Raman Spectroscopic Studies of Gasoline

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Contents

7.1. Introduction

Gasoline taken directly from the refinery is not useable in an internal combusting engine. It would make the engine knock, especially at low temperatures. The gasoline octane number is an experimentally determined value, which defines the antiknock quality. To increase this number TEP (tetraethyl lead) was added for many years to the gasoline. Oxygenates, e.g. methanol, ethanol and MTBE, also exhibit the effect to increase the octane number. MTBE was chosen as a substitute for the very toxic and polluting TEP, among other things because it is cheap to produce. In the recent years there has been a public interest about MTBE, primarily because American investigations have shown that MTBE is able to penetrate the soil and thus pollute the underground water reserves. On January 1st 2000 a new legislation was introduced in Denmark with respect to aromatics in gasoline: the maximum allowed benzene content was fixed to be 1 % and the maximum total aromatic content was 42 %[1]. Before this date there was no restrictions with respect to total aromatic content. Since aromatics also act as octane boosters the legislation caused that more MTBE had to be added to the gasoline.

Danish gasoline is analysed in many different ways. For instance the total aromatic content is determined by a PIONA analyser, which is based on a gas chromatographic method. The parafines (alkanes), iso parafines, olefines (alkenes), naphthenes and aromatics in the gasoline are separated and analysed. The benzene and MTBE contents are also traditionally determined by gas chromatographic methods[1]. Raman spectroscopic studies of gasoline have occasionally been described in the literature, e.g. with respect to octane number and Reid vapour pressure[2,3,4], percent content of oxygen[5] and aromatics[6,7]. It was found of interest in the Ph.D. project to investigate the feasibility of the Raman technique to analyse gasoline by univariate data treatment. The present Chap. 7.2 is concerned with Raman spectroscopic studies of MTBE content in gasoline. The chapter summarises some of the work presented in our publication "Determination of methyl tertiary butyl ether (MTBE) in gasoline by Raman spectroscopy". In Chap. 7.2 is also included some considerations about determination of MTBE in water, Chap. 7.2.4. Chap. 7.3 concerns further Raman spectroscopic studies of gasoline, primarily with respect to aromatics, and some considerations on the contents of sulphur compounds are also included, Chap. 7.3.1.

7.2 Determination of Methyl Tertiary Butyl Ether (MTBE) in Gasoline by Raman Spectroscopy

7.2.1 The Raman Spectrum of Pure MTBE

A pure MTBE[i] sample (>99.9 % by vol., Fischer) stored in a 0.2 ml injection glass sealed with an Al stopper was placed under the microscope for Raman measurement. The FT-IR spectrum of the sample was also obtained. These spectra are presented in Fig. 7.1.
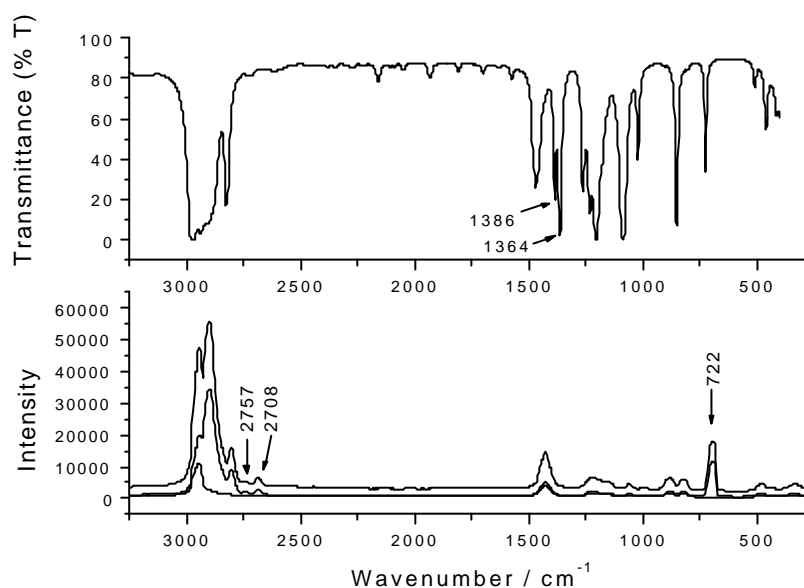

Fig. 7.1. FT-IR spectrum and Raman spectra of the MTBE sample. The FT-IR spectrum was acquired by use of a Fourier transform infrared spectrometer (Perkin Elmer FT-IR 1760X). The spectrum consisted of 4 scans at 4 cm^{-1} resolution. The cell used was a 0.0125 mm liquid cell with KBr windows. The Raman spectra were acquired by use of the 2nd monochromator and the 514.53 nm$_{hir}$ line of the Ar-ion laser as the excitation source. The upper Raman spectrum was obtained with no polarizer and the lower Raman spectra were obtained by use of a polarizer in the scattered beam. The sample was placed in the microscopic position.

The IR active symmetric CH$_3$ "umbrella" deformation at ~1375 cm^{-1} splits up in two bands in tert- butyl compounds, ~1391-1381 cm^{-1} and ~1368-1366 cm^{-1}, and the one with lowest wavenumber is the most intense[8a]. This point was also mentioned in Chap. 4.3.2, in the study of the Oppanol compound. The splitting is clearly seen (indicated with arrows) in the FT-IR spectrum shown above. The two Raman active overtones (2í) of the splitting are

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[i] MTBE (methyl tertiary butyl ether): CH$_3$OC(CH$_I$)$_3$

also observed, but they are relatively weak (indicated with arrows at ~2757 cm^{-1} and ~2708 cm^{-1}). The band at ~722 cm^{-1} is due to the C-C symmetric stretching involving the tertiary carbon in the tert-butyl group[5,9]. Thus it can be concluded that the two overtone bands and the band at ~722 cm^{-1} might candidate to be used to search for MTBE in the Raman spectra of gasoline. The two overtone bands however were so weak that they were not expected to be detected.

7.2.2 The Raman Spectra of Octane 98 Gasoline Samples

Several unleaded octane 98 gasoline samples were collected from different local gasoline stations (North Zealand) during the spring / summer 1998. Raman spectra of the gasoline samples were at first obtained by visible light excitation (514.53 nm$_{air}$ line of the Ar-ion laser). All of the gasoline samples were fluorescing resulting in a broad background in the Raman spectra. An example of such a fluorescent gasoline Raman spectrum will be presented in Chap. 7.3 (Fig. 7.3). Attempts to correct for the fluorescence backgrounds were done by means of mathematical data manipulation (first, second and third order polynomials were introduced to make a smooth background curve that could be subtracted from the spectra). Even though this correction resulted in remarkably better spectra, it was not at all possible to detect the two overtone bands at ~2757 cm^{-1} and ~2708 cm^{-1}, and neither the band at ~722 cm^{-1} was observed. Thus it was decided to investigate how large the MTBE content should be to make the bands visible in a Raman spectrum of such a home-made "artificial" gasoline mixture.

