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Ab initio Calculation of the Conformations and Vibrational Spectra of 2-Phenylbutane

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Abstract

Molecules with internal degrees of rotation are of particular interest to understand the behavior of synthetic or natural polymers. With the extremely rapid increase in floating point performance of modern computers we are able to calculate a subspace of the Born-Oppenheimer hypersphere for quite large molecules with *ab initio* methods. We choose 2-Phenylbutane as an elementary model for Polystyrene (PS), because it possesses two internal degrees of freedom, that are highly relevant for PS. These are the rotation of the benzene ring and the chain like motion of the ethylgroup.

We minimized the energy of one conformation with respect to all internal coordinates and used different basis function sets. From that the standard gaussian type basis 3-21G elaborates as an optimum function set regarding computing time and accuracy. With the help of multidimensional search

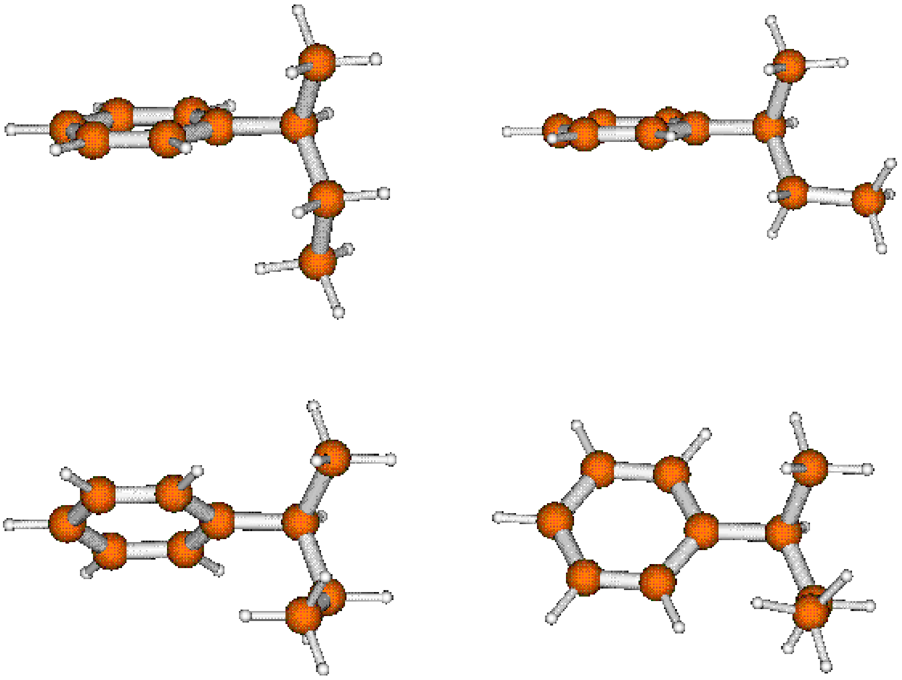

Figure 1. *Conformations of 2-Phenylbutane calculated with GAUSSIAN92 at 6-31G.*
a: T (ΔE=0.0 kJ/mol)
b: G^+ (ΔE=3.7 kJ/mol)
c: G^- (ΔE=7.9 kJ/mol)
d: G_2^- (ΔE=19.9 kJ/mol)

PDB-files available:
0373f01a.pdb
0373f01b.pdb
0373f01c.pdb
0373f01d.pdb

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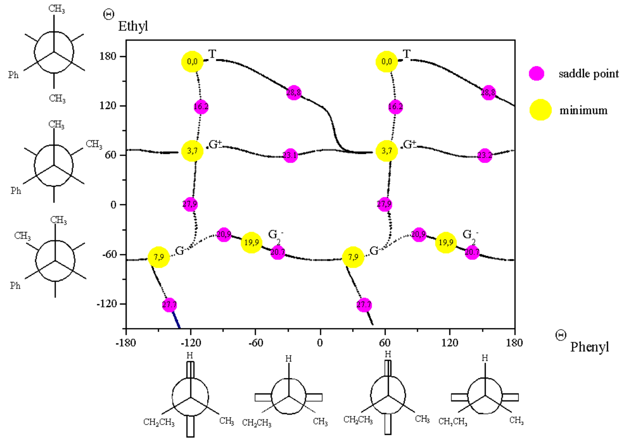

Figure 2. *Changes of the internal torsion angles along the IRC between the calculated minimum and saddle point structures. The Newman projections for different torsion angles are shown to give an idea of the conformational structure within the plot.*

