



# Computational and quantum chemical study on high-frequency dielectric function of *tert*-butylmethyl ether in mid-infrared and near-infrared regions



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## ABSTRACT

Complex dielectric function of *tert*-butylmethyl ether (TBME) was determined and analyzed in a broad spectral region covering mid-infrared (MIR) and near-infrared (NIR) regions (6500–560 cm<sup>-1</sup>). Spectra of the complex electric permittivity and complex molecular polarizability have been derived from complex refractive index spectra. The molar vibrational polarization ( $P^{vib}$ ) corresponding to individual modes has been estimated based on the data derived from fitting damped harmonic oscillator model to the experimental complex permittivity spectrum. Factors determining the dielectric functions due to vibrational resonance absorptions corresponding to fundamental and non-fundamental (overtone and combination modes) modes were taken into account. Direct comparison of contributions to total  $P^{vib}$  value stemming from corresponding fundamental and non-fundamental modes has been carried out and discussed for the first time. In order to identify overtones and binary combination modes, quantum chemical calculation of the vibrational spectrum of *tert*-butylmethyl ether was performed for MIR and NIR regions. Fully anharmonic approach by means of generalized second-order vibrational perturbation theory (GVPT2) was applied on DFT-B2PLYP/SNST level. An accurate reproduction of experimental data was achieved with subsequent assignment of fundamental and non-fundamental bands, which enabled detailed discussion of relations between dielectric contributions of fundamental and non-fundamental modes of *tert*-butylmethyl ether.

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## 1. Introduction

Dielectric properties, including electric permittivity and molecular polarizability, are important parameters of materials, and various methods of determination have been proposed for different physical mediums [1,2,3,4]. The importance of these properties has been growing in recent years due to their significance in the field of photonics and in development of novel optical materials [5,6,7,8,9]. The dielectric properties studied in this work, electric permittivity and molecular polarizability, depend on wavelength of the interacting electromagnetic wave. In case of non-absorbing spectral regions of any given material, its dielectric functions present a monotonic course, with usually gentle decrease of the function value towards higher wavelength; this can be described as ‘normal dispersion’ of dielectric function [10]. Moreover,

the dielectric function is complex; the imaginary part corresponds to the absorption of energy in medium. Within regions of normal dispersion, the imaginary part of the function is equal to zero. In case of mid-infrared (MIR) and near-infrared (MIR) regions, within which most molecular liquids exhibit resonance absorption, the real and imaginary parts of the dielectric functions change rapidly. These regions of non-monotonic change of the spectral curves are often referred to as regions of ‘anomalous dispersion’ [10]; within the boundaries of anomalous dispersion the characterization of electric permittivity or any related property is not straightforward. However, the complex electric permittivity is closely related to complex refractive index, which in turn can be obtained by spectroscopic methods. Different approaches to the determination of complex refractive index in the MIR region have been reported, with two of them coming in forward as the most reliable ones; these use either ATR or transmittance methods [11,12,13,14,15]. The ATR-based method is very sensitive to high precision of control of the incidence angle, among other limitations, but allows for investigation of complex species, including aqueous solutions [16,17].

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Transmittance approach requires the use of quantitative thin-film technique in the MIR region, due to high values of absorption index in the fundamental vibrations region. However, for most molecular liquids in bulk phase the thin-film transmittance spectroscopy approach offers considerable advantages.

Moreover, knowledge of the complex electric permittivity spectrum allows determining the macroscopic molar vibrational polarization value of the medium ( $P^{vib}$ ). The characterization of polarization of any media is most often limited to the determination of electronic, and eventually ionic, and orientational polarization contributions. The contribution to the total polarization stemming from vibrational polarization is less significant than other contributions; certainly it is not negligible, however. In the past,  $P^{vib}$  values were reported for numerous molecular liquids. These studies were limited, however, to entire spectral subregions, narrowed by boundaries of normal dispersion [18,19]. There were attempts to ascribe  $P^{vib}$  values corresponding to individual bands, but only for smaller molecules, which give relatively simple vibrational absorption lineshapes [20]. Moreover, these studies were limited to fundamentals in the MIR region.

*tert*-Butylmethyl ether (TBME; methyl *tert*-butyl ether, MTBE; 2-methoxy-2-methylpropane) is well known for its application in the role of oxygenated fuel additive [21]. It is also widely used solvent and reaction constituent in the pharmaceutical and chemical industry and research [22,23,24]. The significance of TBME is well highlighted by the amount of monographs published so far [21,25,26] and the fact that high impact papers reporting on TBME influences on health are published on regular basis [27,28,29]. Aliphatic ethers generally do not self-associate in neat liquid phase, and spectroscopic properties of TBME are in particular insensitive to concentration effects, due to sterical hindrance. Hence, the theoretical spectra of TBME can be more reliably used for approximation of experimental data obtained in neat liquid phase. Therefore, it offers a good basis for establishing the approach to the detailed analysis of dielectric properties of molecules over MIR-NIR regions, which is reported in this study.

