optical cavity methods below 300 nm. Iyaksov and coworkers used cavity ring-down spectroscopy with a dye laser to measure Rayleigh scattering cross sections of N₂, CH₄, and SF₆ between 198 and 270 nm. Prior work with broadband cavity instruments includes a deep-UV CEAS instrument using a mercury atomic emission lamp (254 nm) to measure gaseous mercury and ozone with detection limits of 8.1 and 8.4 ppbv, respectively, in 10 s acquisition time, an IBBCAES system combining a laser-driven light source (LDLS) and LED to measure acetone between 272 and 292 nm with an LOD of 8 ppmv in 1 s acquisition time, and a deep UV-LED system at 280 nm that achieves an LOD of 3.7 ppbv with a FWHM of 11 nm, and the operation status was 5.3 V forward bias.

The aim of this work is to build on these prior studies and demonstrate that IBBCAES is a useful approach for highly sensitive measurements of sample extinction at deep-UV wavelengths. We describe an LED IBBCAES spectrometer operating in the 252–286 nm wavelength range, which achieves an LOD of 3.7 × 10⁻⁷ cm⁻¹ with a 60 s acquisition time, a sensitivity high enough to be valuable for studying many compounds that absorb strongly at these wavelengths. We demonstrate that this instrument can be used to make sensitive, real-time measurements of aromatic compounds, specifically the important environmental pollutants BTX, and has potential applications in laboratory research, emissions monitoring, and other combined applications.

2. EXPERIMENTAL SECTION

2.1. Instrument Setup. The IBBCAES approach was first described by Fiedler et al. and has been applied in many studies. In this work, the deep-UV IBBCAES instrument comprised three subsystems: the light source, optical cavity, and detection module (Figure 1a). The light source was a 255 nm LED (HSE255H-M807X, Hasunopio, China) with an FWHM of 11 nm, and the operation status was 5.3 V forward voltage and 0.17 A current. The LED was mounted on a thermostat and driven by a constant current source to minimize current and temperature fluctuations. The thermostat was stabilized to 15 ± 0.1 °C using a PID controller.

The light emitted from the LED was collected and focused by a lens (f = 35 cm) into a high-finesse optical cavity formed by a pair of high-reflection (HR) mirrors (Layertec GmbH). The reflectivity of the HR mirror between 250 and 280 nm was specified by the manufacturer to be greater than 0.995. The cavity mirrors were separated by 96.7 ± 0.02 cm. Light transmitted through the cavity was focused by another lens (f = 75 cm), filtered by a short-pass filter (Semrock FF01-300/ SP-25; transmission >70% between 255 and 290 nm), and coupled into a quartz fiber bundle. The fiber bundle was 1.5 m long and consisted of 20 × 200 µm core fibers (Figure 1a). The fibers were vertically arranged at the entrance slit of an imaging spectrograph to optimize light coupling and maximize the signal.

The detection module was a grating spectrograph (Andor SR-303i-B, Oxford Instruments) with a CCD detector (Andor DH343T-18 U-E3, Oxford instruments) cooled to −25.0 °C to minimize the dark current. The detector’s Micro-Channel Plate (MCP) image intensifier can be varied to amplify the signal intensity. The spectrograph had a 1200 L mm⁻¹ diffraction grating (300 nm blaze) and covered the range between 252 and 286 nm. The wavelength resolution was 0.74 nm, based on a fit to the 253.65 nm emission line of a commercial mercury lamp (Hg-I, Ocean Optics).

2.2. Sample Handling. Samples were introduced in a quartz flow tube (25 mm inner diameter) with a separation of 69.7 cm between the inlet and outlet (Figure 1b). The concentration of benzene, toluene, m-xylene, and p-xylene was generated by mixing a flow of N₂ (>99.9999% purity) with the output of a gas cylinder comprising 1.0 ± 0.02 ppmv for benzene, 1.02 ± 0.02 ppmv for toluene, 1.00 ± 0.02 ppmv for m-xylene, and 1.02 ± 0.02 ppmv for p-xylene (Dalain Special Gases). Flow rates of the N₂ and aromatic gas mixture streams were controlled by mass flow controllers (MFC). The flow rates of BTX gases were controlled at 1000 sccm, and the N₂ flow rate was controlled at 666, 250, and 0 sccm, respectively. Thus, the BTX gas was diluted to 600, 800, and 1000 ppbv at about 298 ± 1 K and 101 ± 1 kPa. One hand of the cavity was connected to a buffer bottle, from which sample was drawn into the cavity at a flow rate of 800 sccm (controlled by an MFC) by a pump. Excess gas in the buffer bottle was discharged to the fume hood. MFC were calibrated by a flow meter (Gilibrator-2, Sensidyne).