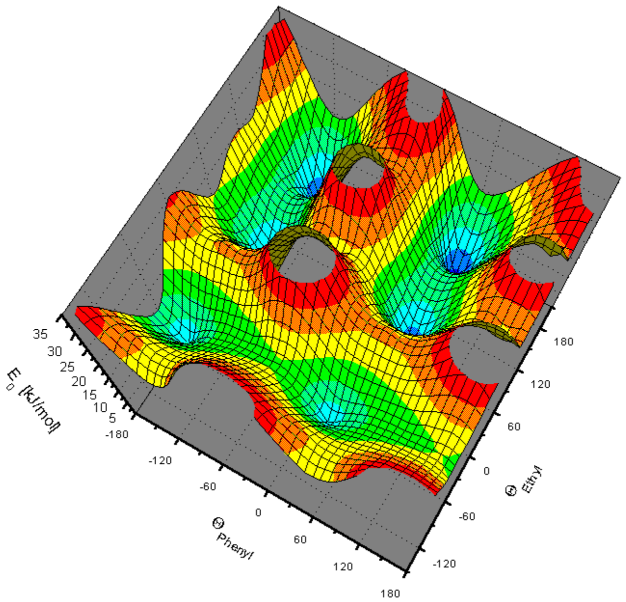

Figure 3. *3 dimensional representation of the Born-Oppenheimer hypersphere for 2-Phenylbutane. The contour is calculated from the IRC coordinates shown in fig. II.*

algorithms, that are available in the GAMESS [1] and GAUSSIAN92 [2] program packages, we were able to calculate 4 different conformations of the 2-Phenylbutane that are energetically relevant (figures 1a-d). In a more extensive search we show that it is possible to calculate the saddle point structures between the minima without restricting the minimization to any coordinate. The calculated intrinsic reaction coordinate (IRC) between the saddle points and the minima provide a detailed view in the Born-Oppenheimer hypersphere of 2-Phenylbutane (figure 2). A three dimensional representation of this energy landscape in dependence of the two internal rotational degrees of freedom is calculated that gives a further inside into the flexibility of the studied molecule (figure 3). Our investigation proofs that the assumption of rigid rotors in molecules with more than 1 internal degree of rotation is - especially for PS - a crude approximation.

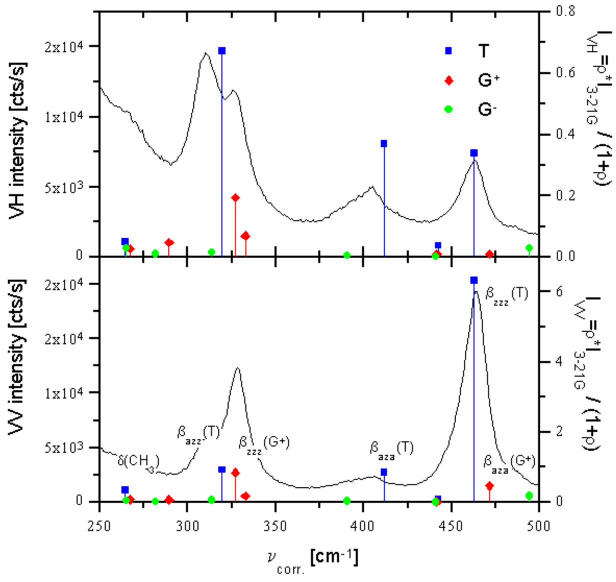

Figure 4. *Calculated Raman active vibrations in the region of CCC bending modes. The polarized and depolarized intensities are in agreement with the experimental data, that are also shown in the figure.*

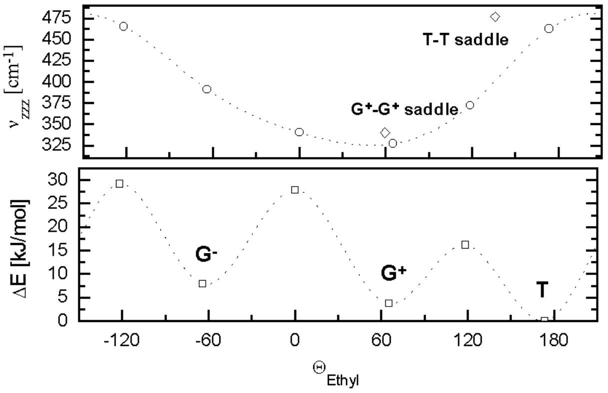

Figure 5. *The calculated frequencies of the 'in phase' CCC bending mode* ν_{zzz} *are showing a large variation with the torsion angle of the butane chain.*

We verify the level of energy relaxation in the calculated conformations by performing a normal coordinate analysis at the minimum and saddle point structures. The calculated polarized and depolarized Raman spectra are in agreement with our experimental data (figure 4). We characterized the measured bandstructure of the strong symmetric ring breathing vibration as a superposition of the vibrations of different conformers. The coupling of the two CCC-bending modes of the chain leads to a normal vibration whose frequency is highly dependent on the conformation of the chain (figure 5), which can be used to monitor the internal rotation of 2-Phenylbutane with Raman spectroscopy [3].

The analysis of the normal vibrations of 2-Phenylbutane with ab initio calculations give a quantitative view of the complex vibrational Raman spectra. With the help of these investigation we are able to show in an Raman experiment the freezing of an internal mode of 2-Phenylbutane during the glass transition [4].

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