In the present study we have aimed at investigation of dielectric properties of MTBE throughout the MIR and NIR spectral regions, and to further explore its vibrational properties, including a detailed analysis of non-fundamental bands. A detailed reproduction of MIR and NIR spectra through quantum mechanical calculation of non-fundamental vibrations is being presented for TBME; these results are being subsequently used for a detailed analysis of dielectric spectra and molar vibrational polarization corresponding to weak, non-fundamental bands. In our previous work we characterized the complex refractive index of TBME over NIR and MIR regions and provided thorough band assignments for fundamentals [30]. Basing on the previous study, we obtained the spectra of complex dielectric permittivity and complex molecular polarizability, which will be reported here. Subsequently, molar vibrational polarization ( $P^{vib}$ ) of TBME will be derived. By employing the recently developed algorithm of simultaneous fitting of the real and imaginary parts of the damped harmonic oscillator model to the experimental data [31], contributions to  $P^{vib}$  value stemming from individual vibrational modes will be calculated. We will make a novel attempt to analyze the impact of non-fundamental modes on the dielectric properties of TBME in the MIR and NIR regions. To enable this, fully anharmonic calculation of theoretical MIR and NIR spectra of TBME will be carried out. By reproducing the spectral lineshape, which includes fundamentals, first overtones and binary combinations, a detailed assignment for NIR-MIR region of TBME will be presented. Moreover, an accurate theoretical reproduction of experimental spectrum will provide additional valuable information about the number of components influencing the experimental spectral envelope, thus supporting the model fitting procedure. Subsequently, comparison of  $P^{vib}$  values arising from fundamentals and their respective overtones and combination bands will be provided as well.

## 2. Materials and methods

### 2.1. Determination of complex dielectric permittivity and complex polarizability spectra

The spectrum of complex electric permittivity, which can be defined as Eq. (1) [10]

$$\hat{\varepsilon}(\nu) = \varepsilon'(\nu) + i\varepsilon''(\nu) \quad (1)$$

is closely related to the spectrum of complex refractive index  $\hat{n}(\nu)$ . Note, that throughout this work, with the aim to keep good accordance with the vibrational properties of TBME, we shall present the dielectric properties as functions of wavenumber  $\nu$ , denoted in  $\text{cm}^{-1}$ . Both parts of the complex electric permittivity are interrelated to each other, satisfying Kramers-Krönig relations (Eqs. (2) and (3)).

$$\varepsilon'(\nu_i) = \varepsilon_\infty + \frac{2}{\pi} P \int_0^\infty \frac{\nu \varepsilon''(\nu)}{\nu^2 - \nu_i^2} d\nu \quad (2)$$

$$\varepsilon''(\nu_i) = -\frac{2\nu_i}{\pi} P \int_0^\infty \frac{\varepsilon'(\nu) - \varepsilon_\infty}{\nu^2 - \nu_i^2} d\nu \quad (3)$$

In Eqs. (2) and (3)  $P$  denotes Cauchy principal value. The real and imaginary parts of the complex electric permittivity can be expressed by, respectively, the real and imaginary parts of the refractive index, following the relations defined in Eqs. (4) and (5).

$$\varepsilon'(\nu) = n^2(\nu) - k^2(\nu) \quad (4)$$

$$\varepsilon''(\nu) = 2n(\nu)k(\nu) \quad (5)$$

The real and imaginary parts of the refractive index,  $n(\nu)$  and  $k(\nu)$  respectively, often referred to as 'optical constants' [11], have been reported for NIR and MIR regions of TBME previously [30].

From the complex electric permittivity the complex polarizability (Eq. (6))

$$\hat{\alpha}(\nu) = \alpha'(\nu) + i\alpha''(\nu) \quad (6)$$

can subsequently be derived, following the Clausius-Mossotti relation, which for Avogadro number  $N_A$  of molecules can be expressed as Eq. (7).

$$\frac{\hat{\varepsilon}(\nu) - 1}{\hat{\varepsilon}(\nu) + 2} \frac{M}{d} = \frac{n^2(\nu) - 1}{n^2(\nu) + 2} \frac{M}{d} = \frac{4}{3} \pi N_A \hat{\alpha}(\nu) \quad (7)$$

In Eq. (7),  $M$  is the molar mass in  $\text{g mol}^{-1}$  and  $d$  is density in  $\text{g cm}^{-3}$ . The relation expressed as Eq. (7) holds for non-polar, isotropic media; it does not hold for any wavelength, but is applicable to the infrared region, since the frequency of radiation is high enough in relation to the frequency of corresponding molecular movement. The real and imaginary parts of the complex molecular polarizability can subsequently be expressed as Eqs. (8) and (9).

$$\alpha'(\nu) = \frac{3M}{4\pi d} \frac{(\varepsilon'(\nu) - 1)(\varepsilon'(\nu) + 2) + (\varepsilon''(\nu))^2}{(\varepsilon'(\nu) + 2)^2 + (\varepsilon''(\nu))^2} \quad (8)$$

$$\alpha''(\nu) = \frac{9M}{4\pi d} \frac{\varepsilon''(\nu)}{(\varepsilon'(\nu) + 2)^2 + (\varepsilon''(\nu))^2} \quad (9)$$

The details of the procedure of determination of complex refractive index and related properties from quantitative thin-film transmittance spectra, in particular the details of the numeric distortion correction procedure, have been explained earlier [13,14,15].

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