7.2.3 The Raman Spectra of Artificial Gasoline Samples

"Artificial" gasoline samples were prepared by mixing heptane with MTBE in different concentrations, 30-100 vol.% MTBE. (Heptane: >99.5 %, Fischer). The mixtures were made volumetrically and contained in 0.2 ml injection glasses sealed with an Al-stopper. Heptane was chosen because it gave little fluorescence. Surprisingly high fluorescence backgrounds were however observed in the Raman spectra. The fluorescence arose from the liquids themselves when mixed. This observation was seen repeatedly.

The characteristic MTBE band at ~722 cm^{-1} was observed in all of the spectra, but only weakly in the spectrum of the 30 vol.% MTBE mixture extensively covered by the fluorescence. It was observed that the more dilute the mixture the weaker became the band

at ~722 cm^{-1}, in comparison to the C-H stretching bands. The correlation between the C-H stretching band areas and the MTBE ~722 cm^{-1} butyl band areas was found by the area ratio method. The total integral under the C-H stretching and the ~722 cm^{-1} bands were found by using the software associated with the Raman instrument[10] (the fluorescence backgrounds were left out by user-guided experimentation). The area ratio, A(722 cm^{-1})/A(C-H stretching bands), was plotted versus the vol.% of MTBE. A clear tendency was observed; The points followed a straight line but scattered with some uncertainty (linear regression forced through the origin gave R^2 of 0.944). It was concluded that the area ratio plots might be used to determine the volumetric MTBE percentage in an unknown binary sample provided the fluorescence was not too strong.

7.2.4 Determination of the Detection Limit of MTBE in Drinking Water

MTBE dissolves in water and is able to penetrate soil and thus pollute the underground drinking water reserves. If that happen it can cause the water to be undrinkable due to poor taste and odour. We thus found it of interest to investigate if it should be possible to detect MTBE in drinking water down to very low concentrations. MTBE / water mixtures were prepared and the Raman spectra of the samples were obtained. Some of these spectra are presented in Fig. 7.2.

In Fig. 7.2 it is seen that it was possible to detect a level of MTBE content in water down to 0.50 vol.% by means of the butyl band at ~720 cm^{-1} without any problems. With respect to the sample containing 0.33 vol.% MTBE the band was faintly seen, and at lower concentrations it was not possible within a reasonable time to detect the band at all. It is therefore concluded that the detection limit of MTBE in water by means of our Raman instrument is on the order of 0.3-0.4 vol.%.
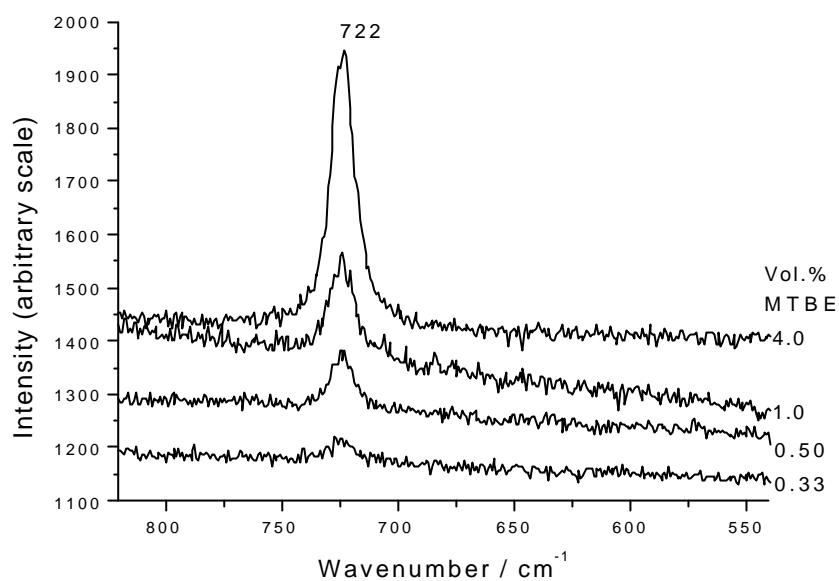
Fig. 7.2. The Raman spectra (820-540 cm^{-1}) of MTBE / water mixtures (0.33, 0.50, 1.0 and 4.0 vol.% MTBE) acquired by use of the 1st spectrograph (1800 grooves per mm) and the 514.53 nm$_{air}$ line of the Ar-ion laser as the excitation source (~200 mW, vertically polarized). The samples were contained in glass ampoules and placed in the macroscopic position (90° collection geometry).

7.3. Further Raman Spectroscopic Studies of Gasoline

7.3.1 Introduction

From the work dealing with determination of MTBE content in gasoline it was concluded that Raman excitation by visible light detection causes a broad fluorescence background in the spectra. Attempts to subtract the fluorescence background were done, but still it was difficult to detect small amounts of MTBE. Thus it was decided to try using the NIR-FT Raman technique (cf. Chap. 2.1) in the studies on gasoline with respect to aromatics. The technique has also been used previously to determine the content of aromatic in gasoline by use of partial least square regression models[7]. The present study was primarily focused on the benzene content in gasoline. The FT-Raman spectrum of a Danish unleaded octane 98 gasoline sample is shown in Fig. 7.3. In the figure the fluorescence Raman spectrum of the same gasoline sample is also included excited with green laser light.
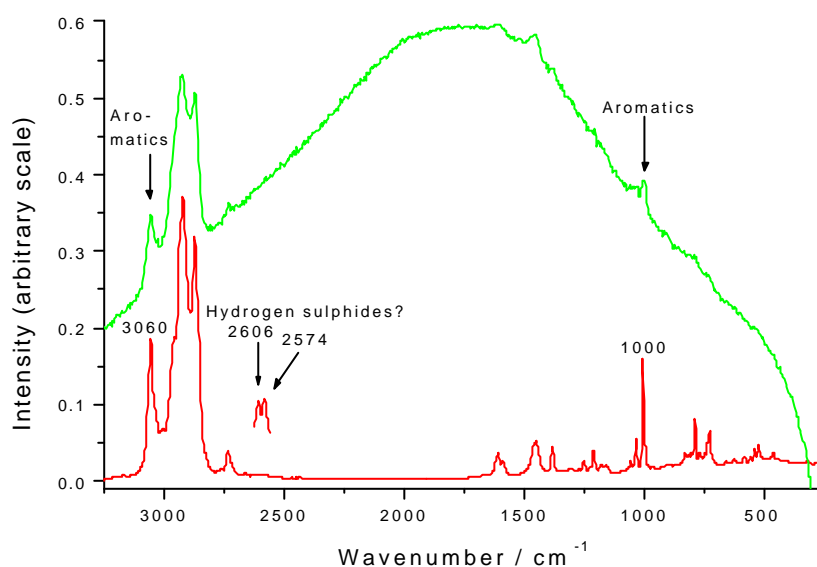