2.3. HR-Mirror Calibration. In IBBCAES systems, the extinction coefficient εext(λ) of the gas sample in the cavity is related to the measured properties and system parameters through the following relation:

\[ ε_{ext}(λ) = -\left(\frac{I_0(λ)}{I(λ)} - 1\right)\left(1 - \frac{R(λ)}{d}\right) + α_{Rayl}(λ) \]  

Here, instrument parameters are the cavity length d, the mirror reflectivity R(λ), the measured reference and sample intensity spectra (I₀(λ) and I(λ), respectively), and the extinction due to the Rayleigh scattering αRayl(λ). The mirror
reflectivity $R(\lambda)$ is essential for quantitative results and must be calibrated. In previous work, $R(\lambda)$ has been determined using different methods based on a known extinction in the cavity. There were also many other different calibration approaches. In this study, we used two approaches to determine the mirror reflectivity, $R(\lambda)$. The first approach used a known gas absorption of SO$_2$ to determine the reflectivity, $R_{\text{SO}_2}(\lambda)$. A 1005 ppm SO$_2$ gas mixture (in N$_2$) was further diluted in a stream of pure nitrogen to 600 and 1000 ppbv with a multigas calibrator (164i, Thermal Fisher). The reflectivity $R_{\text{SO}_2}(\lambda)$ can be determined from:

$$R_{\text{SO}_2}(\lambda) = 1 - a \left( \frac{\sigma_{\text{SO}_2}(\lambda) n_{\text{SO}_2}}{I_{\text{SO}_2}(\lambda)/I_{\text{SO}_2}(\lambda) - 1} \right)$$

where $I_{\text{N}_2}(\lambda)$ and $I_{\text{He}}(\lambda)$ are the measured light intensity when the cavity was filled with nitrogen and a known number density ($n_{\text{SO}_2}$) of SO$_2$, respectively, and $\sigma_{\text{SO}_2}(\lambda)$ is the literature absorption cross section of SO$_2$ convolved to our spectrograph instrument function. This approach gave an uncertainty in $R_{\text{SO}_2}(\lambda)$ of about 4%, which is dominated by the uncertainty in the SO$_2$ cross section.

The second approach used the difference in Rayleigh scattering of two pure gases for another determination of the mirror reflectivity, $R_{\text{Rayl}}(\lambda)$. Pure nitrogen (>$99.999\%$) and pure helium (>$99.999\%$) were used to determine $R_{\text{Rayl}}(\lambda)$ according to eq 3:

$$R_{\text{Rayl}}(\lambda) = 1 - d \left( \frac{I_{\text{N}_2}(\lambda) n_{\text{N}_2} \sigma_{\text{Rayl,N}_2}(\lambda) - I_{\text{He}}(\lambda) n_{\text{He}} \sigma_{\text{Rayl,He}}(\lambda)}{I_{\text{N}_2}(\lambda) - I_{\text{He}}(\lambda)} \right)$$

where $I_{\text{N}_2}(\lambda)$ and $I_{\text{He}}(\lambda)$ represent the measured intensities when either nitrogen or helium, respectively, is in the cavity and $\sigma_{\text{Rayl,N}_2}(\lambda)$ and $\sigma_{\text{Rayl,He}}(\lambda)$ are the Rayleigh scattering cross sections of nitrogen and helium, respectively. The uncertainty of $R_{\text{Rayl}}(\lambda)$ is about 5% and mainly determined by the uncertainty in the scattering cross section of N$_2$ reported by Sneep and Ubachs.

