

Contents lists available at [SciVerse ScienceDirect](http://SciVerse.Sciencedirect.com)

## Chemical Physics Letters

journal homepage: [www.elsevier.com/locate/cplett](http://www.elsevier.com/locate/cplett)

## Aniline-1,4-benzoquinone as a model system for the characterization of products from aniline oligomerization in low acidic media

Claudio H.B. Silva, Daniela C. Ferreira, Rômulo A. Ando, Marcia L.A. Temperini\*

Departamento de Química Fundamental, Instituto de Química da Universidade de São Paulo (USP), C.P. 26077, CEP 05513-970 São Paulo, SP, Brazil

## ARTICLE INFO

## Article history:

Received 29 August 2012

In final form 12 September 2012

Available online 23 September 2012

## ABSTRACT

Increase in the pH medium of aniline polymerization is used for giving products of different morphologies, which are often wrongly attributed to PANI chains. Infrared and Raman spectroscopic data, supported by quantum chemical calculations, show that aniline-1,4-benzoquinone (AnBzq) is a model system for the characterization of the products of aniline oligomerization in low acidic media. The Raman spectra excited at different laser lines reveal the bichromophoric nature of AnBzq, whose absorption bands at 550 nm and 440 nm can be attributed to  $\pi$ - $\pi^*$  transitions of the delocalized benzoquinone and amino-phenyl moieties, respectively.

© 2012 Elsevier B.V. All rights reserved.

## 1. Introduction

Polyaniline (PANI) is a conducting polymer which is easily prepared from aniline and ammonium peroxydisulfate (APS) in strong acidic media [1]. The growth of the polymeric chains occurs by a head-to-tail coupling mechanism [2]. It has been reported that nanostructured PANI provides improved performances for electronic devices such as nonvolatile memory [3,4], capacitors [5–8] and chemical sensors [9–13] in comparison with the bulk polymer. The synthetic protocols proposed in literature to produce PANI of different morphologies clearly demonstrate that the acidity profile of the medium during the reaction plays a major role to determine whether the products consist of PANI chains and/or non-linear oligomeric compounds (also called as oligoanilines) [14–22]. However, such interesting morphologies achieved by several protocols are often wrongly attributed to PANI chains.

Surwade et al. proposed for the first time that aniline could react with peroxydisulfate by a different mechanism (Boylard-Sims rearrangements) [20], which produces intermediate species such as benzoquinone-monoimines. Afterwards, such species would react with aniline by a series of conjugate 1,4-Michael-type reactions, producing an oligomeric system composed by amino-phenyl and benzoquinone-monoimine moieties. Such hypothesis was based on the spectral similarities of the products of aniline-peroxydisulfate system with the products of reaction of aniline and 1,4-benzoquinone (named as AnBzq). Scheme 1 shows the proposed structure for AnBzq system, composed by benzoquinone and amino-phenyl moieties, in accordance to FTIR, Raman and NMR data [21]. Although the spectral features of AnBzq have been

compared with oligoanilines produced by aniline oligomerization by APS acidic media [20–22], a detailed assignment of the vibrational bands of these supramolecular systems has not been performed. In this Letter, it is reported a detailed vibrational assignment of AnBzq, which can be used as a model system to the characterization of products obtained from aniline oligomerization in low acidic media. In addition, the resonance Raman study revealed the bichromophoric nature of this supramolecular system.

## 2. Experimental section

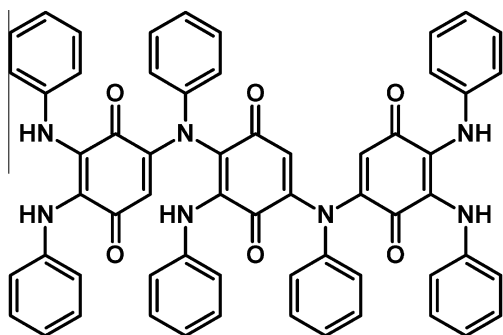
The reaction of aniline monomer (Merck, distilled under reduced pressure) and 1,4-benzoquinone (Aldrich, purified by sublimation at 60 °C) was performed as previously described [20–22]. The reaction mixture of 100 mL of 1.0 mol L<sup>-1</sup> HCl containing 1.0 mL of aniline and 50 mg of 1,4-benzoquinone was stirred at room temperature for 90 min. The brown solid was filtered and dried under vacuum. The product obtained was labeled as AnBzq.