Fig. 7.3. Upper curve (green): The Raman spectrum of an unleaded octane 98 gasoline sample (from the area of Copenhagen), acquired by use of the 2nd monochromator (grating: 600 grooves/mm). The sample was placed in the microscopic position (10 x objective), i.e. 180 ° scattering. The 514.53 nm_{air} line from the Ar-ion laser was used as the excitation source (~200 mW). The obtained spectrum was divided by a factor of hundreds. Lower curve (red): The FT-Raman spectrum of the same gasoline sample. The sample was placed in a little tube of quartz. A small part of the spectrum (2625-2560 cm^{-1}) was blown up by a factor 20.

Aromatics were detected in both of the spectra at ~3060 cm^{-1} and ~1000 cm^{-1}. Before working further with this issue (in Chap. 7.3.3) we need to make some considerations about the two weak bands at (~2606 cm^{-1} and ~2574 cm^{-1}) clearly seen in the blown up part of the FT-Raman spectrum. The two bands probably are due to sulphur compounds.

7.3.2 Detection of Hydrogen Sulphide and Thiols in Gasoline?

Because of the position in a range where not many other compounds occur the two bands at ~2606 cm^{-1} and ~2574 cm^{-1} were interpreted (tentatively) as S-H stretching bands. H_2S bands were previously observed at ~2585 cm^{-1} in the Raman spectra of natural gas samples at high pressures (1.1 – 10.2 MPa$_A$) (see Chap. 4.3, Fig. 4.13.a). As discussed it was surprising that it was possible to detect it at all since H_2S is only present in Danish domestic distributed natural gas at very low concentrations. The Raman spectrum of a home-made H_2S gas sample was also obtained and a band at ~2617 cm^{-1} was observed (Chap. 4.3, Fig. 4.15), in close accordance with the value given in the literature for the gas phase, 2611 cm^{-1}. Thus it was obvious to assign the band at ~2606 cm^{-1} as symmetric S-H stretching (in gas phase). According to Danish gasoline companies the level of *total* sulphur content is typically about 50 ppm (maximum value is 150 ppm). Two methods are traditionally used to reveal hydrogen sulphides, a copper strip corrosion method and a "doctor test", ASTM[ii] 4952. It has however not been possible for us to get information on the level of H_2S content, because that it is not measured routinely. According to the gasoline companies however the level is very low, informed guess: <1 ppm[1]. Hydrogen sulphide is absolutely undesirable in gasoline[1]. Not only H_2S molecules but also hydrogen sulphides are present in gasoline as thiols[iii] (mercaptans). A strong polarized band in the S-H stretching region is found in the Raman spectrum for both the R-SH and Ar-SH sort of thiols. In the liquid phase the S-H stretching vibration is observed at 2590-2560 cm^{-1} for R-SH and at 2580-2560 cm^{-1} for Ar-SH[8b]. The same vibration is observed at 2598-2584 cm^{-1} for R-SH in the vapour phase[8b,11]. It is however presumed that the thiols only are present in gasoline in the liquid state. In the view of this, the two bands observed at ~2606 cm^{-1} and ~2574 cm^{-1} in the gasoline sample was interpreted as S-H stretching in hydrogen sulphide and in alkanethiols. It is quite interesting that the Raman method seems to be suited to measure

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[ii] ASTM:American Society for Testing and Materials
[iii] R-SH (alkanethiols) and Ar-SH (benzenethiols)

sulphur components in gasoline. When studying Raman spectra obtained of other components present in the gasoline, peaks near the S-H stretching area were observed, arising from overtones and combination bands. In a FT-Raman spectrum of o-xylene obtained recently by the author, a weak polarized band was observed ~2578 cm^{-1}. The same weak band has been observed in the literature ~2580 cm^{-1} (exact value was not given)[12a]. This value is very close to the observed band at ~2574 cm^{-1} in the FT-Raman spectrum of gasoline interpreted as discussed above as S-H stretching in thiols. Thus although the above-discussed interpretation is very tentatively it might be extended to other cases. As concluded previously further Raman studies of hydrogen sulphide and hydrogen sulphide mixtures need to be done.

7.3.3 Detection of Aromatics in Gasoline by FT-Raman Spectroscopy

At first it was decided to focus on the determination of benzene contents in gasoline by use of the area ratio method. Benzene was diluted by mixing it with heptane. Seven mixtures were prepared with different known concentration in the range 0.5 – 20 % by volume. The chemicals at hand were: Benzene from Merck (1782) and heptane (>99.5% by vol.) from Fischer. FT-Raman spectra of pure benzene and heptane samples were obtained. These spectra are presented in Fig. 7.4.
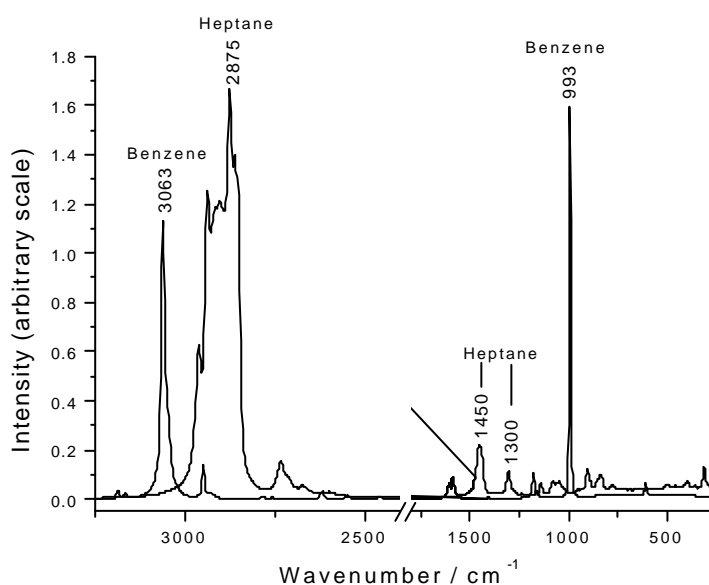

Fig. 7.4. The FT-Raman spectra of a pure benzene sample and a pure heptane sample. The samples were placed in small tube of quartz. Characteristic bands for each sample are indicated with sample name and the wavenumber position.

