In situ detection of benzene molecules with UV absorption spectroscopy

feasability, results and comments

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## Contents

1 Introduction  
   1.1 Motivation ................................................. 2  
   1.2 List of symbols and units .................................. 3  

2 Benzene description  
   2.1 The molecule ............................................... 4  
   2.2 Molecular spectroscopy ...................................... 5  

3 Broadening issues  
   3.1 Natural broadening ......................................... 8  
   3.2 Collision broadening ........................................ 8  
   3.3 Doppler broadening ......................................... 9  
   3.4 Instrument line shape ...................................... 9  

4 Absorption spectroscopy in practice  
   4.1 Integral form ............................................... 10  
   4.2 Differential form ........................................... 10  
   4.3 Practical spectroscopy ..................................... 11  

5 Experimental work  
   5.1 Setup ..................................................... 13  
   5.2 Spectrometry ............................................... 15  
   5.2.1 Spectrometry equipment .................................. 15  
   5.2.2 Low resolution spectrum simulation ...................... 17  
   5.3 Benzene concentration control strategies .................... 19  
   5.3.1 Use of vapor pressure law ................................ 19  
   5.3.2 Cross section calculation .................................. 20  
   5.4 High temperature measurement ................................. 20  
   5.5 Flame measurement ......................................... 20  
   5.5.1 Setup .................................................. 20  
   5.5.2 Combustion reaction ...................................... 21  
   5.5.3 The burner ............................................... 21  

6 Precision analysis  
   6.1 Optical shift .............................................. 23  
   6.2 Noise origin ............................................... 23  
   6.3 Definition of minimal concentrations ....................... 24  
   6.3.1 Importance of standard deviations ....................... 24
## List of Tables

<table>
<thead>
<tr>
<th>Table</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Peaks position (air wavelengths)</td>
<td>7</td>
</tr>
<tr>
<td>5.1</td>
<td>Absorption vs range orders of magnitude</td>
<td>16</td>
</tr>
<tr>
<td>5.2</td>
<td>Calibration lines: spectrometer response is figure (5.7)</td>
<td>18</td>
</tr>
<tr>
<td>7.1</td>
<td>Point per point comparison for Deut Lamp</td>
<td>28</td>
</tr>
<tr>
<td>7.2</td>
<td>Point per point spectra comparison for LED</td>
<td>28</td>
</tr>
<tr>
<td>7.3</td>
<td>Full absorption comparison for Deuterium lamp</td>
<td>30</td>
</tr>
<tr>
<td>7.4</td>
<td>Full absorption comparison for LED</td>
<td>30</td>
</tr>
<tr>
<td>7.5</td>
<td>One point absorption comparison for Deut Lamp</td>
<td>31</td>
</tr>
<tr>
<td>7.6</td>
<td>Maximum concentration point comparison for LED Lamp</td>
<td>32</td>
</tr>
<tr>
<td>7.7</td>
<td>Basic DOAS comparison for Deut Lamp</td>
<td>32</td>
</tr>
<tr>
<td>7.8</td>
<td>Basic DOAS for Deuterium Lamp</td>
<td>33</td>
</tr>
<tr>
<td>7.9</td>
<td>Average peak detection with Deut Lamp</td>
<td>33</td>
</tr>
<tr>
<td>7.10</td>
<td>First derivative comparison for Deut Lamp</td>
<td>34</td>
</tr>
<tr>
<td>7.11</td>
<td>First derivative comparison for LED</td>
<td>35</td>
</tr>
<tr>
<td>7.12</td>
<td>Data for limit of blank</td>
<td>38</td>
</tr>
</tbody>
</table>
# List of Figures

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>The Kekule structures of benzene</td>
<td>4</td>
</tr>
<tr>
<td>2.2</td>
<td>Cyclic formation enthalpies <em>(see the resonance energy = 360-210 kJ/mol)</em></td>
<td>4</td>
</tr>
<tr>
<td>2.3</td>
<td>Absolute differential oscillator strengths for the valence shell photoabsorption of benzene in deeper UV</td>
<td>5</td>
</tr>
<tr>
<td>2.4</td>
<td>Electronics, Vibrational and rotational transitions <em>(<a href="http://www.hyperphysics.phy-atr.gsu.edu">www.hyperphysics.phy-atr.gsu.edu</a>)</em></td>
<td>6</td>
</tr>
<tr>
<td>2.5</td>
<td>Electronic transition vs coupled electronic and vibronic transition <em>(chemwiki.ucdavis.edu)</em></td>
<td>6</td>
</tr>
<tr>
<td>2.6</td>
<td>Benzene 250 nm rovibronic transitions <em>(A^0_n)</em></td>
<td>7</td>
</tr>
<tr>
<td>4.1</td>
<td>10^5 ppm absorbance and raw spectra</td>
<td>11</td>
</tr>
<tr>
<td>5.1</td>
<td>Benzene dilution and monitoring setup</td>
<td>13</td>
</tr>
<tr>
<td>5.2</td>
<td>Cell surpression calibration curve</td>
<td>14</td>
</tr>
<tr>
<td>5.3</td>
<td>LED and Deuterium lamp emission spectra</td>
<td>15</td>
</tr>
<tr>
<td>5.4</td>
<td>Picture of ocean optic USB4000 spectrometer</td>
<td>16</td>
</tr>
<tr>
<td>5.5</td>
<td>Reference spectrum</td>
<td>17</td>
</tr>
<tr>
<td>5.6</td>
<td>Reference peaks</td>
<td>17</td>
</tr>
<tr>
<td>5.7</td>
<td>Spectrometer calibration curve</td>
<td>18</td>
</tr>
<tr>
<td>5.8</td>
<td>Response to a ponctual pulse (pixel 1040)</td>
<td>19</td>
</tr>
<tr>
<td>5.9</td>
<td>Simulated spectrum after downsampling and convolution</td>
<td>19</td>
</tr>
<tr>
<td>5.10</td>
<td>Photographs of premixed C_2H_4/air sooty flames of different stoechiometric ratios</td>
<td>21</td>
</tr>
<tr>
<td>5.11</td>
<td>Overview of a McKenna burner</td>
<td>22</td>
</tr>
<tr>
<td>6.1</td>
<td>Relationship between 0ppm(LoB), LoD, LoQ</td>
<td>25</td>
</tr>
<tr>
<td>7.1</td>
<td>Some ring-based molecules UV spectra</td>
<td>27</td>
</tr>
<tr>
<td>7.2</td>
<td>Accuracy and precision</td>
<td>27</td>
</tr>
<tr>
<td>7.3</td>
<td>Point per point comparison for Deuterium lamp</td>
<td>28</td>
</tr>
<tr>
<td>7.4</td>
<td>Point per point comparison for LED lamp</td>
<td>29</td>
</tr>
<tr>
<td>7.5</td>
<td>Overall absorption comparison for DEUT lamp</td>
<td>29</td>
</tr>
<tr>
<td>7.6</td>
<td>Overall absorption comparison for LED</td>
<td>30</td>
</tr>
<tr>
<td>7.7</td>
<td>Comparing max edge detection</td>
<td>31</td>
</tr>
<tr>
<td>7.8</td>
<td>Comparing max edge detection</td>
<td>31</td>
</tr>
<tr>
<td>7.9</td>
<td>Basic differential spectroscopy for Deuterium Lamp</td>
<td>32</td>
</tr>
<tr>
<td>7.10</td>
<td>Basic DOAS for LED</td>
<td>33</td>
</tr>
<tr>
<td>7.11</td>
<td>Averaging maximum absorption peaks</td>
<td>34</td>
</tr>
<tr>
<td>7.12</td>
<td>Testing first derivative</td>
<td>34</td>
</tr>
<tr>
<td>7.13</td>
<td>Projecting lab spectrum on simulated spectrum</td>
<td>35</td>
</tr>
<tr>
<td>7.14</td>
<td>Correlating lab spectrum and simulated spectrum</td>
<td>36</td>
</tr>
<tr>
<td>7.15</td>
<td>Autocorrelation of high resolution benzene spectrum</td>
<td>37</td>
</tr>
</tbody>
</table>
Abstract

This thesis reports experiments of benzene spectroscopy in the 250 nm region, with the use of UV LED and Deuterium lamp. Since database was found only at usual temperature, concentration measurements were performed at 293 K and then absorbance at high temperature was recorded, although with low precision. Emphasis was put on precision analysis and setup robustness.
Chapter 1

Introduction

1.1 Motivation

Althought benzene is not a major greenhouse gas, its detection is important for environnemntal monitoring.