High-performance liquid chromatograms were obtained for a solution of AnBzq (ca. 5 mg mL<sup>-1</sup>) in tetrahydrofuran (Vetec, 99%) in a Phenomenex column (250 mm × 4.6 mm × 5 μm), by using pressure of 27.0 psi, air flux of 7.0 mL min<sup>-1</sup>, and sample injection of 100 μL min<sup>-1</sup>. The detection was performed at 370 nm in accordance to previous spectroscopic data for AnBzq in solution [20–22]. Electrospray ionization-Time of Flight-Mass spectrometry (ESI-TOF-MS) curves of the solution of AnBzq were obtained using a LC-MS-Bruker Daltonic Esquire 3000 Plus coupled to a high-performance liquid chromatograph.

The electronic absorption spectrum (UV-Vis) was obtained for solid sample dispersed in BaSO<sub>4</sub> (Riedel-de Haën) using a Shimadzu UVPC-3101 scanning spectrophotometer in diffuse reflectance mode. The Raman spectra excited at 568 nm, 514 nm and 458 nm

\* Corresponding author. Fax: +55 11 3091 3890.

E-mail address: [mlatemp@iq.usp.br](mailto:mlatemp@iq.usp.br) (M.L.A. Temperini).



Scheme 1. Proposed structure for AnBzq compound (based on ref [21]).

(mixed Ar<sup>+</sup> and Kr<sup>+</sup> ions laser, Coherent INNOVA 70C spectrum) were obtained using a Jobin-Yvon T64000 triple spectrometer, with a liquid nitrogen cooled CCD detector. The spectral resolution was 4 cm<sup>-1</sup> and the laser power was kept at 10–15 mW. Potassium sulfate (Cinética Química, used as received) was used as the internal standard (AnBzq/K<sub>2</sub>SO<sub>4</sub> mass ratio of 1/70). The baselines of the Raman spectra were corrected for a better comparison of the relative intensities. FTIR spectra of solid samples dispersed in KBr pellets were recorded on a Bomem MB100 spectrometer with resolution of 4 cm<sup>-1</sup>.

Density functional theory calculations (DFT) were performed by using Gaussian 03 package [23]. The ground state geometries were optimized with B3LYP hybrid functional using 6-31+G(d) as basis

sets and no imposition of symmetry [24–26]. Theoretical vibrational spectra were calculated at the same level of theory and no imaginary wavenumbers were obtained, indicating that optimized geometries are in the minimum of the potential energy surfaces. Vibrational spectra were plotted as gaussian curves with FWHM of 5 cm<sup>-1</sup> and a scaling factor of 0.9648 for harmonic vibrational wavenumbers [27]. Raman intensities were calculated from Raman activities according to ref [28].

### 3. Results and discussion

The HPLC curve in Figure 1A shows that AnBzq solution presents a single elution peak of retention time at 3.2 min. The ESI-TOF-MS curve in Figure 1B for the solution eluted at 3.2 min indicates that AnBzq is composed mostly by a product of *m/z* 948, but a weaker peak at *m/z* 664 was also detected. The same retention time indicates similar structural features for these two components. Therefore, HPLC coupled to ESI-TOF-MS data suggest that AnBzq is a supramolecular system, which the major product presents a molecular weight of 948 Da. Such results are in accordance to gel permeation chromatography data reported by Surwade et al. [20].

Figure 2A shows the FTIR spectrum of AnBzq. Taking into account that AnBzq is a complex supramolecular system, the FTIR spectrum shows a relatively low number of bands. Moreover, the comparison of FTIR and Raman (Figure 2B) spectra shows that intense bands in the former spectrum are weaker in the latter. The presence of additional functional groups in AnBzq could give rise to several vibrational modes at same wavenumber range, such as the stretching mode of benzenoid rings and bending mode of N–H groups in FTIR spectrum (1480–1520 cm<sup>-1</sup>). Such complex features clearly show that the assignment of the FTIR and Raman spectra is not straightforward. Therefore, the spectroscopic study of supramolecular systems such as AnBzq and oligoanilines should be performed in more detail in order to provide unambiguous structural information.