Suitable bands, i.e. characteristic bands in which the area can be easily determined, were searched for. The choices with respect to benzene were, as indicated in the figure, the ~3063 cm^{-1} (C-H symmetric stretching) and ~993 cm^{-1} (C-C stretching) bands. With respect to heptane the ~1450 cm^{-1} (C-H bending) and ~1300 cm^{-1} (-$(CH_2)_5$- in phase twist)[8a] bands were chosen. Even though the heptane band at ~2875 cm^{-1} is overlapped by several bands, it was decided to include it to get experience with peak fitting by the Microcal Origin[13]. The FT-Raman spectra of all the prepared benzene / heptane mixtures were obtained. These spectra are shown in Fig. 7.5.
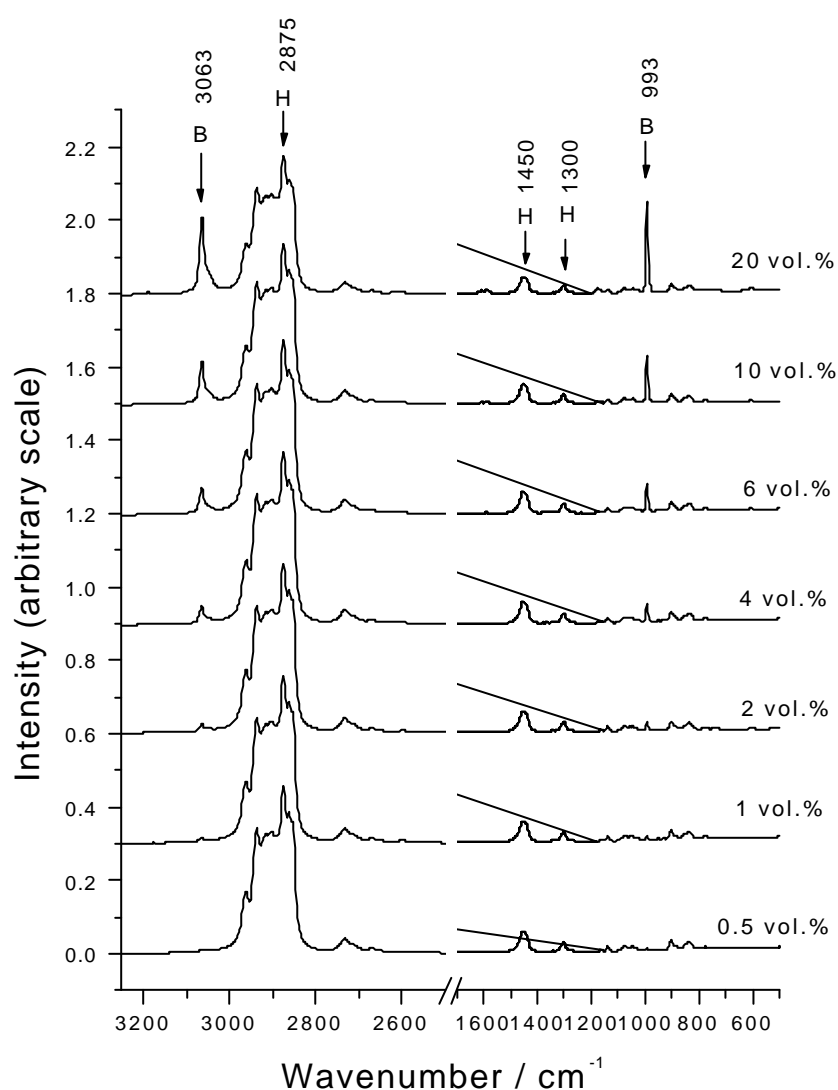

Fig. 7.5. The FT-Raman spectra of the benzene / heptane mixtures as a function of benzene concentration. The letter B indicates benzene bands and the letter H heptane bands.

It is clearly seen in Fig. 7.5 that the intensity of each of the two benzene bands (at ~3063 and ~993 cm^{-1}) increases relatively to the heptane bands as the benzene concentration increases. The intensity relations between the benzene bands and the heptane bands as a function of the benzene concentration in the mixtures were investigated. At first, areas of selected bands (indicated with arrows in the Figure) were determined by means of the Microcal Origin peak fitting module (PFM)[13]. The areas of the bands at ~3063 cm^{-1}, ~1450 cm^{-1}, ~1300 cm^{-1} and ~993 cm^{-1} could be determined without any complications. Because of the overlap of several bands in the C-H stretching region however some care must be applied, when resolving the band at ~2875 cm^{-1}. In Fig. 7.6 we present seven overlapping heptane C-H stretching bands from the upper FT-Raman spectrum shown in Fig. 7.5 (i.e. the 20 vol. % benzene mixture). The bands were resolved by the PFM and this result is also presented in Fig. 7.6. The Lorentz function was used as the fitting function.
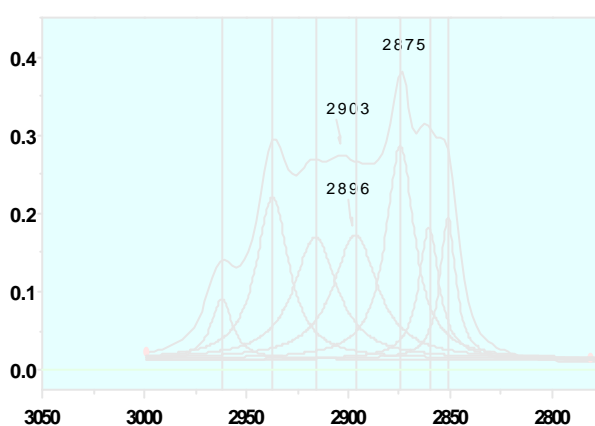

Fig. 7.6. <u>Upper curve</u>: The FT-Raman spectrum of a benzene / heptane mixture (20 vol.% benzene) in the aliphatic C-H stretching region (3000-2550 cm^{-1}). <u>Lower curves</u>: The resolved heptane bands (fitting function: Lorentz). Correlation coefficient: 0.99673.

