



Vibrational spectra and structure of isopropylbenzene

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ABSTRACT

Infrared spectra (4000–400 cm⁻¹) and Raman spectra (1700–40 cm⁻¹) of the liquid and two crystalline solids of isopropylbenzene (cumene) and isopropylbenzene-d₁₂ have been recorded. The spectra indicate that in the liquid and crystalline solids isopropylbenzene exists in planar conformation only (C–H bond is in the plane of the benzene ring). An assignment of the observed band wave numbers both isopropylbenzene and isopropylbenzene-d₁₂ is discussed by comparison with normal mode wave numbers and IR intensities calculated from ab initio 6-31G (d) force fields.

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1. Introduction

Molecular structure and conformational mobility of isopropylbenzene (cumene) have been challenged in several studies. Various experimental and theoretical methods have been applied, yet the data obtained so far do not allow one to interpret the conformational behavior of this molecule unequivocally.

An electron diffraction study of a series of isopropylbenzenes in the gas phase [1] has shown that the molecules of this class occur in two stable conformations. The C–H bond can be in the plane of the benzene ring (the planar or *p*-conformation, Fig. 1a) and at some angle along the C(sp²)-C(sp³) bond, in particular, it can be perpendicular to the benzene ring (the orthogonal or *o*-conformation, Fig. 1b). Spectra of cumene and other alkylbenzenes, obtained with the help of the Time of Flight Mass Spectroscopy (TOFMS) technique were investigated in [2]. In the spectrum of cumene, only one intense line was observed in the region of 37668.5 cm⁻¹, which was interpreted as the presence of a single *p*-conformation. A number of authors [3,4] conducted theoretical simulations of isopropylbenzene. Ab initio calculations using a Hartree-Fock self-coordinated field with an STO-3G basis [3] have shown that *p*-conformation is preferable, with the global minimum on the potential curve corresponding to it. The calculated barrier to internal rotation was found to be of 14.5 kJ/mol. In Ref. [4] using a 6-31G basis set and optimizing the conformation at $\varphi = 90^\circ$, it has been obtained that the energy of *o*-conformer is 13.4 kJ/mol higher than that of the *p*-conformer.

To our best knowledge, there is only a single study of conformational stability in cumene by means of infrared spectroscopy [5]. Main attention there was given to the analysis of the spectra between 1140 and 1170 cm⁻¹, where IR spectrum of the liquid exhibits two absorption bands: 1148 cm⁻¹ and 1160 cm⁻¹. The authors claimed that some of the bands “freeze-out” upon crystallization. Relying on this fact, they concluded that there is a dynamic equilibrium of the two cumene conformations in the liquid phase. Unfortunately, no sufficient experimental evidence (either spectra or tables) is given in the paper to prove the conformer’s disappearance upon crystallization. The provided survey spectra of the liquid and crystal are insufficient for drawing any conclusion regarding possible conformational inhomogeneity in cumene. Thus, conformational stability of cumene in different phases, its vibrational spectra and their interpretation still represent a challenge for spectroscopists.

In this work we performed a new study of vibrational spectra of isopropylbenzene (Cum) and its fully deuterated analog (Cum-d₁₂). The goal of the study is to establish stable conformations of this compound in condensed and crystalline phases.

2. Experimental

Fourier-transform infrared spectra were collected using a Bruker spectrometer Tensor-27 at a resolution of 1 cm⁻¹ and the number of scans of 32. The liquid samples were droplets squeezed between KBr plates. Cryogenic studies were carried out using a standard cryostat. The temperature was registered by a platinum thermometer. The temperature was maintained with an accuracy of ± 1 K.

Raman spectra in the region 50–1700 cm⁻¹ were collected using a modified spectrometer DFS-52 equipped with a double mono-

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