The intensity of the cavity at 1 s integration time is shown in Figure 2a. A wide spectral range from 250 to 295 can be achieved. As shown in Figure 2b, the reflectivity of the mirror exceeded 99.63% at its center near 266 nm. The averaged precision was fundamentally limited by low light levels and longer averaging implies that more photons are measured. The system gain setting also influenced instrument precision for a given measurement time, with a higher gain producing better precision for a given integration time. The maximum precision of the instrument was $2.3 \times 10^{-7}$ cm$^{-1}$ without the MCP image intensifier (Gain = 0); the precision improved to $1.1 \times 10^{-7}$ cm$^{-1}$ using the MCP image intensifier with Gain = 1800. The retrieval precision of the DUV-IBBCEAS system to BTX over a 60 s acquisition time was estimated by fitting the zero air spectrum to the BTX absorption cross sections reported by Fally et al.

3. RESULTS AND DISCUSSION

3.1. System Performance. The optimal integration time for an instrument is commonly determined by calculating the Allan deviation:

$$\sigma^2_{\alpha}(t) = \frac{1}{2(M-2)} \sum_{i=1}^{M-2} [\alpha_{i+1}(t) - \alpha_i(t)]^2$$

where $t$ is the integration time, $M$ is the number of time series, and $\alpha_i(t)$ is the absorption coefficient in each subset from $i = 1$ to $i = M - 2$. The Allan deviation $\sigma_{\alpha}(t)$ is the square root of $\sigma^2_{\alpha}(t)$. A total of 20,000 reference spectra with 1 s exposure time were continuously measured over 5 h while the cavity was filled with pure nitrogen (>99.999%).

System sensitivity increased with integration time up to 1000 s (Figure 3). This result is not surprising because the system sensitivity was fundamentally limited by low light levels and longer averaging implies that more photons are measured. The system gain setting also influenced instrument precision for a given measurement time, with a higher gain producing better precision for a given integration time. The maximum precision of the instrument was $2.3 \times 10^{-7}$ cm$^{-1}$ without the MCP image intensifier (Gain = 0); the precision improved to $1.1 \times 10^{-7}$ cm$^{-1}$ using the MCP image intensifier with Gain = 1800. The retrieval precision of the DUV-IBBCEAS system to BTX over a 60 s acquisition time was estimated by fitting the zero air spectrum to the BTX absorption cross sections reported by Fally et al.

A histogram analysis of 600 zero measurements is
cross sections of benzene, toluene, m-xylene, and p-xylene at room temperature and at different pressures and resolutions.

### 3.2.1. Benzene

The absorption coefficients were measured over a 30 min integration time. The absorption coefficients of benzene at 600, 800, and 1000 ppbv obtained in this work are shown in Figure S1(a). Figure 4a shows that the absorption coefficient at 252.96 nm is linearly correlated with concentration ($R^2 > 0.999$). The intercept (6.88 $\times$ 10$^{-3}$ cm$^{-1}$) and its standard deviation (1.95 $\times$ 10$^{-3}$ cm$^{-1}$) are both small.

The UV absorption of benzene is attributed to the $S_1(1B_{2u}) \rightarrow S_0(1A_{1g})$ electronic transition. $^{36}$ Narrow vibrational transitions dominate in this range, and spectral resolution strongly affects the measured spectrum. The absorption cross section of benzene measured in this work is compared against prior work in Figure 4b. Two major absorption peaks are apparent in our measurement window. The position of the absorption peaks reported in our study is consistent with the data of Fally et al.$^{36,39}$, whereas the spectrum reported by Olive$^{40}$ is shifted $-0.2$ nm compared to others. For highly structured spectral features, the instrument resolution has a large effect, and high-intensity structures are apparent in the high-resolution measurements of Fally et al.$^{36}$ These features are smoothed out at coarser resolution. Indeed, the resolution of our instrument is a factor of 4 or more lower than other measurements. The absorption cross section of recent literature convolved to this work’s resolution is shown in Figure S2.

The absorption cross-sections reported in this work were the mean value obtained by averaging the absorption cross-sections of three concentrations (600, 800, and 1000 ppbv) and were in good agreement with cross sections obtained by linear regression analysis.

