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The vibrational spectra and conformations of ethylbenzene

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Abstract

Infrared spectra (4000–250 cm^{-1}) of the liquid, amorphous, crystalline solids and solutions in liquid krypton and Raman spectra (2500–20 cm^{-1}) of the liquid as well as the amorphous and crystalline solids of ethylbenzene and its deuterated analogue—ethylbenzene-d_{10} have been recorded. The spectra indicate that in the liquid and amorphous solids a small amount of a second conformer is present, whereas only one conformer remains in the crystalline phases. Assignments of the observed band wave numbers are discussed by comparison with normal mode wave numbers and IR and RS intensities calculated from ab initio 6-31G force fields and optimised geometries for both conformers for two species. All of the normal modes of conformers have been assigned.

Keywords: Ethylbenzene; Ethylbenzene-d_{10}; Infrared spectra; Raman spectra; Ab initio; Conformational analysis

1. Introduction

The different conformations of the ethylbenzene (EB) have been the subject of several experimental and theoretical investigations.

The literature contains considerable experimental data on the conformational properties of EB, which have been studied extensively by various experimental techniques. Experimental as well as theoretical methods imply contradicting results for conformational properties of EB.

An electron diffraction study [1,2] indicates that the one conformation of EB exists (the bond C(sp^3)–C(sp^3) is in the plane, which is orthogonal to the benzene ring plane—*o*-conformation). Indirect evidence from electronic spectra (time-of-flight spectroscopy) [3], low- [4] and high-resolution microwave spectroscopy [5] of EB were interpreted in terms of the *o*-conformation. This conformation was found to be the most stable by ^{1}H NMR spectroscopy [6,7].

Using NMR spectroscopy, the authors [6] concluded that the barrier of internal rotation in EB is insensitive to the polarity and internal pressure of the solvent (acetone-d_6, CCl_4, CS_2 and perfluoromethylcyclohexane).

Vibrational spectroscopy, infrared (IR) and Raman were used to solving conformational behaviour of EB, too. The assignment of the observed IR and Raman bands of EB and other alkylbenzenes in spectral interval 650–200 cm^{-1} was made in [8]. Raman spectra of toluene, EB and *n*-propylbenzene in a liquid state were also measured at room temperature by Yamakita [9]; assignment of some experimental bands was made.

IR spectra of EB have been investigated in liquid, solid phase and CS_2 solution [10]. Two solid phases A and B, which was distinguished by IR spectra, were observed. Authors analysed spectral region from 1050 to1030 cm^{-1}, where two bands at 1034 and 1040 cm^{-1} were recorded. In the liquid phase the relative intensities of these bands varied with temperature. One band of this doublet is present only in solid phase A, whereas another band is present in the solid phase B. Authors maintain that the IR spectrum of the liquid sample can be obtained by superposition of the spectra of both crystalline forms. This fact was interpreted by the existence of a different conformations in each crystal phase, and in the liquid phase EB exists as a mixture of two conformers—orthogonal and planar (in the latter, C(sp^3)–C(sp^3) bond is in the plane of the benzene ring).

Normal coordinate analysis, using GF-matrix method, was carried out only for *o*-conformer [11,12].

Ab initio calculations [6,13,14] predicted the only stable *o*-conformation of EB. Caminati [4] carried out ab initio

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