

Force dependence of the infrared spectra of polypropylene calculated with density functional theory



Michael F. Pill ^{a, b}, Alfred Kersch ^a, Hauke Clausen-Schaumann ^{a, b}, Martin K. Beyer ^{c, *}

^a Munich University of Applied Sciences, Department of Applied Sciences and Mechatronics, Lothstr. 34, 80335 Munich, Germany

^b Center for Nanoscience (CeNS), Geschwister-Scholl-Platz 1, 80539 Munich, Germany

^c Institut für Ionenphysik und Angewandte Physik, Leopold-Franzens-Universität Innsbruck, Technikerstraße 25, 6020 Innsbruck, Austria

ARTICLE INFO

Article history:

Received 19 August 2015

Received in revised form

22 February 2016

Accepted 22 March 2016

Available online 26 March 2016

Keywords:

Mechanochemistry

Infrared spectroscopy

Mechanical strain

Mechanophore

ABSTRACT

The force dependence of the infrared spectrum of isotactic 3,5-dimethylheptane, which serves as a model molecule for polypropylene, was investigated with quantum chemical calculations using the External Force is Explicitly Included (EFEI) method. Normal modes were analyzed with respect to the force dependence of their frequencies and intensities. In general, the frequencies exhibit a monotonic increase or decrease with force, depending on the way the external force is modifying the bonds involved in the normal mode vibration. The behavior of the intensities is in many cases non-monotonic. This is attributed to the force-dependent coupling and mixing of modes, which leads to irregular behavior of the intensities. To compare the calculations with experimental results the modes were broadened with a Lorentzian, and superimposed to simulate the infrared spectrum. The experimentally observed force dependence is in qualitative agreement with the calculated values. Due to the occasionally counteracting behavior of normal modes, peaks originating from several normal modes may move, split, coalesce, emerge or disappear under the influence of an external force.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

The stability of molecules exposed to an external force is a particularly relevant for applications like e.g. biodegradable polymeric materials, force sensing, or self-healing materials [1–6]. Besides mechanochemical reactions, which lead to irreversible change, i.e. polymer degradation, many properties of molecules change reversibly when mechanical stress is applied at low force levels. In this area, infrared spectroscopy of stressed polymers is particularly well investigated experimentally [7–28]. However, so far no theoretical description of these measured force-dependent infrared spectra is available.

On the theoretical side mechanochemistry is described with *ab-initio* molecular dynamics simulations and with static density functional theory (DFT) calculations and theoretically with quantum chemical calculations [29–44]. Methods describing the influence of force are CONstrained Geometries simulate External Force (COGEF) [45], External Force is Explicitly Included (EFEI) [30,31] or Force Modified Potential Energy Surface (FMPES) [46].

With the EFEI method the reaction paths of a variety of chemical reactions were calculated, e.g. ring opening [30–32] or hydrolysis reactions [33,34]. In a recent study by Stauch and Dreuw, the force dependence of the UV/VIS absorption spectrum as well as the infrared (IR) and Raman spectra of two model chromophores were investigated [47]. It was found that the convoluted spectra change upon application of force, both in the frequency and intensity of the peaks. However, no experimental data are available to compare these theoretical predictions with.

Here we analyze how the force dependence of peak positions and intensities in convoluted infrared spectra relates to the behavior of individual vibrational modes. Isotactic 3,5-dimethylheptane was chosen as a model molecule for polypropylene, because a large volume of experimental data is available on this particular polymer for comparison with our calculations [7–28]. The EFEI method is used, where the potential energy surface (PES) on which the vibrational spectrum is calculated includes the external mechanical potential. The work is limited to harmonic approximation, because current quantum chemical packages do not allow for the calculation of anharmonic effects on the EFEI-PES. Especially at high forces, where anharmonic effects will be pronounced, this would be highly desirable.

* Corresponding author.

E-mail address: martin.beyer@uibk.ac.at (M.K. Beyer).

Nevertheless, valuable insight can be gained into the behavior of vibrational modes of polymers exposed to mechanical strain.

IR spectra on the EFEI-PES are also required to calculate the Arrhenius pre-factor in transition state theory for modeling the kinetics of mechanochemical reactions [34], as well as for the calculation of the free energy of a molecule [48]. This links the current work to the ongoing efforts in quantitative polymer mechanochemistry, which are experimentally based on single molecule force spectroscopy with the atomic force microscope [29,49–64].

2. Computational methods

As DFT [65] method the B3LYP functional [66,67] together with Ahlrich's SVP basis set [68] was used. The computations were done with TURBOMOLE 6.3 [69]. To implement the EFEI method [30,31], TURBOMOLE was interfaced with a script that modifies the geometry optimization module (relax) and the module for the numerical calculation of second derivatives (NumForce) [70]. Essentially, the calculation of analytical gradients is modified by adding the mechanical potential (cf. SI for details). The stretching force was applied to the terminal carbon atoms, Scheme 1. It should be noted that a frequency calculation with a COGEF optimized geometry on the non-modified Born-Oppenheimer PES will lead to erroneous results, since standard quantum chemical codes assume that the second derivative calculation is done on a stationary point of the Born-Oppenheimer PES.