- In itself, benzene vapors are known as human carcinogen and mutagen. But benzene is still used, for polystyrenes, epoxy resines polycarbonates, nylons. The critical limits are set 1 ppm for 8 hr/day and 500 ppm for immediate danger. A fingerprint is hence needed for air monitoring.

- As a volatile organic compound, benzene is a precursor of tropospheric ozone. Ozone is known for becoming a pollutant at high concentration and constituent of city smog.

- Benzene is also a precursor of soot particle formation process. Its monitoring is thus needed to design particulate matter reduction strategies [3], especially in the UV [4].

- An interesting fact is that aromatic species are of great importance for astronomical studies ([5]). Indeed although transmission difficulties, benzene UV-spectroscopy have been performed on Jupiter and Titan surface (see [6], [7], [8]) to investigate prebiotic chemistry for example.

The aim on this study is to discuss the use of UV LED and deuterium lamp as a low-cost alternative to Laser spectroscopy techniques for flame chemistry monitoring. Indeed a major issue for combustion engine is the production of soot particles whose formation process includes the formation of benzene rings. Furthermore, this non-intrusive method (by opposition to sampling) has to be checked in terms of robustness and precision. Focus will be hold on absorption spectrum behaviour and recognition to enhance detection.
### 1.2 List of symbols and units

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
<th>Unit</th>
<th>Order of mag.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda$</td>
<td>wavelength</td>
<td>nm</td>
<td>250 nm</td>
</tr>
<tr>
<td>$\tilde{\nu}$</td>
<td>wavenumber</td>
<td>cm$^{-1}$</td>
<td>40 000</td>
</tr>
<tr>
<td>$\nu$</td>
<td>optical frequency</td>
<td>GHz</td>
<td>$c \times \tilde{\nu} = 100$ GHz</td>
</tr>
<tr>
<td>$n_{\text{specie}}$</td>
<td>optical index</td>
<td>$\emptyset$</td>
<td>1</td>
</tr>
<tr>
<td>$\alpha_{\text{specie}}$</td>
<td>refractivity</td>
<td>$\emptyset$</td>
<td>$10^6 (n - 1) \approx 00$</td>
</tr>
<tr>
<td>$N_i$</td>
<td>number of molecules in state $</td>
<td>i\rangle$</td>
<td>cm$^{-3}$</td>
</tr>
<tr>
<td>$\tilde{\nu}$ transition wavenumber</td>
<td>cm$^{-1}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\sigma_{\lambda(\text{specie})}$</td>
<td>cross section</td>
<td>Mb</td>
<td>$10^{-18}$ cm$^2 = 1$ Mb</td>
</tr>
<tr>
<td>$T$</td>
<td>temperature</td>
<td>K</td>
<td>300 K</td>
</tr>
<tr>
<td>$g_i$</td>
<td>statistical weight of state i</td>
<td>$\emptyset$</td>
<td></td>
</tr>
<tr>
<td>$A$</td>
<td>absorbance</td>
<td>$\emptyset$</td>
<td>0.1</td>
</tr>
<tr>
<td>$L(x,\gamma_L)$</td>
<td>lorentzian profile</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$G(x,\sigma_G)$</td>
<td>gaussian profile</td>
<td>$\emptyset$</td>
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Chapter 2

Benzene description

2.1 The molecule

Benzene ($C_6H_6$) is a liquid hydrocarbon (crystallization at 5.5°C and ignition at 520°C), isolated by M. Faraday in 1825 in illuminating gases. This species is the knownest specie of aromatic species group, defined today by high stability molecules with a cyclic, planar system (more precisely the Hückel rule needs $4n+2$ $\pi$ electrons).

The hexagonal structure of benzene have been checked in 1931 with X-Rays. The bond were equally 0.140 nm long, ie between simple and double bond lengths. Indeed, before quantum mechanics, benzene structure was described by Kekule forms as shown in 2.1.

Figure 2.1: The Kekule structures of benzene

The delocalization between the two forms allows more stability as shown in figure 2.2

Figure 2.2: Cyclic formation enthalpies (see the resonance energy = 360-210 kJ/mol)
Benzene molecule major property is its highly symmetry, allowing many (30) normal modes among which ten are degenerated [9]. The UV progression matching with the LED emission is in the 250 nm.

A more complete UV spectrum is given by [10] is shown on figure 2.3 and shows another absorption peak at 175 nm.

![Figure 2.3: Absolute differential oscillator strengths for the valence shell photoabsorption of benzene in deeper UV](image)

### 2.2 Molecular spectroscopy

The overall energy of a molecule is a combination of electronic, vibrational and rotational energies as shown in picture 2.4.

Under *Born-Oppenheimer approximation*, it consists in a simple addition of theses states. But spectroscopy work is based on a break of Born-Oppenheimer approximation. Indeed, *the transitions used in this work are enabled by the coupling of rotational and electronic transitions*. Indeed below the first ionization threshold, the photoabsorption oscillator threshold is mainly composed of three electronic transitions:

- a very weak band \( ^1B_{2u} \leftarrow ^1A_{1g} \) at 4.9 eV
- a stronger band \( ^1B_{1u} \leftarrow ^1A_{1g} \) at 6.19 eV
- a very intense band \( ^1E_{1u} \leftarrow ^1A_{1g} \) at 6.96 eV

The \( S_1\left( ^1B_{2u} \right) \leftarrow S_0\left( ^1A_{1g} \right) \) electronic transition is detailed further in [11], [12], [13] and used in [14]. The idea is that an asymmetric ring breathing vibration mode is excited enough (1 quantum) to allow \( \nu_1 \) totally symmetric ring-breathing vibration mode by “perpendicular-band one-photon absorption”. This interrelation of vibrational and electronic interaction is called *vibronic coupling* and is neglected in the *Born-Oppenheimer approximation*. 
Vibronic transitions are depicted in picture 2.5 (from [11]).