It is seen that the bands can be well resolved. According to the horizontal lines included in the figure it is obvious that the wavenumber position for each band is the same before and after it has been resolved, except for one band. The band seemed to be at a wavenumber position of ~2903 cm^{-1} before it was resolved and at ~2896 cm^{-1} after it was resolved. This tendency was reproducible in all of the obtained FT-Raman spectra of the methane / heptane mixture presented in Fig. 7.5.

The areas of the bands at ~3063 cm^{-1}, ~2875 cm^{-1}, ~1450 cm^{-1}, ~1300 cm^{-1} and ~993 cm^{-1} were all determined. The baselines were all estimated by "free form". All the determined areas are listed in Appendix E. The area ratio, A(benzene band) / A(heptane band), was plotted as a function of the benzene concentration. This work is presented in Fig. 7.7. As it is seen there is an obvious linear correlation between area ratio and the benzene concentration. Thus it was concluded that the presented curves can be used for a determination of the benzene contents in benzene / heptane mixtures. It was furthermore concluded that it should be possible by the same area ratio method to determine the benzene contents in gasoline. Before we go further, into this issue however some considerations had to be done.

Besides benzene there are other aromatics present in gasoline, that is methylbenzene (toluene), ethylbenzene and dimethylbenzene (xylene) isomers (ortho-, meta- and para-xylene) to mention the simplest. Benzene and these simple aromatics are often given as the acronym BTEX in the literature. The FT-Raman spectrum of a pure benzene sample was shown in Fig. 7.4. It was decided to obtain FT-Raman spectra of the "TEX" too. The chemicals were provided: toluene (PA, Ferak 01548), ethylbenzene (PA, Fluca 03030), o-xylene (S, Merc 808697), m-xylene (PA, Fluca 95672) and p-xylene (PA, Fluca 96682). The FT-Raman spectra were obtained of all of the samples. The C-H stretching parts of the spectra (3100–2800 cm^{-1}) are presented in Fig. 7.8. In the figure are also included the FT-Raman spectrum of an octane 98 gasoline sample (shown in Fig. 7.3) and the FT-Raman spectrum of benzene (shown in Fig. 7.4). The gasoline spectrum is presented as a dashed curve and the benzene spectrum as a dotted curve.

The above discussed area method to determine benzene content in heptane (or gasoline) was e.g. based on the aromatic C-H stretching band at ~3063 cm^{-1}. As it is seen in the Fig. 7.8 each of the aromatics has a band near this wavenumber position. In fact the bands are so close to each other that it (so far) not has been possible to resolve them. It is therefore concluded that the band at ~3063 cm^{-1} is useless, when determining the *benzene* content in gasoline by the discussed area ratio method. But the possibility remains that the band could be used in a determination of the total aromatic content.
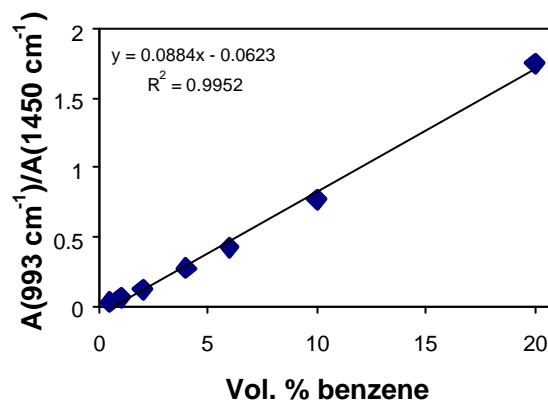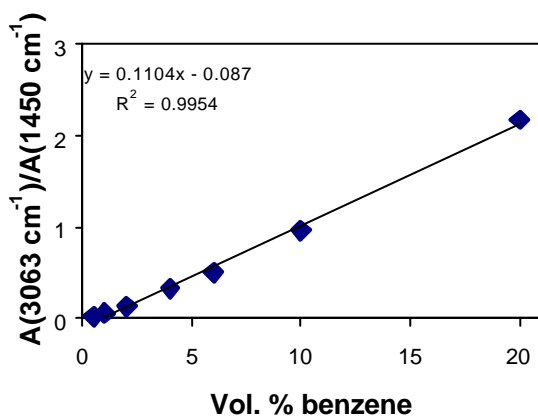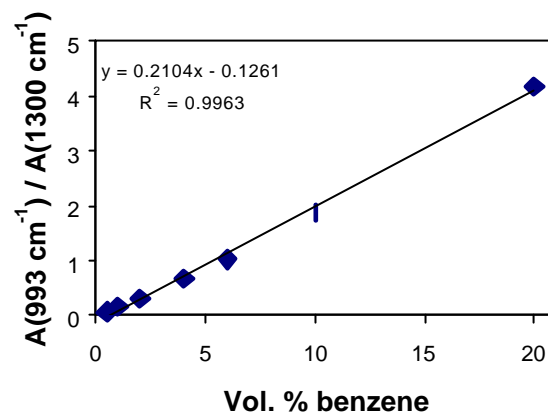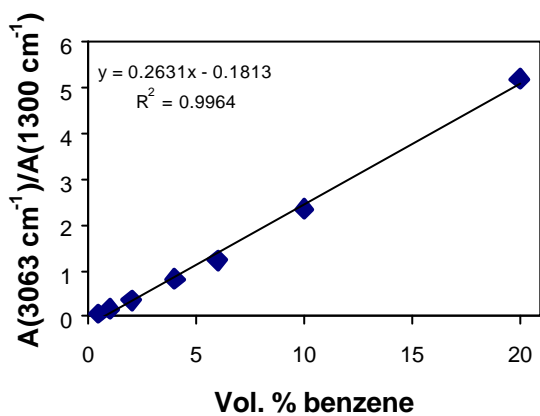
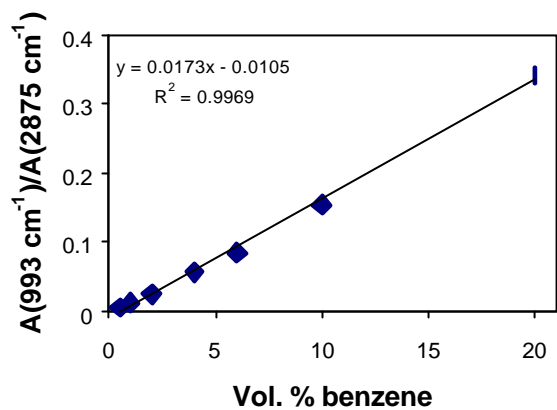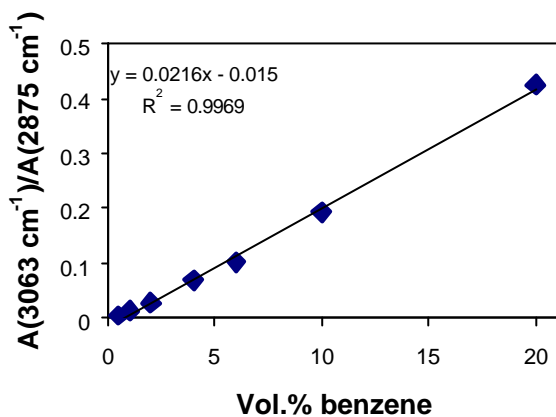**Fig. 7.7** The area ratio A(benzene) / A(heptane) as a function of benzene concentration by volume.

