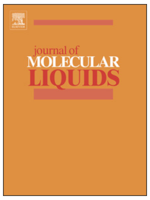
Journal of Molecular Liquids 196 (2014) 26–31

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq



# Vibrational analysis of neat liquid *tert*-butylmethylether

K.B. Beć *, A. Kwiatek, J.P. Hawranek

*Faculty of Chemistry, University of Wrocław, F. Joliot-Curie 14, 50-383 Wrocław, Poland*

ARTICLE INFO

*Article history:*
Received 16 January 2014
Accepted 26 February 2014
Available online 14 March 2014

*Keywords:*
IR dispersion
Complex refractive index
Neat liquid *tert*-butylmethylether (TBME)
Thin film IR spectra
Low temperature matrix IR spectra
Anharmonic vibrational analysis
B2PLYP/N07D

ABSTRACT

Among aliphatic ethers, the most known is *tert*-butylmethylether (TBME), mainly for its significance in the fuel industry. It was the subject of numerous investigations, including industrial, environmental and medical studies. The literature however is lacking of any insightful infrared studies of TBME in neat liquid phase. In this work we determined the optical constants of TBME, from transmission studies in the IR range (11,700–560 $cm^{-1}$). The use of quantitative thin film recording techniques was essential due to the high absorption of neat liquids in the MIR range. Low temperature matrix investigation was also carried out, to elucidate details of the vibrational spectrum of TBME. The experiment was supported by an anharmonic vibrational analysis including the simulation of experimental spectrum, based on the B2PLYP/N07D level of theory. The chosen method delivered good results with a relatively modest computational cost.

## 1. Introduction

The wide utilization of *tert*-butylmethylether (TBME) in the fuel industry [1,2] in the past years led to numerous studies of its physico-chemical properties [3,4], as well as environmental [5–7] and medical [8] research. In past decades the worldwide annual production volume of TBME reached 18 million tons [9], and over 3 million tons in the EU only [10]. Surprisingly the infrared properties of liquid *tert*-butylmethylether were never deeply investigated. In this work we aimed to obtain an insight into the vibrational properties of the studied ether through a broad spectral range complex refractive index measurements and a detailed vibrational analysis, with the hope to a better understanding of factors determining the vibrational spectra of TBME in the neat liquid phase. The determination of these data required the use of thin-film quantitative techniques in the MIR region due to strong absorption in the studied region. The determined $k(\nu)$ spectrum revealed broadened bands in several spectral regions. With the hope to elucidate more details in the vibrational spectrum of TBME, a low temperature matrix isolation investigation was carried out. Experimental data were supported by a detailed anharmonic vibrational analysis. The final band assignment procedure was based on a spectrum modeled with the use of the DFT-B2PLYP/N07D computational method and also PED analysis. The obtained results allowed for a detailed band identification in the vibrational spectrum of *tert*-butylmethylether.

The results of investigation reported here are also indispensable for the determination of high frequency dielectric properties of *tert*-butylmethylether in the liquid phase.

## 2. Experimental

The TBME sample was of the highest purity available from Aldrich, additionally dried and stored over molecular sieves under nitrogen. The density of TBME measured on an Anton Paar DMA 48 density meter was 0.7353 $g \cdot cm^{-3}$ at 298.15 K and the refractive index at sodium D-line was 1.36684 also at 298.15 K.

NIR and MIR spectra were recorded on a Nicolet Magna 860 FT-IR/Raman spectrometer. To minimize the effect of possible drift, the empty chamber was measured as a reference spectrum before and after the sample measurement. All measurements were carried out at controlled temperature 298 K.

Due to strong absorption bands, the MIR spectra were recorded in thin film cells assembled for the purpose of this work from KBr windows polished to high flatness, monitored in sodium light on a glass optical flat. The spacers were prepared out of aluminum foils of required thickness. The geometrical parameters of the cell cavity were determined by fitting the experimental interference spectrum of the empty cell with the theoretical ones, using the procedure based on the earlier derived algorithm. Several KBr cells were used with a thickness ranging from 4 to 8 μm. The resolution was set at 0.5 $cm^{-1}$ and a scan number of 512 was chosen to ensure a good signal to noise ratio.