Absorption spectrum can be found (fig 2.6) and major peaks on Table 2.1.
Figure 2.6: Benzene 250 nm rovibronic transitions ($A_0^0$)

<table>
<thead>
<tr>
<th>source</th>
<th>Fally [15]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_0^0$ position</td>
<td>38610</td>
</tr>
<tr>
<td>$B_0^0$ position</td>
<td>39533.5</td>
</tr>
<tr>
<td>$A_1^0$ position</td>
<td>40455.8</td>
</tr>
<tr>
<td>$A_2^0$ position</td>
<td>41377</td>
</tr>
<tr>
<td>grating</td>
<td>0.2</td>
</tr>
<tr>
<td>$(\nu_1 + n \times \nu_0) \times \text{cm fit}$</td>
<td>$38611 + n \times 922.3$</td>
</tr>
</tbody>
</table>

Table 2.1: Peaks position (air wavelengths)
A transition is never a line in the final spectrum. Following phenomena occurs:

### 3.1 Natural broadening

From Heisenberg uncertainty principle

\[ \Delta E \Delta t \sim h \]  \hspace{1cm} (3.1)

which is equivalent to

\[ \Delta \nu \Delta t \sim 1 \]  \hspace{1cm} (3.2)

it can be deduced that an energy level can never be determined precisely because of the finite lifetime \( \Delta t \). Thus the line profile is broadened over a natural width \( \Delta \lambda \):

\[ \Delta \lambda = \frac{\lambda^2}{2\pi c} \left( \frac{1}{\Delta t_i} + \frac{1}{\Delta t_f} \right) \]  \hspace{1cm} (3.3)

where \( \Delta t_i \) and \( \Delta t_f \) are the initial and final state lifetime, respectively. This effect leads to a Lorentz profile function:

\[ \Phi(\nu) = \frac{\gamma}{4\pi^2} \frac{1}{(\nu - \nu_0)^2 + (\gamma/4\pi)^2} \]  \hspace{1cm} (3.4)

\( \gamma \) being related to spontaneous decay rates \( A_{ij} \) of the excited state \( |i \rangle \) into all lower states \( |j \rangle \). The order of magnitude is the nanosecond, so that the broadening is \( \frac{\gamma}{8\pi} \) so \( \frac{\gamma}{8\pi c} \), with an order of magnitude \( 10^{-3} \text{ cm}^{-1} \)

### 3.2 Collision broadening

Another lorentzian broadening can be explained by collisions: distorting the energy level and thus also called pressure broadening. Nethertheless, its calculation is immediate only for atoms or ions. In this case magnitude depends on the \( \nu_{\text{col}} = \nu_{\text{th}} n \sigma_{\text{col}} \) where \( \nu_{\text{th}} = \sqrt{2k_B T/m} \) is the thermal speed of the atoms, \( n \) its density and \( \sigma_{\text{col}} \) their cross-section for collisions. From above it can only be deduced that it exists a broadening proportional to the number density of particles and their average speed.

\[ \nu_{\text{col eff}} = \nu_0 \frac{P}{P_0} \sqrt{\frac{T_0}{T}} \]  \hspace{1cm} (3.5)
Also, it should be pointed out that since this broadening may come from various particle interaction $V_k(r) = h \frac{C_k}{r^k}$, its expression $\Delta E \sim 1/r^k$ may differ much according to experimental conditions:

- $k=2$ linear Stark broadening for emitter/electric field interaction
- $k=3$ resonance broadening when perturbing particle is of the same type as the emitting one
- $k=6$ Van der Waals broadening when their forces are dominant
- etc..

### 3.3 Doppler broadening

A gaussian broadening is due to the thermal velocity of particles. Due to the Doppler effect. A Doppler width is hence defined:

$$\Delta \tilde{\nu}_D \equiv \tilde{\nu}_0 \frac{3k_B T}{mc} \sqrt{3}$$

which is equal to $\sim \tilde{\nu}_0 \times 10^{-6}$ so $0.04 \text{ cm}^{-1}$. Absorption line profile due to Doppler broadening is:

$$\phi(\tilde{\nu}) = \frac{1}{\sqrt{\pi} \Delta \tilde{\nu}_D} \exp\left(-\frac{(\tilde{\nu} - \tilde{\nu}_D)^2}{\Delta \tilde{\nu}_D}\right)$$

### 3.4 Instrument line shape

Indeed the spectrometer himself has to be known when using database. In same way slit experiment show diffraction patern, an instrumental response has to be taken into account when comparing spectrometer result and spectrum form database, which is created by deconvolving with ILS. The adaptation (convolution) will be discussed on page 18.

Although not used, it should be stated out that gaussian and lorentzian broadening is usually computed by convolving gaussian and lorentzian profile. It is called the **Voigt profile** (written $V = G \otimes L$):

$$V(\lambda, \sigma_G, \gamma_L) = \int_{-\infty}^{\infty} G(\lambda', \sigma_G) \times L(\lambda - \lambda', \gamma_L) \, d\lambda'$$
Chapter 4

Absorption spectroscopy in practice

4.1 Integral form

When an electromagnetic wave $I_\nu$ travels through an absorbing sample, its intensity decrease along $z$ by:

$$T_\nu = \frac{I_{z, \nu}}{I_{0, \nu}} = \exp(-\alpha_{mix}(\nu)z) \quad (4.1)$$

$T_\nu$ is called the transmittance and $\alpha_{mix}(\nu) = \alpha_{mix}(\nu, T, N)$ is the attenuation coefficient:

$$\alpha_{mix}(\nu) = \sum_{\text{species}} \frac{N_{\text{specie}}}{N_{\text{tot}}} \alpha_{\text{specie}}(\nu) \quad (4.2)$$

Also, absorbance is worth noting:

$$A = -\ln \frac{I}{I_0} \quad (4.3)$$

4.2 Differential form

A deeper definition of absorption could be helpful for this work, as regard the flame condition. It is well worth noting that for each specie the absorption coefficient $\alpha_{\nu}$ for a transition $|i\rangle \rightarrow |k\rangle$ with population densities $N_i$ and $N_k$ and statistical weights $g_i$ and $g_k$ is related to the absorption cross section $\sigma_{ik}$ by [16]:

$$\alpha(\nu) = (N_i - \frac{g_i}{g_k} N_k) \sigma_{ik}(\nu) \quad (4.4)$$

Indeed the absorption coefficient is a function of the population inversion

Some temperature considerations can be drawn since Boltzmann distribution applies:

$$N_i = \frac{g_i}{Q(T)} N \exp(-\frac{E_i}{k_BT}) \quad (4.5)$$

with Q(T) being the partition function, still unable to be approximated in our region:

$$Q(T) = \sum_{i=0}^{\infty} g_i \exp(-\frac{E_i}{k_BT}) \quad (4.6)$$
Temperature dependance

Unfortunately, no theoretical temperature dependance can be derived from this since the partition function cannot be approached at these wavelengths (\( \frac{N_c}{k_B T} \simeq \frac{\hbar \nu}{0.025 \text{eV}} \simeq 500 \)). Nethertheless, it can be also derived that for our case the population inversion is not different from the population.

Saturation

As seen after, detection will be made in the 10 → 1000 ppm region. At 10^5 ppm there is no obvious linearity of the absorbance against concentration that can be seen on the 10^5 ppm spectrum 4.1. Indeed self-absorption occurs.

![Figure 4.1: 10^5 ppm absorbance and raw spectra](image)

4.3 Practical spectroscopy

The attenuation coefficient described in 4.1 depends on:

- wavelength
- sample composition
- temperature

Here gaz composition will be the main factor.

Absorption spectrum

The crux of the problem is of course to know the absorption spectrum of benzene. For this project only usual temperature database have been found [15]. Hence, a part of the project is to outline high the benzene high temperature spectrum (up to 450 Celsius degree).
Gaz mixture absorption

The absorption coefficient of a gaz mixture is simply:

\[ \alpha_{\text{mix}}(\lambda) = \alpha_{\text{air}}(\lambda) + C_{\text{benzene}} \alpha_{C_6H_6}(\lambda) \]  

(4.7)

The concentration is calculated relative to air: the unit is part per million. Concerning absolute concentration, reciprocal cubic centimeter (some times normalized at amagat: 1 amg = 0.269 × 10^20 cm\(^{-3}\)).