The CH$_3$ symmetric stretching vibration band occurs near 2882-2862 cm^{-1} (and the antisymmetric near 2972-2952 cm^{-1})[8a]. In the FT-Raman spectrum of the octane 98 gasoline sample the symmetric stretching band was observed at ~2875 cm^{-1}, as seen in Fig. 7.8. With respect to the toluene and xylene isomers however the CH$_3$ symmetric stretching bands were observed at a lower wavenumber position ~2863 cm^{-1}. For molecules with one or more CH$_3$ groups attached directly to a benzene ring, two bands are regularly observed in the Raman spectra, at positions near 2925 cm^{-1} and 2865 cm^{-1}. These two bands are assigned as the overtone (2í) of the CH$_3$ bending vibration at ~1450 cm^{-1} in Fermi resonance with the CH$_3$ symmetric stretching vibration[14]. This phenomenon is clearly seen in the FT-Raman spectra of toluene and the xylene isomers shown in Fig. 7.8 (the overtone at ~2920 cm^{-1} and the CH$_3$ symmetric stretching at ~2863 cm^{-1}). Because of the Fermi resonance the overtone bands occur with a relatively high intensity and the CH$_3$ symmetric stretching bands with relatively low intensities. Thus it was decided that the band at ~2875 cm^{-1} should be used in the area ratio method, but some uncertainty might arise due to the CH$_3$ symmetric stretching bands belonging to the aromatics.
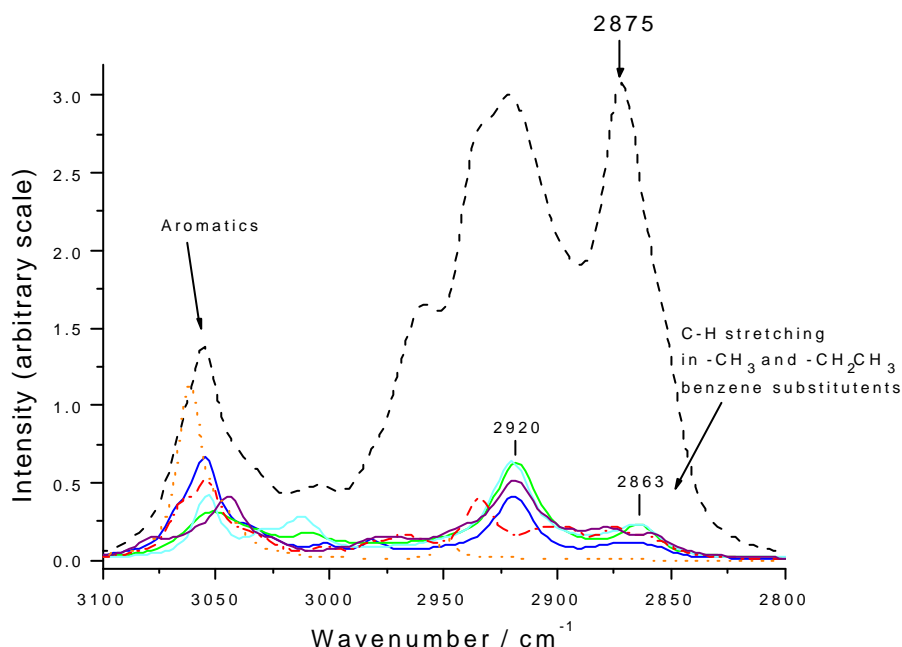

Fig. 7.8. The FT-Raman spectra (3100-2800 cm^{-1}) of toluene, ortho-, meta- and para-xylene (lower curves), ethylbenzene (dashed dotted curve), benzene (dotted curve) and an octane 98 gasoline sample (dashed curve).