Spectra in the NIR range were measured on the same instrument. A $CaF_2$ beamsplitter with the MCT-A detector (in the region 11,700–8000 $cm^{-1}$) and DTGS detector (in the 8000–4000 $cm^{-1}$ region). The resolution was maintained on a 0.5–1 $cm^{-1}$ level, depending on the recorded subregion. Thermostated quartz cells (Hellma) of 5 and 10 mm thickness were used in the upper NIR region (11,700–8000 $cm^{-1}$); in the lower region, cells of 0.1 and 0.5 mm thickness were used. The absorbance spectrum of the liquid was obtained by subtraction of the empty

---

* Corresponding author. Tel.: +48 71 3757 249; fax: +48 71 3282 348.
*E-mail address:* krzysztof.bec@chem.uni.wroc.pl (K.B. Beć).

http://dx.doi.org/10.1016/j.molliq.2014.02.028
0167-7322/

cell spectrum from the spectrum of the cell filled with the liquid. Subsequently, the absorbance spectrum was recalculated to yield the spectrum of the absorption index $k(\nu)$.

FT-Raman spectra were measured on a Nicolet Magna 860 FTIR spectrometer interfaced with a FT-Raman accessory. The samples were illuminated by a Nd:YVO$_4$ laser line at 1.064 nm with a power of 0.2–0.3 W. A CaF$_2$ beamsplitter was used in combination with an InGaAs detector. The interferograms were averaged over 1024 scans. The resolution of the spectra was 2 cm$^{-1}$.

Infrared spectra of TBME in argon and nitrogen matrixes were recorded in a reflection mode on a Bruker 113v FT-IR spectrometer equipped with a liquid N$_2$ cooled MCT detector (4000–400 cm$^{-1}$). The resolution of collected spectra was set as 0.5 cm$^{-1}$ and the concentration of TBME/matrix gas mixtures varied in the range 1/100–1/800. Gas mixtures were prepared by standard manometric techniques and sprayed onto a gold-plated copper mirror held at 17 K during matrix deposition by a closed cycle helium refrigerator (Air Products, Displex 202A). The matrixes were maintained at the temperature of 12 K during infrared spectra collection. The spectra of matrixes after their annealing to 33 K for 10 min were also recorded.

## 3. Data processing

From the transmission spectra in the entire measured region, the spectra of both components of the complex refractive index:

$$\hat{n}(\nu) = n(\nu) + ik(\nu) \tag{1}$$

were obtained by the use of the procedure described previously [11,12]; $i = \sqrt{-1}$ and $\nu$ denotes wavenumbers [cm$^{-1}$] throughout this work. The spectrum was processed as a whole from 11,700 to 560 cm$^{-1}$. To begin with, the experimental $k(\nu)$ spectrum was corrected for dispersion distortion. To ensure a good accuracy for the $k(\nu)$ spectrum, the reference point needed for the preliminary processing of data with the use of the dispersion distortion correction procedure was taken at the sodium D-line (589.6 nm). At the second stage, the $n(\nu)$ spectrum was calculated using several values of the refractive index in the visible region and the modified Kramers–Krönig procedure [13].

The spectra of the complex refractive index are required for the determination of high frequency dielectric properties of studied liquid, which are in progress. Moreover, the accurate determination of the absorptive properties of a liquid can be based only on the absorption index spectrum $k(\nu)$, because of strong distortion of thin layers transmission spectra [11].