Database

The reference UV absorption spectrum was published in 2008 by Fally [15]. It should not be forgotten to adapt the database to the refractive index and hence compare all spectra within vacuum unit

\[ \lambda_{\text{vacuum}} = \lambda_i \times n_i \]  

(4.8)

The refractivity in this paper is assumed to be nearly 300 in accordance to the second Edlen equation while the present spectrometer was calibrate using a few spectral lines as described pages 18 and 17.

Limitations of Beer-Lambert law

Indeed the linearity of the Beer-Lambert law may be limited by chemical and instrumental factors. Although neglected, these effects are worth noting:

- deviations in absorptivity coefficients at high concentrations due to electrostatic interaction between molecules
- scattering of light due to particulates in the sample
- fluorescence or phosphorescence in the sample
- changes in refractive index at high concentration
- stray light
Chapter 5

Experimental work

5.1 Setup

The chosen method for preparing nitrogen vapor with known benzene ppm concentration is to act on dilution of benzene vaporized flux in a benzene-free flux. A sketch can be seen on figure 5.1

![Benzene dilution and monitoring setup](image)

**Figure 5.1: Benzene dilution and monitoring setup**

**Preparing Φ₁ and Φ₂**

The nitrogen gaz supply was divided in two tubes and connected to Flow mass controlers, whose orders of magnitude were typically

- 0.5 L/min for Φ₁
- 15 then 40 L/min for Φ₂
Φ₁ flux was then passing through a liquid benzene bottle, thus generating a flux with a fixed benzene concentration due to known vapor pressure [17], [18].

\[
ppm = 10^6 \frac{10^A - B}{P_{bottle}}
\]  \hspace{1cm} (5.1)

\[
ppm \approx 100000 \times \frac{P_{atm}}{P_{bottle}}
\]  \hspace{1cm} (5.2)

Indeed \( P_{bottle} \to 120\% \ P_{atm} \) when maximum \( \Phi₂ \) (see fig 5.2). Another correction could come from the presence of nitrogen in the setup, thus maybe changing the application of the Antoine law as a specy gas/liquid interface with unique .

![Figure 5.2: Cell suppression calibration curve](image)

**Filling the sample**

**Room temperature**

The two flux were mixed and passed through tubes (5 mm internal diameter), and then along sample (12 cm long, 4 cm wide) and then sent to the hood, as regard benzene toxicity recommendations.

**High temperatures**

For high temperature experiments, the flux was instead connected to a vertical heating pipe connected to an horizontal 18 cm long sample. A problematic issue was the thin exit hole (4 mm wide), leading in theory to a high velocity beam. Nethertheless, perfect gas law was applied with constant pressure and varying temperature to calculate benzene density.
5.2 Spectrometry

5.2.1 Spectrometry equipment

Lamps

255 nm-centered LED (narrow) and Deuterium lamp (broad) were used for the 240-260 nm progression (Fig 5.3). Light emission shall be explained:

- Deuterium lamp is based on creating an arc, exciting the molecular Deuterium in the bulb to a higher energy state. Light is emitted as a relaxation.
- LED are basically consist of a junction of p-type and n-types materials, creating in our case a large gap $E_g = \frac{e h}{\lambda e} = 4.86 \, V$

![Figure 5.3: LED and Deuterium lamp emission spectra](image)

CCT spectrometer description

A spectrometer is made of three basic components:

- collimating optics at the input
- a diffraction grating
- focusing optics: different wavelength must be sent to different pixel

The USB4000 spectrometer is Crossed Czerny-Turner (CCT) based and thus include these three elements. Its composition is detailed in figure 5.4.

Optical resolution depends on:

- 1: connector
- 2: entrance slit ($\approx 200 \, \mu m$)
Table 5.1: Absorption vs range orders of magnitude

<table>
<thead>
<tr>
<th>spectral range</th>
<th>mean cross section (Mb)</th>
<th>mean (Δλ ≈ 5 nm) absorbance with 1000 ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>all (37300-41800 cm⁻¹)</td>
<td>0.1696</td>
<td>0.0509</td>
</tr>
<tr>
<td>biggest peak, reference window (0.2 cm⁻¹)</td>
<td>5.58</td>
<td>1.67</td>
</tr>
<tr>
<td>biggest peak, USB4000 window (8 cm⁻¹)</td>
<td>2.36</td>
<td>0.71</td>
</tr>
</tbody>
</table>

- 3: filter to block second and third order or to balance color
- 4: mirror that collimates the beam to the grating
- 5: grating

Resolution is about assumed nearby 0.3 nm. Sampling of diffracted light depends on:

- 6: mirror focuses beam on detector plane
- 7: lenses to focus the light from the tall slit onto shorter detector elements
- 8: detector array
- 9: further filters

Spectrometer performances

Reference spectrum

General

A FTIR spectrum of benzene has been performed by Fally [15] in 2008 plotted in Figure 5.5 and discussed in Figure 5.6.

This spectrum has two main structures:

- distinct and sharp $A_{1u}$ peaks with common progression (they can represent several vibrational transitions)
- rotational transitions, near, accompanying each vibrational transition

Table 5.1 gives tabulated absorbance in interesting spectral ranges.
5.2.2 Low resolution spectrum simulation

vacuum unit calibration

A shift between HITRAN and Fally spectra can be observed; bigger than central peak width and thus requiring calibration. In that purpose some spectral lamp have emission lines in this region, such as Hg at 253 nm. I decided to convert both USB4000 spectrometer and Fally FTIR ([15]) to vacuum wavelength; USB4000 being calibrated with spectral line and Fally data converted by Edlen formula (5.3)

\[
\frac{\lambda_{\text{vac}}}{\lambda_{\text{air}}} = 1.00008342 + \frac{2.40603 \times 10^{-2}}{130 - (1\mu m/\lambda_{\text{air}})^2} + \frac{1.55957 \times 10^{-4}}{38.9 - (1\mu m/\lambda_{\text{air}})^2}
\]  (5.3)

Following lines were recorded see table (5.2):
Table 5.2: Calibration lines: spectrometer response is figure (5.7)

<table>
<thead>
<tr>
<th>Element</th>
<th>Vacuum Wavelength</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>213.925</td>
</tr>
<tr>
<td>Hg</td>
<td>253.652, 296.728, 302.15</td>
</tr>
<tr>
<td>Cd</td>
<td>326.106</td>
</tr>
</tbody>
</table>

**Database convolution**

It is indeed crucial for the experimental absorption spectrum to be compared with a trustworthy reference spectrum. Solutions were:

- finding accurate smoothing window length
- building instrumental response from known parameter
- recording instrumental response from spectral lamp

No accurate clue on spectrometer with optical fiber could be found thus a simple recording of spectral line was performed. Also a change of the spectrometer sensitivity in the 240-260 nm should be checked. The simulated spectrum is defined by:

\[
S_{out} = S_{input} \otimes ILS
\]  

(5.4)
$S_{out}$ being the low sampled and low resolution simulated spectrum and $S_{input}$ being the low sampled spectrum without instrumental broadening from database. Discrete convolution of $V = U \otimes Q$ being:

$$v(k) = \sum_j u(j)q(k-j) \quad (5.5)$$

The ILS is crucial for comparing the lab results to others. For that purpose I looked for some reference gas whose monitoring would be easy and trustworthy, but I only achieved to work on spectral line: the low pressure mercury lamp 253 nm line (see output 5.8). Netherthless it can be considered as purely instrumental broadened peak. Indeed the sampling is nearly 0.05 nm in the 250 nm region thus represents to $8 \text{ cm}^{-1}$ while the 253 nm line broadening is fitted [19] at $\approx 3 \times 10^{-4} \text{ cm}^{-1}/\text{Torr} = 0.2 \text{ cm}^{-1}/\text{P atm}$. (The final low res, low sampled is (see fig 5.9):