The FT-Raman spectra of the BTEX and the octane gasoline spectrum are presented in Fig. 7.9 in the wavenumber ranges of 1080-960 cm^{-1} (A) and 860-700 cm^{-1} (B).
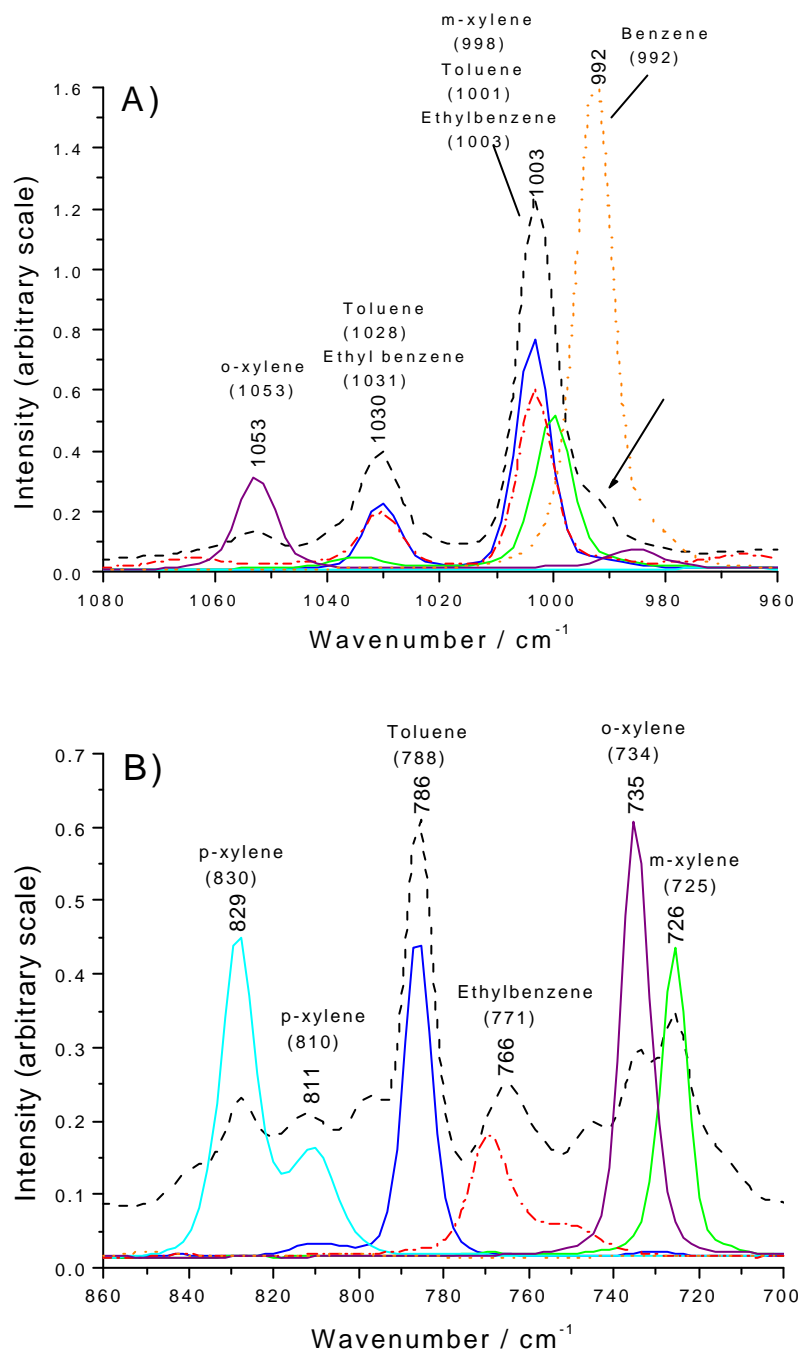

Fig. 7.9. The FT-Raman spectra of toluene, ortho-, meta- and para-xylene (solid curves), ethylbenzene (dashed doted curve), benzene (dotted curve) and the octane 98 gasoline sample (dashed curve). Wavenumbers in parentheses are values given in the literature[12a,b]. A) 1080-960 cm^{-1}, and B) 860-700 cm^{-1}.

At first it was investigated if the benzene C-C stretching band at ~993 cm^{-1} could be used as a suitable band in the area ratio method. The bands due to aromatics are clearly seen in the FT-Raman spectrum of the gasoline sample, shown in Fig. 7.9.A. The most intense one in the spectrum is the band at ~1003 cm^{-1} arising from vibrations in m-xylene, toluene and ethylbenzene. Very close to this band the benzene C-C stretching vibration is observed at ~993 cm^{-1} as a shoulder. Attempts to resolve the two bands, in the same way as described previously, were done successfully as shown in Fig. 7.10.A. The area of the band at ~993 cm^{-1} was determined to 0.09931 cm^{-1}·counts. Even though the band at ~2875 cm^{-1} in FT-Raman spectrum of the gasoline sample is not a "pure" heptane band, it was decided to try to use it in the are ratio method to see if the magnitude of the content in the gasoline as determined comes out well.

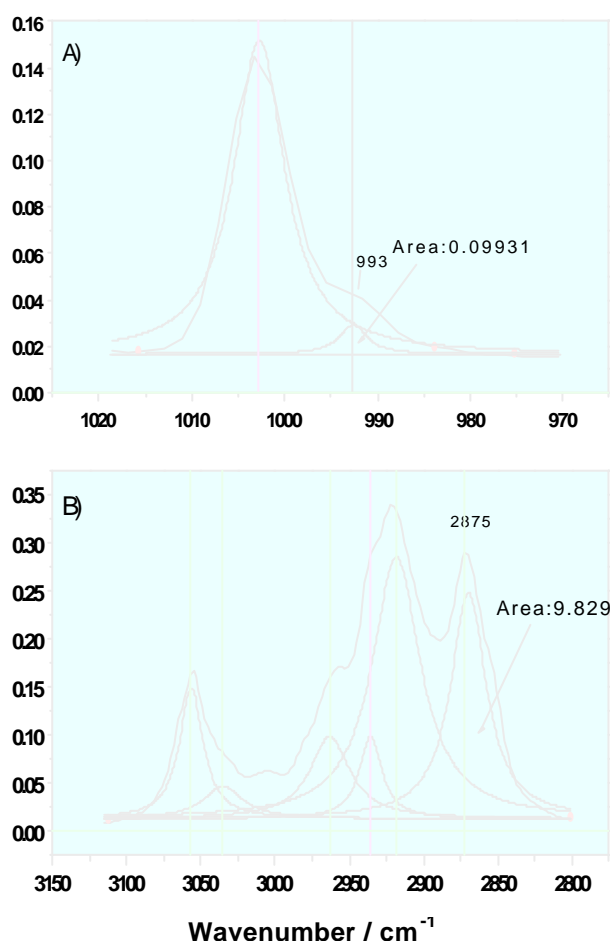**Fig. 7.10.** FT-Raman spectrum of the octane 98 gasoline sample. A) The resolved benzene band at ~993 cm^{-1}. Correlation coefficient: 0.98738. B) The resolved CH$_3$ symmetric stretching band ~2875 cm^{-1}. Correlation coefficient: 0.99444.

At first the gasoline band at ~2875 cm^{-1} was resolved from the other C-H stretching bands in the wavenumber range 3120-2600 cm^{-1}, as shown in Fig. 7.10.B. The area of the band was determined to 9.829 cm^{-1}·count. Thus the area ratio between the two bands were determined to 0.0101.

$$\frac{A(993cm^{-1})}{A(2875cm^{-1})} = \frac{0.09931}{9.829} = 0.0101$$

By using the equation indicated in the Fig. 7.7.b (y = 0.0173x – 0.0105, found by linear regression) the vol.% benzene (x) was calculated to be 1.2 %. The magnitude of the value seems reasonable, but the value is probably lower. It was however included in this chapter for illustrative reasons.