### 3.2.2. Toluene

The agreement between the absorption cross-sections of Etzkorn et al.$^{39}$, Koban et al.$^{41}$, Olive$^{40}$, and Trost et al.$^{38}$ is generally good, while the cross section reported by Fally et al.$^{36}$ is lower than other studies.

### 3.2.3. m-Xylene

The absorption coefficients of m-xylene at 600, 800, and 1000 ppbv obtained in this work are shown in Figure S1(c). The three absorption coefficients at 271 nm are compared in Figure 6a and also highly linear with concentration ($R^2 > 0.999$) with a small y-intercept 5.78 $\times$ 10$^{-8}$ cm$^{-1}$ (standard deviation of 8.22 $\times$ 10$^{-8}$ cm$^{-1}$).

The absorption cross-section of m-xylene measured in this work is shown in Figure 6b, together with the spectra of Bolovinos et al.$^{32}$, Trost et al.$^{38}$, Etzkorn et al.$^{39}$, Olive$^{40}$, and Fally et al.$^{36}$. The agreement between our cross section and those of Etzkorn et al.$^{39}$, Koban et al.$^{41}$, and Olive$^{40}$ is generally good, while the cross section reported by Fally et al.$^{36}$ is lower than other studies.

### 3.2.4. p-Xylene

The agreement between the absorption cross-sections of Etzkorn et al.$^{39}$, Koban et al.$^{41}$, Olive$^{40}$, and Fally et al.$^{36}$ is generally good, while the cross section reported by Fally et al.$^{36}$ is lower than other studies.
3.2.4. p-Xylene. The absorption coefficients of p-xylene at 600, 800, and 1000 ppbv obtained in this work are shown in Figure S1(d), and the three absorption coefficients at 273 nm are compared in Figure 7a. The absorption was linear with concentration ($R^2 > 0.999$) with a small y-intercept $1.82 \times 10^{-7}$ cm$^{-1}$ with a standard deviation of $4.17 \times 10^{-7}$ cm$^{-1}$.

Figure 7. (a) Dependence of the p-xylene absorption coefficient on the different concentrations at 272.79 nm. The correlation coefficient of the linear regression is $R^2 > 0.999$. (b) p-Xylene absorption cross section from this work and recent literature spectrum.\cite{36,38,40,42}

The absorption cross section of p-xylene measured in this work is shown in Figure 7b, together with the spectra of Bolovinos et al.,\cite{40} Trost et al.,\cite{38} Etzkorn et al.,\cite{39} Olive,\cite{40} and Fally et al.\cite{42} The agreement between the spectrum in this work, and the spectra reported by literature are good over this region. The spectrum reported by Trost et al.\cite{38} was marginally higher than other values.

3.2.5. Uncertainty of Cross Section. The uncertainty in our absorption cross-section measurements was estimated using standard uncertainty propagation. The uncertainty of extinction coefficient $\varepsilon$, can be calculated by eq 5:\cite{16}

$$\Delta \varepsilon = \frac{\partial \varepsilon}{\partial d} \cdot \Delta d^2 + \frac{\partial \varepsilon}{\partial (1 - R)} \cdot \Delta (1 - R)^2 + \frac{\partial \varepsilon}{\partial \delta} \cdot \Delta \delta^2 + \frac{\partial \varepsilon}{\partial (1 - I)} \cdot \Delta (1 - I)^2$$

$$= \left( \frac{\Delta d}{d} \right)^2 + \left( \frac{\Delta (1 - R)}{1 - R} \right)^2 + \left( \frac{\Delta \delta}{\delta} \right)^2 + \left( \frac{\Delta (1 - I)}{1 - I} \right)^2$$

$$= \varepsilon \left( \frac{\Delta d}{d} \right)^2 + \varepsilon \left( \frac{\Delta (1 - R)}{1 - R} \right)^2 + \varepsilon \left( \frac{\Delta \delta}{\delta} \right)^2 + \varepsilon \left( \frac{\Delta (1 - I)}{1 - I} \right)^2$$

(5)

where $\Delta d$, $\Delta (1 - R)$, and $\Delta \delta$ are the uncertainties in the cavity length, mirror reflectivity, and spectral intensity, respectively. The relative uncertainties in eq 6 are 1% for $d$, 6.4% for $1 - R$ (according to the uncertainty of $R$), and 3.5% for intensity fluctuations at a 1 min integration time. The overall uncertainty in the extinction measurement is therefore around 9.8% and is dominated by the uncertainty in the mirror reflectivity.