![Figure 5.8: Response to a ponctual pulse (pixel 1040)](image1)

![Figure 5.9: Simulated spectrum after downsampling and convolution](image2)

### 5.3 Benzene concentration control strategies

ranges of benzene concentration we achieved by mixing two flux:

- $\Phi_1$ is a nitrogen flux passing through a liquid benzene bottle
- $\Phi_2$ is a direct nitrogen flux

#### 5.3.1 Use of vapor pressure law

**Physical property**

saturation pressure is tabulated with Antoine coefficients:

$$P_s = 10^A-B/(T+C) \quad (5.6)$$
ppm calculation

ppm value in $\Phi_1$ is $\approx 10^5$ ppm through saturation vapor law:

$$n_{ppm} = 10^6 \times \frac{P_s}{P_{inside}}$$  \hspace{1cm} (5.7)

Feasability

The saturation phenomenon is much dependent from pressure which has an important dynamic part. Indeed a calibration curve must be performed: see 5.2

- $\Phi_1$ is expressed in percent of 0.5 L/min
- $\Phi_2$ is expressed in percent of 15 L/min

5.3.2 Cross section calculation

The absorption is still based on $A = \sigma N_b L$ with $N_b \propto N_{tot}$. Perfect gas law leads to:

$$\sigma_{\lambda} = A_{\lambda} \times \frac{450 \times 10^6 \text{ppm}}{P_{atm}} \times \frac{P}{293 K}$$  \hspace{1cm} (5.8)

unit of $\sigma$ being $10^{-18}$ cm$^2$

5.4 High temperature measurement

Measurement up to 400 degree Celsius (under ignition point) have been performed. Following change in the setup where:

T-tube

A T-tube (17 cm long, 50 cm high) was used to heat flux, working up to 450 C sufficently enough to heat big flux.

Temperature measurement

A thermocouple type N (14 percent Nickel) was used with reference junction at usual temperature. A broadly fitted equation of the thermal voltage in mV with temperature in Kelvin degree is:

$$V_T(T) - V_T(298) \simeq 21.6 \times 10^{-3}(T - 298) + 12 \times 10^{-6}(T - 298)^2$$  \hspace{1cm} (5.9)

5.5 Flame measurement

5.5.1 Setup

Sooty flame absorption measurement have been performed by Ramsia and Bo ([20]). The setup has following characterisitics:
5.5.2 Combustion reaction

The overall combustion reaction for an ideal, stoechiometric combustion process of an hydrocarbon is:

\[
C_xH_y + (x + 0.25y)O_2 \rightarrow xCO_2 + 0.5yH_2O \quad (5.10)
\]

Here \(x = 2\) and \(y = 4\) since ethene will be used. Of course not all carbon and hydrogen are oxydized during the combustion process. Some species remain partially oxydized to form CO and H₂. Furthermore, their reaction path can lead to the production pollutants like PAHs and soot. Benzene is an important aromatic specy, but it should be underlined that radicals are important in these reaction paths. An immediate factor of soot formation is the *equivalence ratio* as described after. Effects on flames are shown on Fig 5.10 (from [21]).

\[
\Phi = \frac{(n_{fuel}/n_{ox})}{(n_{fuel}/n_{ox})_{stoech}} = \frac{n_{fuel}/n_{ox}}{(x + 0.25y)} \quad (5.11)
\]

which is to say that:

- if air-fuel is less than \(\Phi\), the mixture is rich
- else, it is a lean mixture

![Figure 5.10: Photographs of premixed C₂H₄/air sooty flames of different stoechiometric ratios](image)

5.5.3 The burner

Among other type (Glder, Santoro), the McKenna burner present flat flames along on a large (6 cm diameter) disk. The idea of porous surface is sketch on figure 5.11. Fuel and oxydizing agent are brought by tubes with \(\alpha \times 15\) L/min for air and \(\beta \times 2\) L/min for ethene. Equivalence ratio is thus equal to \(3 \times \frac{\beta}{21 \times \alpha \times 15}\). Absorption measurements were hold 1 cm above the burner: at this distance benzene is expected to appear according to simulations.
Figure 5.11: Overview of a McKenna burner
Chapter 6

Precision analysis

6.1 Optical shift

The Beer-Lambert law needs a second qualifying in the wavelength/wavenumber axis:

Orders of magnitude

As seen before, the UV region is very sensitive to refractive index effects compared to peak narrowness. The database is filled with vacuum wavelengths and experiments were performed in nitrogen vapor. A useful definition is the refractivity:

\[ \text{ref} = 10^6 (n - 1) \]  

(6.1)

its effect on our spectra is:

\[ \Delta \tilde{\nu} = \tilde{\nu} - \tilde{\nu}_0 = \text{ref} \times \tilde{\nu}_0 \sim \frac{\text{ref}}{25} \text{ cm}^{-1} \]  

(6.2)

A basic calibration was performed with spectral lamps as seen before on Fig (5.2) an emphasis is put on the uncertainty of the wavelength scale.

6.2 Noise origin

Instrumental noise

generally optical receiver signal to noise ratio is expressed as:

\[ \text{SNR} = \frac{\bar{m}^2}{\bar{m} + \sigma_q^2} \]  

(6.3)

- \( \bar{m} \approx 30000 \) being the mean number of photons detected during resolution time: \( \bar{m} = \eta \Phi T \)
- \( \sigma_q \) being a dimensionless noise parameter derived from Thermal noise \( \sigma_i^2 = 4k_B T \frac{B}{R} \)

T is found 1MHz and \( \eta \) is broadly \( 10^{-2} \)
Johnson noise

The random electron motion due to temperature is usually limited. It was recorded as the standard deviation of a serie of background spectra:

\[ \sigma_{\text{thermal}} = \sqrt{\frac{4k_B T}{R}} \]  

(6.4)

Which was found to be \( \approx 40 \) counts to be compared to the 35000 counts of the lamp during the 0.1 second period.

Shot noise

Shot noise is a major noise when . Its standard deviation is the square root of the average number of incoming photon, this leading to a SNR equal to \( N/\sqrt{N} = \sqrt{N} \). This value is thus no problem for our experiment.

Source flicker noise

It consist in a voltage variation to source; compensated by stabilized voltage supply or double beam spectrometer. Here neglected too.

Effects of slit widths

Narrow slit width may:

- increase detail in absorbance spectrum
- increase the peak absorbance values
- decrease photon flux thus increasing noise
- but are necessary to resolve fine details

Stray radiation

Stray radiations were neglected but it may be the explanation to high deviation between setup at different moments.

Denoising

At this point only background noise was substracted. Due to the low sampling of the spectrometer, no further smoothing has been performed. Nevertheless an attempt of filtering high frequencies considewred as noise has been performed.

6.3 Definition of minimal concentrations

6.3.1 Importance of standard deviations

Each ppm value (at 0 ppm, at limit of detection, at limit of quantification) has \( \sigma \) standard deviation around its mean value (see 6.1). Classically, limit of detection and limit of quantification are calculated as multiple of the 0 ppm standard deviation, whose being related to the total SNR (see fig 6.1.
Figure 6.1: Relationship between 0ppm(LoB), LoD, LoQ

**Limit of Blank**

The $LoB$ is the highest apparent concentration expected to be found when 0 ppm replicates are tested

$$LoB = \text{mean}_{0\text{ppm}} + d_{LoB} \times \sigma_{LoB}$$  \hspace{1cm} (6.5)

the distance $d$ here and below as to be discussed (1.645 for LoB representing 95%, or 3 for 99%).