Then it was decided to turn the attention to the FT-Raman spectra of toluene, ethylbenzene and the xylene isomers. There was, as it can be seen in Fig. 7.8 and 7.9.A, a high degree of band overlap in the spectra of toluene and ethylbenzene. The same was the case for the xylene isomers as also concluded in the literature[15]. Characteristic bands for each compound were searched for in the FT-Raman spectra. In the wavenumber range of 860-700 cm^{-1} it was observed that toluene has a characteristic band at ~786 cm^{-1} and ethylbenzene one at ~766 cm^{-1}. Furthermore para-, orto- and meta-xylene have characteristic bands at ~829 cm^{-1}, ~735 cm^{-1} and ~726 cm^{-1} respectively. Unfortunately one cannot be sure that the octane 98 gasoline band at ~726 only arises due to vibrations in meta-xylene. As described in the previous chapter, MTBE shows a band at ~722 cm^{-1} due to symmetric C-C stretching vibrations involving the tertiary carbon in the tert-butyl group. It seems probable that the band at ~726 cm^{-1} in the FT-Raman spectrum of the gasoline sample could be a combination of vibrations in both meta-xylene molecules and MTBE molecules. Moreover another characteristic m-xylene band, which can be easily resolved, was found at ~278 cm^{-1}, as shown in Fig. 7.11. Even though there is a high degree of spectral overlap between the aromatic compounds, it ought to be possible (by means of the above given characteristic bands) to determine the content of each compound by means of the area method.
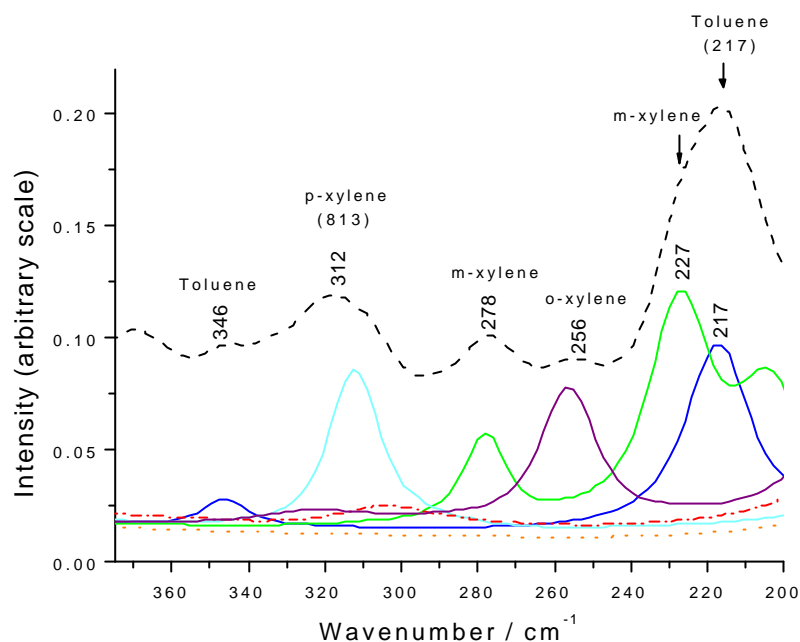
Fig. 7.11. FT-Raman spectra (375-200 cm^{-1}) of toluene, ortho-, meta- and para-xylene (solid curve), ethylbenzene (dashed dotted curve), benzene (dotted curve) and the octane 98 gasoline sample (dashed curve). Wavenumbers in parentheses are values given in the literature[12a,b], (parentheses indicate that an exact value is given in the literature).

7.4. Conclusions

The Raman spectroscopic studies of gasoline were found to be very interesting and informative. One aim was to investigate whether Raman spectroscopy using visible light excitation could be used to determine the MTBE contents in gasoline samples. Two overtone bands (from the symmetric CH$_3$ umbrella deformation) at ~2757 cm^{-1} and ~2708 cm^{-1}, plus a band at ~722 cm^{-1} arising from vibrations in the tert-butyl group, were characteristic for the Raman spectrum of MTBE. The two overtone bands were too weak to be detected in the Raman spectrum of the examined gasoline sample. The band at ~722 cm^{-1} however was so intense that it ought to be observed if MTBE was present, even at low concentrations. Because of the broad fluorescence backgrounds in the spectra it was concluded that the sensitivity of the Raman method in the present version is not particularly high. The MTBE was not detected at all in any of the obtained Raman spectra of several gasoline samples. The Raman spectra of the "artificial" gasoline samples (prepared by mixing heptane with MTBE) were also influenced by a fluorescence background but to a

lesser degree. The detection limit of the band at ~722 cm^{-1} in these mixtures was in our experimental setup determined to be around 30 vol.% MTBE. The ratio between the area of the band at ~722 cm^{-1} and all of the C-H stretching bands were plotted as a function of the MTBE content. A clear linear correlation was found, but with some uncertainty (R square was 0.944). Finally the detection limit of MTBE in drinking water was determined to 0.3-0.4 vol.% MTBE.

In our spectroscopic studies of gasoline samples with respect to aromatics, the FT-Raman technique was chosen because of the fluorescence under visible light excitation. Two weak bands were observed at ~2606 cm^{-1} and ~2574 cm^{-1} in the Raman spectra of the gasoline samples. It was concluded that such bands might arise from S-H symmetric stretching in hydrogen sulphide and thiols, respectively. "Artificial" gasoline samples were prepared by mixing heptane with benzene. FT-Raman spectra of these samples were acquired. It was obvious that two benzene bands at ~3063 cm^{-1} and ~993 cm^{-1} increased in intensity relatively to three chosen heptane bands at ~2875 cm^{-1}, ~1450 cm^{-1} and ~1300 cm^{-1}, as the benzene content in the mixture was increased. The bands (i.e. the two mentioned benzene bands and the three heptane bands) were resolved and areas determined. The area ratio, A(benzen band) / A(heptane band), was plotted as a function of the benzene content and clear linear correlations were found in all six plots (tendency lines determined by regression gave R square of order 0.996).

In addition to the FT-Raman spectra of an octane 98 gasoline sample and a benzene sample, FT-Raman spectra of toluene, ethylbenzene and the xylene isomers were also obtained. All these spectra were compared. It was with success possible to resolve the benzene band at ~992 cm^{-1} in the FT-Raman spectrum of the gasoline sample. The area of this band was determined and so was the CH$_3$ symmetric stretching band in the same spectrum. The area ratio was determined and an estimate of the benzene content was given (probably below 1.2 vol. benzene). Finally characteristic bands for toluene, ethylbenzene and the xylene isomers were found. With that in mind it should be interesting to determine the contents of these compounds in gasoline, also by Raman spectroscopy. In further work with Raman spectroscopic studies of gasoline it should be very interesting to remeasure a series of gasoline samples with exactly known composition.

7.5. References

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