The calculated vibrational frequencies in harmonic approximation were used without scaling to analyze their force dependence. To compare convoluted spectra with experimental results a scaling factor of 0.9614 [71] was used.

Vibrational frequencies and infrared absorption intensities as a function of force were calculated from 0 to 4 nN in steps of 0.1 nN. For comparison with experiment, the absorption lines were broadened with a Lorentzian and superimposed, with a standard deviation of 17 cm^{-1} and 2000 sampling points. Peak positions in these convoluted spectra were identified with a peak-finder tool, which searches for local maxima.

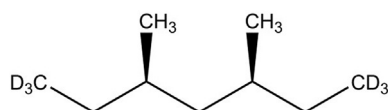
In experimental studies of IR spectroscopy on stressed polymers [18–20], the change in the frequency was described with a linear fit, eq. (1a), with σ the applied stress and α_x the mechanically induced frequency shifting coefficient. For a single molecule the stress in eq. (1a) is replaced by the force f , eq. (1b). The coefficients α_x are used for comparison between experiment and theory.

$$\nu(\sigma) = \nu_0 + \alpha_x \sigma \quad (1a)$$

$$\nu(f) = \nu_0 + \alpha_x f \quad (1b)$$

3. Results and discussion

The linear alkane 3,5-dimethylheptane ($\text{CD}_3\text{C}_7\text{H}_{14}\text{CD}_3$) (Scheme 1) was chosen as a model molecule for isotactic polypropylene, as a compromise between system size and computational costs. A symmetric molecule was chosen to reduce the complexity of the spectra. First, the force dependence of the frequencies and infrared



Scheme 1. Isotactic 3,5-dimethyl heptane.

intensities of all normal modes of this molecule was investigated individually. Then the spectral lines originating from these vibrational modes were broadened with a Lorentzian and superimposed to simulate IR spectra for comparison with the experimental results. To minimize artifacts due to the short length of the model molecule, the vibrational modes of the methyl end groups were decoupled from the rest of the molecule by replacing hydrogen with deuterium. The vibrational frequencies of the CD_3 stretching and bending modes lie around 2000 cm^{-1} and 1100 cm^{-1} , respectively.

3.1. Force dependence of harmonic vibrational frequencies and infrared intensities

From experiment it is known that peaks in the infrared spectrum exhibit quite variable force dependence. Their intensity may increase or decrease with increasing force, and the frequency may be red- or blue-shifted. To get a systematic understanding of the origin of this behavior, quantum chemistry allows for analyzing the behavior of individual vibrational modes contributing to the absorption lines.

Since nearby modes behave differently, an unambiguous method is required to follow an individual mode through the calculations with increasing forces. Quantum chemical packages sort the modes according to their vibrational frequency, which means the number assigned to a mode by the software may change with force. In order to follow an individual mode over the investigated range of 0–4 nN, the dot product of the displacement vectors is calculated. It is close to 1 for corresponding modes, see SI for details.

The force dependence of four representative modes is discussed in detail. Frequencies (left) and intensities (right) are shown in Fig. 1: (A) C–C stretching mode along the backbone at 984 cm^{-1} , (B) collective C–H wagging mode at 1355 cm^{-1} , (C) C–H bending mode at 1466 cm^{-1} and (D) asymmetric C–H stretching mode at 3051 cm^{-1} . The force dependences of all other modes are summarized in SI (Table S4). The frequencies change monotonically over a small range, but the intensities may change dramatically, in a non-monotonic way.

The biggest effect is seen in the C–C stretching vibration along the backbone, Fig. 1A. The frequency decreases almost linearly from 984 cm^{-1} to 913 cm^{-1} , while the intensity stays almost constant up to 0.8 nN, and drops linearly to near zero around 2.5 nN, followed by a moderate increase towards 4 nN. The frequency drop is also significant for the C–H wagging vibration, Fig. 1B, from 1355 cm^{-1} to 1307 cm^{-1} at 4 nN. The intensity shows little force dependence up to 2.6 nN, followed by a sharp drop to half the original value for the rest of the investigated force range. The frequency of the C–H bend, Fig. 1C, also exhibits a negative force dependence, from 1466 cm^{-1} to 1453 cm^{-1} at 4 nN. The intensity is overall weak, and exhibits a linear increase from 1.8 nN to 4 nN. The C–H stretch, Fig. 1D, on the other hand, exhibits an increase in frequency with force, from 3051 cm^{-1} to 3067 cm^{-1} , while the intensity fluctuates in an erratic manner between 10 and 40 km mol^{-1} .

For Fig. 1C, the force dependence of the frequency is quite smooth, but a number of nearly degenerate modes are present with very similar force dependence. The force-dependent coupling of these modes may explain the relatively irregular behavior of the intensities. The same argument applies to the erratic fluctuations of the intensities in Fig. 1D.

Fig. 2 shows the force-dependent frequencies of all vibrational modes in the fingerprint region from 800 to 1500 cm^{-1} . Many frequencies are only weakly force-dependent, but some change drastically by around 25 cm^{-1} per nN. Particularly interesting are regions where modes become nearly degenerate due to mechanical

Download English Version:

<https://daneshyari.com/en/article/5201208>

Download Persian Version:

<https://daneshyari.com/article/5201208>

[Daneshyari.com](https://daneshyari.com)