The uncertainty in the absorption cross section must also account for the uncertainty in the concentration of each species ($\Delta N$):

$$\left( \frac{\Delta \sigma}{\sigma} \right)^2 = \left( \frac{\Delta \varepsilon}{\varepsilon} \right)^2 + \left( \Delta N \right)^2$$

(6)

The uncertainties in the concentrations of gas cylinder are 2% for benzene, toluene, m-xylene, and p-xylene according to the manufacturer. The uncertainty in flowrate is 0.35% F.S. according to the manufacturer and calibrated by a flow meter (Gilibrator-2, Sensidyne). And the combined uncertainty in absorption cross sections is thus 10.0% for all four gases at a resolution of 0.74 nm.

3.3. Measurement of Xylene Isomers. The least-squares spectral fitting method was used to demonstrate that deep-UV spectral analysis could be used to quantify the concentrations of different xylene isomers at the same time. The optimized spectral fitting window was from 258 to 278 nm. A third-order polynomial was applied to fit the shape of the background spectrum, which was mainly produced by the spectral dependence of the mirror reflectivity and from sample scattering. The reported absorption cross sections of xylene in this work were used to retrieve the concentration of xylene isomers. As shown in Figure 8a, five sets of m-xylene/p-xylene mixtures diluted by standard gas cylinders were measured with an integration time of 60 s. During the experiment, the fractional flow rate of p-xylene was reduced in a stepwise manner (80, 60, 50, 40, and 20%); the fractional flow rate of m-xylene was increased sequentially from 20, 40, 50, 60, and 80%. The uncertainty of retrieved concentration was dominated by absorption cross section and reflectivity.

Figure 8b,c,d shows an example of the spectral fitting of a spectrum of the m-xylene and p-xylene mixture measured 83 min from the start of the experiment. The retrieved mixing ratios of m-xylene and p-xylene were 493 ± 12 ppbv and 505 ±
5 ppbv, respectively. The corresponding fitting residual is in the range of $\pm 7.6 \times 10^{-7}$ cm$^{-1}$.

3.4. Discussion. The instrument presented in this work represents an important advance in the application of broadband optical cavity techniques to deep-UV wavelengths. We applied our system to quantify the important anthropogenic environmental pollutants BTX. Nevertheless, we emphasize that the method has general application to other compounds that absorb in this region, as well as to particle extinction measurements. This work therefore has broad applicability to a range of applications and research fields, whether for air quality or emissions monitoring, pure or applied laboratory research, or other technological applications. In the following, we discuss considerations around the BTX measurements presented in this work, propose instrumental improvements and measurement strategies, and assess their use in different applications.

The $1\sigma$ measurement precisions of the DUV-IBBCEAS system over a 60 s acquisition time (7.2 ppbv ($1\sigma$) for benzene, 21.9 ppbv ($1\sigma$) for toluene, 10.2 ppbv ($1\sigma$) for m-xylene and 4.8 ppbv ($1\sigma$) for p-xylene) are already sufficient to be relevant to a range of applications, including fence-line and continuous emissions monitoring of these species. It also provides a potentially useful tool for analytical chemistry in combination with pre-concentration or chromatographic approaches. These ideas will be explored in future work to monitor atmospheric BTX.

Several strategies are possible to further improve the system sensitivity. Our spectrometer used a relatively low-resolution configuration to increase light throughput owing to the challenges of working with low light levels in the deep UV. Although there is a trade-off between resolution and optical throughput, higher resolution spectra would be advantageous for capturing highly structured spectral features (for benzene, in particular) with improved sensitivity and selectivity.

Light source intensity is a major technical challenge in this spectral region. The advantages of deep-UV LEDs are that they are relatively inexpensive light sources, produce stable emission intensities with careful control of temperature and current and do not need extensive spectral filtering. Other light sources with deep-UV output could prove advantageous for some applications. LDLS or Xe flashlamps have relatively high-intensity DUV output and could be useful alternative sources but would require stringent filtering to remove unwanted wavelengths from the optical system. Deuterium lamps would be challenging to use at these wavelengths because they are not particularly bright.