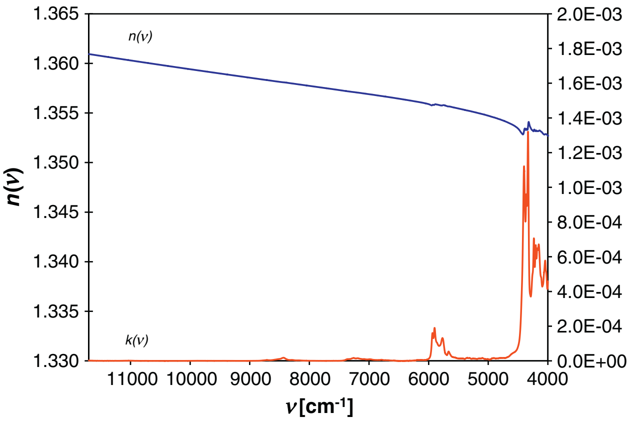


**Fig. 1.** Spectrum of the complex refractive index of TBME in the NIR range (11,700–4000 cm$^{-1}$).

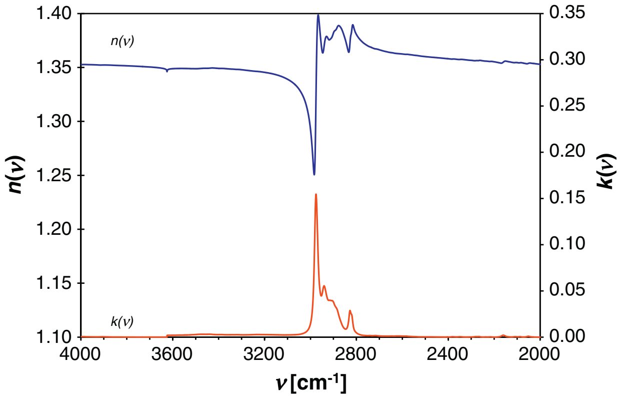


**Fig. 2.** Spectrum of the complex refractive index of TBME in the upper MIR range (4000–2000 cm$^{-1}$).

## 4. Results and discussion

### 4.1. Complex refractive index in the NIR range (11,700–4000 cm$^{-1}$)

The complete spectrum of the complex refractive index of TBME in the measured NIR range (11,700–4000 cm$^{-1}$), covering the first and second overtone regions, is presented in Fig. 1.

As can be seen for the studied ether, the NIR bands are very weak except for bands in the region 6000–4000 cm$^{-1}$. In general, the range between 6000 and 5600 cm$^{-1}$ reflects well the doubled 3000–2800 cm$^{-1}$ region. The analysis of overtones for the studied molecule was not the aim of this work and will not be presented here. However, the $\hat{n}(\nu)$ spectrum had to be determined in the NIR region, since its knowledge is essential for an accurate determination of the $\hat{n}(\nu)$ spectrum in the MIR region [13].

### 4.2. Complex refractive index in the MIR range (4000–560 cm$^{-1}$)

Spectra of the complex refractive index of TBME separated into the upper MIR region (4000–2000 cm$^{-1}$) and lower MIR region (2000–560 cm$^{-1}$) can be found in Figs. 2 and 3, respectively. The detailed discussion of the MIR range will be presented later in this paper. The Raman spectrum is presented in Fig. 4.

### 4.3. Matrix isolation studies

The determined absorption index spectrum reveals several broadened bands, mainly in the 2940–2870 cm$^{-1}$ region and in the 1500–1350 cm$^{-1}$ region. With the aim to achieve a higher level of detail

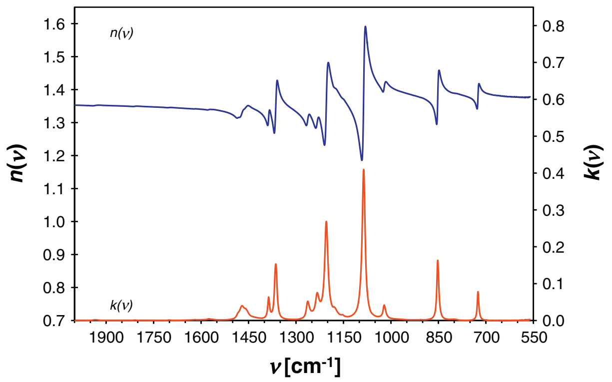


**Fig. 3.** Spectrum of the complex refractive index of TBME in the lower MIR range (2000–560 cm$^{-1}$).