**Lower limit of detection**

The $LoD$ is the lowest quantity of a substance that the setup will distinguish from its absence. As above,

$$LoD = LoB + d_{LoD} \times \sigma_{LoD}$$  \hspace{1cm} (6.6)

**Lower limit of quantification**

The $LoQ$ is the lowest quantity of a substance that the setup will detect with prerequired bias and imprecision (20% for example)

$$LoQ = LoD + d_{LoQ} \times \sigma_{LoQ}$$  \hspace{1cm} (6.7)
Chapter 7

Results

7.1 Usual temperature concentration measurements

7.1.1 Data processing

After denoising, an absorption spectrum with basic denoising is saved as a \( \sim 400 \) points array. In theory, it represents the \( [a_1..a_n] = \sigma(\lambda)LN \times 10^{-6} \text{ppm} \) to be compared to database \( [b_1..b_n] = \sigma(\lambda)LN \times 10^{-6} \), \( N \) being the gaz mix concentration and \( \text{ppm} \) its benzene concentration in part per million. An interesting step was to choose a method to extract one number of it. Tested methods were:

- classic \( \frac{1}{n} \sum_{i=1}^{n} \frac{a_i}{b_i} \)
- overall band absorption \( \frac{\sum_{i=1}^{n} a_i}{\sum_{i=1}^{n} b_i} \)
- selected band portion absorption: \( \frac{\max([a_1..a_n])}{\max([b_1..b_n])} \)
- differentiated spectra comparison
- correlation spectroscopy
- projection matrix
- analysis of autocorrelated spectrum

Following graphs are made:

- of a logarithmic scale of the ppm values for the x-axis
- of the attenuation length and the calculated density/expected density for the y-axis

At first glance, little sampling of LED absorption measurement was made, but in fact many were lost due to air reference spectrum fast unwanted variations. It should be kept in mind that the 240-260 nm is not a fingerprint of benzene, but rather of the \( \pi \to \pi^* \) transition. For example polycyclic aromatic (see 7.1) have strong absorption in that region.

A first plot is the absorption length as a function of the ppm sent by the mixing system. The absorption length is the inverse of the absorbance with length normalized at 1 meter, but also with total density \( N \) normalized at 1 amagat (number density at 1 atm and 0 C). Also, standard deviation and mean values will be checked as precision and accuracy as drawn in fig 7.2. A good idea would be to calculate them for each ppm \( 10^n \) ppm order of magnitude.
7.1.2 Mean point-by-point comparison

For Deuterium Lamp

I decided for each spectrum to select point \textit{a priori}:

- points whose $\sigma \geq 10\%$ of maximum
- points whose $\sigma \leq 50\%$ of maximum
This was done to prevent from both noisy signal but also the narrow bands whose position could not be efficiently matched. Such reduced spectrum has $\approx 40\%$ points less but $\approx 20\%$ more mean value. Also since the process is dividing lab spectra and reference spectrum, no typical absorbance could be drawn as seen in figure 7.3, the results is much more precise than accurate.

![Figure 7.3: Point per point comparison for Deuterium lamp](image)

<table>
<thead>
<tr>
<th>ppm range $10^n \rightarrow 10^{n+1}$</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>mean val / expect val</td>
<td>2.14</td>
<td>1.20</td>
<td>1.40</td>
</tr>
<tr>
<td>standard deviation in %</td>
<td>157</td>
<td>42</td>
<td>54</td>
</tr>
</tbody>
</table>

Table 7.1: Point per point comparison for Deut Lamp

### For LED

Same algorithm but with less broader array. As seen in fig 7.4

<table>
<thead>
<tr>
<th>ppm range $10^n \rightarrow 10^{n+1}$</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>mean val / expect val</td>
<td>3.46</td>
<td>2.62</td>
<td>0.88</td>
</tr>
<tr>
<td>standard deviation in %</td>
<td>62</td>
<td>102</td>
<td>117</td>
</tr>
</tbody>
</table>

Table 7.2: Point per point spectra comparison for LED

#### 7.1.3 Mean overall absorbance comparison

This method is suposed to be among the most robust. Results are presented below
For Deuterium Lamp

See fig 7.5. This method still shows a big uncertainty on low concentration. It seems no better measurement can be made.

Figure 7.4: Point per point comparison for LED lamp

Figure 7.5: Overall absorption comparison for DEUT lamp
Table 7.3: Full absorption comparison for Deuterium lamp

<table>
<thead>
<tr>
<th>ppm range 10^n \rightarrow 10^{n+1}</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>mean val / expect val</td>
<td>2.20</td>
<td>1.21</td>
<td>1.43</td>
</tr>
<tr>
<td>standard deviation in %</td>
<td>178</td>
<td>44</td>
<td>11</td>
</tr>
</tbody>
</table>

Figure 7.6: Overall absorption comparison for LED

As seen in fig 7.6, precision is better in low concentrations than in in higher ones. This may result from low number of points.

Table 7.4: Full absorption comparison for LED

<table>
<thead>
<tr>
<th>ppm range 10^n \rightarrow 10^{n+1}</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>mean val / expect val</td>
<td>1.58</td>
<td>1.25</td>
<td>0.63</td>
</tr>
<tr>
<td>standard deviation in %</td>
<td>24</td>
<td>48</td>
<td>70</td>
</tr>
</tbody>
</table>

7.1.4 Simple max edge detection

For Deuterium

Here is used the maximum absorption point, which represents the average absorption on a 0.05 nm range. The maximum is 1 compared to the 0.16 mean value of the full 240-260 nm range. Looking for the maximum allows to get rid of refractivity uncertainties. As seen in fig 7.7,

For LED

For, LEDS, high concentration measurements are poorly accurate as seen on fig 7.8; but with constant standard deviation.
Figure 7.7: Comparing max edge detection

<table>
<thead>
<tr>
<th>ppm range $10^n \rightarrow 10^{n+1}$</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>mean val / expect val</td>
<td>2.22</td>
<td>1.34</td>
<td>0.97</td>
</tr>
<tr>
<td>standard deviation in %</td>
<td>86</td>
<td>59</td>
<td>19</td>
</tr>
</tbody>
</table>

Table 7.5: One point absorption comparison for Deut Lamp

Figure 7.8: Comparing max edge detection
### Table 7.6: Maximum concentration point comparison for LED Lamp

<table>
<thead>
<tr>
<th>ppm range $10^n \rightarrow 10^{n+1}$</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>mean val / expect val</td>
<td>1.75</td>
<td>1.23</td>
<td>0.42</td>
</tr>
<tr>
<td>standard deviation in %</td>
<td>28</td>
<td>44</td>
<td>36</td>
</tr>
</tbody>
</table>

#### 7.1.5 Basic DOAS

Here is computed the difference of the previously used maximum absorption $A(\lambda_{max})$ by $A(\lambda_{max} - 1 nm)$; in other word a basic differential spectroscopy.

