

Analysis of the Vibrational Spectrum of P-Methyl Styrene Based on IR, Raman and INS Data and *Ab Initio* and DFT Calculations

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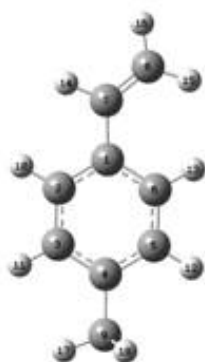
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An investigation of the geometric structure, force field and fundamental vibration wavenumbers of p-methylstyrene molecule (Fig.) has been carried out by using *ab initio* and density functional theory (DFT) and scaling methods. The experimental data used as reference in the scaled force field have been those from IR, Raman and Inelastic Neutron Scattering (INS) spectra recorded by us.

In the harmonic oscillator approach, the fundamental vibrational wavenumbers, IR intensities and thus the predicted IR spectra of the p-methylstyrene were calculated by using DFT/B3LYP method with 6-31G* and 6-311++G** basis set. The vibrational wavenumbers calculated with DFT/B3LYP were scaled by using two different methods: 1) The SQM method developed by Pulay et al. [1, 2] 2) The wavenumber-linear scaling method (WLS) proposed by Yoshida et al. [3] This all has allowed us to propose a new assignment which checks and extends the existing one [4, 5].

The WLS method uses linear relationships between the scaling factor, defined as the ratio between observed and calculated frequencies, and the calculated ones. This method turns out to be a very useful tool for a fast approach to the assignment of the vibrational spectrum of p-methylstyrene. As for SQM method, the scaling procedure has been carried out in different steps. First a unique scale factor, 0.928 as recommended for B3LYP/6-31G* level was used regardless of the internal natural coordinates. Then this unique factor was refined in order to fit the experimental frequencies. Afterward, a set of 9 independent scale factors associated with the natural internal coordinates was used; and finally this set was also refined in order to reproduce the experimental frequencies.



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