For applications where lower absorption sensitivities would suffice, light throughput could be raised by using lower reflectivity mirrors in the optical cavity, resulting in greater throughput and higher time resolution, at the cost of a shorter effective light path length and lower sensitivity.

In addition to the technological challenges described above, absorption by ozone is also at its maximum in this spectral region and could prove challenging for working with ambient air samples. Appreciable absorption by O$_3$ in a sample would reduce the overall instrument sensitivity. An O$_3$ denuder in the inlet line could circumvent this issue, albeit at the cost of greater system complexity. Alternatively, sample preconcentration could be used to attain much higher sensitivities and avoid some interferences while retaining almost real-time measurement capability. We will explore the application of the DUV-IBBCEAS system to the measurement of ozone concentrations in future work.

The influence of other atmospheric constituents on system performance should also be considered. The common atmospheric pollutant NO$_2$ has an absorption cross section between 250 and 280 nm that is around two orders of magnitude lower than ozone and BTX species. Unless present in much higher concentrations than BTX, the influence of NO$_2$ absorption on the retrieval of BTX concentration will be negligible. However, aerosol extinction, mainly from Mie scattering, can exceed $10^{-6}$ cm$^{-1}$ in a polluted environment. Such high extinctions will substantially reduce the effective path length of light in the cavity and hence lower the instrument sensitivity. In our instrument, for instance, the effective path length at 266 nm is ca. 189 m under minimal aerosol conditions but decreases to below 160 m when the aerosol extinction coefficient is $10^{-6}$ cm$^{-1}$. To minimize the effect of ambient aerosols, a simple solution is to install a particle filter in the inlet stream.

This work shows the potential of the IBBCEAS approach for measurements of absorbing gases in the deep UV. Many other volatile species absorb between 250 and 280 nm, notably carbonyl species and other small aromatics, SO$_2$ (as used to calibrate our instrument), organic reaction intermediates and radicals (like the ethyl, benzyl, and phenyl radicals, the phenoxy radical, and the phenyl, methyl, and benzyl peroxy radicals), and a range of chlorine oxide species (ClO, ClOO, ClOOCl, Cl$_2$O, Cl$_3$O$_2$). For research applications, spectroscopic methods would have exceptional sensitivity to these highly unstable species and the ability to measure them in situ would be valuable tools.

It is also worth pointing out that the 200–230 nm spectral region is particularly important for the measurement of the key environmental gases NH$_3$, SO$_2$, isoprene, and NO, even if commercially available DUV LEDs cannot yet attain such short wavelengths, and mirror reflectivities are worse at these short wavelengths. Some active DOAS systems have already demonstrated high sensitivity in this region with light paths of 100 m, which is useful for sampling particularly sticky gases like NH$_3$.

4. CONCLUSIONS

This study presented a novel IBBCEAS system for the measurement of BTX. Combined with the 255 nm LED, optical cavity, and short-pass filter, a spectral range from 250 to 295 nm was achieved. The absorption cross sections of benzene, toluene, p- and m-xylene measured with the spectrometer were in good agreement with previous work by others. We demonstrated the application of the system to the simultaneous retrieval of mixtures of m-xylene and p-xylene. The extension of the approach to other species of scientific and technological interest, as well as ways to optimize the spectrometer for different purposes, was discussed.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.analchem.1c04940.

Figure S1, the absorption coefficient of BTX; Figure S2, the absorption cross section of benzene (PDF)
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Author Contributions

M.W. was in charge of investigation, data curation, formal analysis, validation, and writing the original draft. R.V. was in charge of conceptualization, methodology, writing, review as well as editing. W.Z. performed the conceptualization and funding acquisition. J.C. was in charge of conceptualization, methodology, investigation, supervision, funding acquisition, writing, review, and editing.

Funding

This work was supported by the National Natural Science Foundation of China (Grant Nos. 91544225, 51776129), the National Key Research and Development Program of China (Grant Nos. 2017YFC0211504 and 2018YFC0213800).

Notes

The authors declare no competing financial interest.

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