**For DEUT Lamp**

see fig 7.9

<table>
<thead>
<tr>
<th>ppm range $10^n \rightarrow 10^{n+1}$</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>mean val / expect val</td>
<td>2.19</td>
<td>1.35</td>
<td>0.93</td>
</tr>
<tr>
<td>standard deviation in %</td>
<td>75</td>
<td>60</td>
<td>22</td>
</tr>
</tbody>
</table>

### Table 7.7: Basic DOAS comparison for Deut Lamp

**Figure 7.9: Basic differential spectroscopy for Deuterium Lamp**

**For LED**

As seen in fig 7.10 the low concentration measurement are catastrophic with a negative trend. Benzene of course did not lase. Nethertheless the failure for LED measurements should be investigated.
7.1.6 Average peak detections

Due to LED limited width, averaging peak height was only performed with Deuterium lamp. Result is plotted in fig 7.11 on page 34.

<table>
<thead>
<tr>
<th>ppm range $10^n \rightarrow 10^{n+1}$</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>mean val / expect val</td>
<td>-0.46</td>
<td>1.00</td>
<td>0.42</td>
</tr>
<tr>
<td>standard deviation in %</td>
<td>103</td>
<td>50</td>
<td>38</td>
</tr>
</tbody>
</table>

Table 7.8: Basic DOAS for Deuterium Lamp

7.1.7 First derivative

At this point only maximum point detection was used. Derivating spectra is a technique to enhance detecting overlapping spectra ([22], which is not the case here.

For Deuterium

As seen on table 7.12 only first derivative showed a reliable attenuation/ppm correlation. Second derivative plot showed as for LED basic DOAS. Indeed derivative spectroscopy needs a very reliable reference spectrum.
Figure 7.11: Averaging maximum absorption peaks

<table>
<thead>
<tr>
<th>ppm range 10&lt;sup&gt;n&lt;/sup&gt; → 10&lt;sup&gt;n+1&lt;/sup&gt;</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>mean val / expect val</td>
<td>3.04</td>
<td>1.58</td>
<td>0.94</td>
</tr>
<tr>
<td>standard deviation in %</td>
<td>126</td>
<td>83</td>
<td>30</td>
</tr>
</tbody>
</table>

Table 7.10: First derivative comparison for Deut Lamp

Figure 7.12: Testing first derivative
For LED

As concern LED, the table shows underestimate ppm values at high concentrations that may come from the close self-absorption zone.

<table>
<thead>
<tr>
<th>ppm range $10^n \to 10^{n+1}$</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>mean val / expect val</td>
<td>1.92</td>
<td>1.65</td>
<td>0.37</td>
</tr>
<tr>
<td>standard deviation in %</td>
<td>44</td>
<td>175</td>
<td>25</td>
</tr>
</tbody>
</table>

Table 7.11: First derivative comparison for LED

### 7.1.8 Projecting spectra

When present species are known and need to have their relative concentration known, an idea is to not only to consider the absorbance as a sum of weighted tabulated spectra, but to build new basis to project the record spectrum on. An immediate basis is an orthogonal one: it means, for each species $1..k$ with sampled spectrum $\sigma_k$, to create the array $e_k$ defined as follow:

$$u_1 = \sigma_1 e_1 = \frac{u_1}{\|u_1\|} u_k = \sigma_k - \sum_{i=1}^{k-1} \frac{\langle u_j, \sigma_k \rangle u_j}{\langle u_j, u_j \rangle}$$  \hspace{1cm} (7.1)

$\langle u_j, \sigma_k \rangle$ being of course the scalar product between the two vectors. Results can be seen on fig 7.13

![Figure 7.13: Projecting lab spectrum on simulated spectrum](image)

It is worth noting that another way it to minimize cross-correlation between basis vectors. This idea is developp in the Principal component analysis [23].
7.1.9  Correlation

Here is pictured performances of cross correlation, although corrections have been ignored: see fig 7.14

![Figure 7.14: Correlating lab spectrum and simulated spectrum](image)

7.2  Interest for the benzene progression structure

The pulsation (stretching) structure of benzene can be used to segregate benzene spectrum from other species, and thus could not be really tested here.

7.2.1  Autocorrelation function

Indeed a property of benzene UV spectrum is its $922\, \text{m cm}^{-1}$ pseudo-period. May it be considered as its fingerprint? This property is insensitive to:

- error of constant refractivity (not for higher order)
- broadening uncertainty

Autocorrelation is correlating the spectrum with itself, *ie* producing a vector $R[m]$:

$$R_{xx}(m) = \sum_{n=0}^{N} x_{n+m} \times x_{n}$$  \hspace{1cm} (7.2)

In our case, for $m = 922 \times$ sampling rate, the product rises. Normalization being made by dividing each argument by its euclidian norm. Result can be seen on figure 7.15 with original Fally ([15]) as argument data while figure 7.16 is calculated form simulated spectrum with constant wavenumber step. *Here is a finger print of benzene to be implemented for detection.* Autocorrelation shall be usefull to distinguish benzene from other polycyclic species.
The idea of autocorrelation method is to autocorrelate a noisy spectrum and to look for a $\approx 922 \text{ cm}^{-1}$ repetition. Autocorrelating shall create a peak $R_{x \text{ ppm}}(922)$ above the noise. I think a wise formula formulation is:

$$R_{x \text{ ppm}}(922) = R_{x \text{ ppm}}(0) - \alpha \times 10^{-6} x$$

(7.3)

calibration being:

- $R_{x \text{ ppm}}(0)$ for the white noise contribution
- $\alpha$ for the the calibrated first autocorrelation peak (up to 0.9)

Nethertheless, the high temperature broadening reduces the interest of this method as shown on Fig 7.17

### 7.2.2 Use of acoustic recognition schemes

Along with the failure of classical deconvolution, the idea of considering benzene as a particular sound to be detected among noise rose. The interesting value should be the filtered power spectral density. The power
Figure 7.17: Benzene autocorrelation function along temperature (Celsius)

<table>
<thead>
<tr>
<th>Function</th>
<th>mean</th>
<th>std</th>
</tr>
</thead>
<tbody>
<tr>
<td>LED</td>
<td>145 ppm</td>
<td>160 ppm</td>
</tr>
<tr>
<td>DEUT</td>
<td>180 ppm</td>
<td>180 ppm</td>
</tr>
</tbody>
</table>

Table 7.12: Data for limit of blank

Spectral density of our range is:

$$P(\omega) = \frac{1}{\sqrt{2\pi}} \sum_{n_{\min}}^{n_{\max}} S_n e^{i\omega n} |^2$$  \hspace{1cm} (7.4)

and by wisely cutting (filtering) the benzene spectrum around its main component, it should be possible to detect (hardly quantize) the presence of benzene.

### 7.3 Limit of detection

#### 7.3.1 Limit of blank results

Chosen detection method was the mean absorbance (ie the least problematic) 0 ppm spectra between 246.5 and 259 nm for LED and 246 to 262 for DEUT taken the same day with the same setup. Mean detected values and standard deviations are shown on table 7.12.

An order of magnitude of 150 ppm absorbance is, using the mean value of this progression:

$$A(150 \text{ ppm}) = 12 \times 15010^{-6} \times 0.2510^{20} \times 0.210^{-18} = 910^{-3}$$ \hspace{1cm} (7.5)

$$\frac{I}{I_0} = 0.991$$ \hspace{1cm} (7.6)

Such bad results need qualifying in terms of detection method.

#### Limit of detection results

Limit of detection is usually expressed as a multiple of the blank results standard deviation. A more robust value is the basic fluctuations recorded as the standard deviation of background spectra: $n_{std} \approx 40 \text{ counts}$ to be
compared to the $3 \times 10^4$. The corresponding absorbance is $1.3310^{-3}$ ans, with usual particle density, gives a concentration sensitivity of $4.5 \text{ ppm} \rightarrow 20 \text{ ppm}$ depending of either peak or average absorbance values are used. Indeed, without further denoising, this limit can be compared to results in section 7.1.

7.4 High temperature

7.4.1 Miscellaneous

On figure 7.18 on page 39, the average behaviour of the absorbance can be seen at different temperatures.

![Figure 7.18: Benzene absorbance 25 C → 450 C](image)

The 7eV absorption band is of course prominent compared to the 5eV progression, but it is really located in deeper UV and the Deuterium lamp broadly start emitting at these wavelengths (see fig 7.19 on page 39).

![Figure 7.19: Spectrum of a benzene cell with deuterium lamp light](image)

An idea of broadening can be seen on fig 7.20 on page 40.

Density and length corrected spectra are presented on picture 7.21. Z-axis is the cross-section convolved with the instrument line shape.
Figure 7.20: Some absorption spectra at different temperature (no density correction)

Figure 7.21: broadened cross section spectrum vs temperature

7.4.2 Some facts

The effects of temperature on cross section are mainly a shift and a broadening. An idea of the shift is plotted on figure 7.22 on page 41. The shift is found by comparing each spectrum to the low temperature spectrum: either by cross-correlating or by comparing their maximum.

Also, the mean absorbance of this progression is plotted on figure 7.23 on page 41. Indeed benzene has a strong absorption baseline in the UV when temperature rises. For example benzene absorption at 274 nm has been proposed for temperature monitoring in a patent [24]. Figure 7.24 on page 41 shows that the absorption peak do not change much their amplitude with temperature.

7.4.3 Raw deconvolution

Deconvolving high temperature spectra generally give bad results due to high “frequencies” transform as seen in fig 7.25 or with inverse fourier transform 7.26. Many filters, such as Wiener filter are available as soon as proper definition of noise is given in term of minimal frequency.
Figure 7.22: Redshift of benzene absorption

Figure 7.23: Mean absorbance ($235.3 \rightarrow 289.7 \text{ nm}$) at different temperatures

Figure 7.24: Ground to peak absorption difference
Figure 7.25: Failed deconvolution

Figure 7.26: Raw ifft
### 7.4.4 Improving high temperature database

Deconvolving spectra with Instrument line shape being too difficult, an idea was to define a temperature function $\Theta_{T_i \rightarrow T_j}$, $Abs$ being the recorded absorption:

$$Abs(T_j) = Abs(T_i) \otimes \Theta_{T_i \rightarrow T_j}, \quad (7.7)$$

and since the convolution product is linear and commutative:

$$Abs(T_j) = \sigma(T_j) \otimes ILS \times LN = \sigma(T_i) \otimes ILS \times LN \otimes \Theta_{T_i \rightarrow T_j} = (\sigma(T_i) \otimes \Theta_{T_i \rightarrow T_j}) \otimes ILS \times LN \quad (7.8)$$

$$\sigma(T_j) = \sigma(T_i) \otimes \Theta_{T_i \rightarrow T_j} \quad (7.9)$$

Nevertheless, the result was not satisfying neither. It can be due to:

- bad sampling length
- need for cutting some frequencies (see Wiener Filter)

This needs deeper work on noise characterization. One interest of autocorrelation is therefore its robustness.

### 7.5 Flame measurement

#### species

Among flame components, emphasis should be put on:

- remaining $C_2H_4$
- $C_2H_2$ Acetylene, shown on graph 7.27 may be responsible for the slope
- radicals like $OH$, although absent in the 240-270 nm region
- intermediate products like $C_3H_3$, $C_3H_4$, $C_6H_6$ and maybe polycyclic molecules

Main flame reactions are sketched on figure 7.28, from [2]. Benzene main reaction paths are expected to come from $C_3H_3$, $a-C_3H_4$ and $p-C_3H_4$. Due to lack of data, no spectral basis could efficiently represent the mixture.

#### attenuation spectra

Attenuation ($m^{-1}$) spectrum are shown on fig 7.29.

Unfortunately, no clue on absorption of benzene magnitude compared top other species absorption could be drawn, thus forbidding to perform comparison of a absorption sample points with simulated one. Only $OH 310$ nm absorption can be seen. Needed algorithm for full detection is projection of predominant species at flame temperature. Also it should be underlined that that the flame temperature reach high orders of magnitude (1500 K) compared to previous experiment (750 K) ([25]). Another value to remember is the 12 nm soot particle size, leading to an effective Mie scattering cross-section equal to:

$$\sigma_{eff} = \frac{10\pi}{3} (\frac{2\pi}{\lambda})^4 (\frac{d}{2})^6 = 20 \text{ Mb}! \quad (7.10)$$

Also, it should be underlined that the setup did not allow to efficiently compare flame regions; pre-flame height being small compared to the beam radius (see fig 7.30).
benzene detection

As seen above, the only hope to fully detect benzene would be to have a 200 nm centered light source, 20 nm broad and to perform voigt deconvolution to segregate it from the flame mixture. Furthermore, the spectrum of a mix of cyclic hydrocarbons (benzene, toluene...) could be used instead of benzene to fit better. Nevertheless, autocorrelation method has been investigated in the 250-280 nm region (absorption is shifted) and gave the following plot (7.31):

This graph is the autocorrelation of the flattening, ie the residue of a polynomial fit in the benzene absorption region. It gives another outlook on the $\Phi = 2 \rightarrow \Phi = 2.5$ behaviour (discontinuity). Indeed a specie seems to
Figure 7.29: Sooty flame spectra

Figure 7.30: $C_5H_6$ (circles) and $C_6H_6$ (triangles) formation zone (from [2])

appear above noisy bottom, with $\approx 340 \text{ cm}^{-1}$ pulsation in comparison to benzene.

after fitting this, further species could be segregated. But noise is still high.
Figure 7.31: Residue autocorrelation in the benzene absorption region
Chapter 8

Conclusions and recommendations

Conclusions

This work gave fact on benzene UV spectrum and its quantitative spectroscopy. Order of magnitude for accuracy and precision were checked such as detection methods. High temperature behaviour was detailed although not in the form of a database due to bad deconvolution performance. Also, the use of the 250 nm band could not give any result in flame, due to the broadening combined to its low density. The only way for sufficient segregation is to work in the 200 nm region with a laser (most probably frequency doubled) both for efficient precision and voigt profile deconvolution but also, more simply, for a reduced sampling surface as regard the tiny preflame height.

further work recommendations

Benzene concentration monitoring

Indeed the saturation vapor method may suffer from inaccuracies such as:

- the vapor pressure law may depend of the gaz mixture
- some benzene may remain fixed to tubes and pollute next measurements

from this it should be performed a full correlation spectroscopy with a calibration gas bottle.

UV-source

The first fact that arise is that I worked on the 5 eV progression while a 7 eV absorption band is times higher. Thus an emphasis on new deep UV light sources should be put on further work.

Normalization

The setup much suffered from inaccuracies due to a change (magnitude, shift) of the probe light compared to the 0 ppm one. In other word, no real spectrum averaging could be done for low concentration monitoring.

Work in the energy domain

Such as the original data, it would be useful to use $\frac{1}{x}$ units to enhance correlation.
**Calibration**

Calibration of spectrometer should be carefully done regarding the wavenumber/wavelength scale but also the instrument line shape (instrumental response).

**pulsation detection**

The $922 \text{ cm}^{-1}$ pseudo-period should be investigated further, with good filtering skills to achieve a Temperature-related convolution function.
Bibliography