DFT calculations were performed for a model structure composed by three phenyl moieties coupled by amino groups to one benzoquinone moiety (An3Bzq1). It is proposed that theoretical vibrational spectra of this relatively simple model structure may provide adequate data for the assignment of FTIR and Raman spectra of AnBzq. The optimized geometry and the calculated vibrational spectra of An3Bzq1 are presented in Figure 2. It is clearly observed that the intensities and wavenumbers of the most intense bands in the experimental FTIR spectrum at 1566, 1505–1489 and 1288 cm<sup>-1</sup>, spectrum A, are well reproduced in the calculated IR spectrum (bands at 1567, 1514–1496 and 1280 cm<sup>-1</sup> in spectrum C). Moreover, the comparison of the calculated IR and Raman spectra also shows that the intense bands in the former spectrum are weaker in the latter.

The vibrational assignment (Table 1) shows that the intense bands at 1566 and 1505–1489 cm<sup>-1</sup> observed in the IR spectrum are due to νC=C of benzoquinone moiety and βN–H of amine groups, respectively. Based on our assignment (Table 1), the IR bands of oligoanilines at ca. 1500 cm<sup>-1</sup> reported in literature [16–18,29,30] should be assigned to βN–H vibrations and not to νC=C of benzenoid rings. It is important since these previous assignments were proposed in comparison with emeraldine forms of PANI, causing a misleading interpretation that new morphologies obtained are formed by chains of PANI. Moreover, DFT calculations indicate that the Raman bands of AnBzq at 1676 and 1633 cm<sup>-1</sup> are due to the benzoquinone moieties, whereas the band at 1601 cm<sup>-1</sup> is mostly due to the amino-phenyl moieties.

As previously reported in literature [20,21], the electronic spectra of AnBzq and oligoanilines systems in solution are very similar.

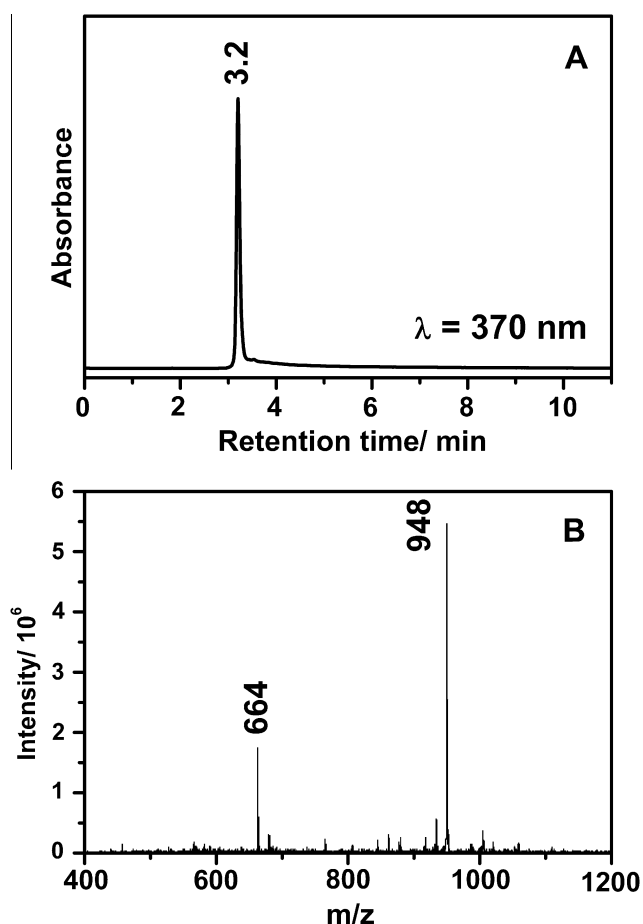


Figure 1. (A) HPLC curve ( $\lambda = 370$  nm) for the solution of AnBzq in THF. (B) ESI-TOF-MS curve of the eluted solution at 3.2 min.

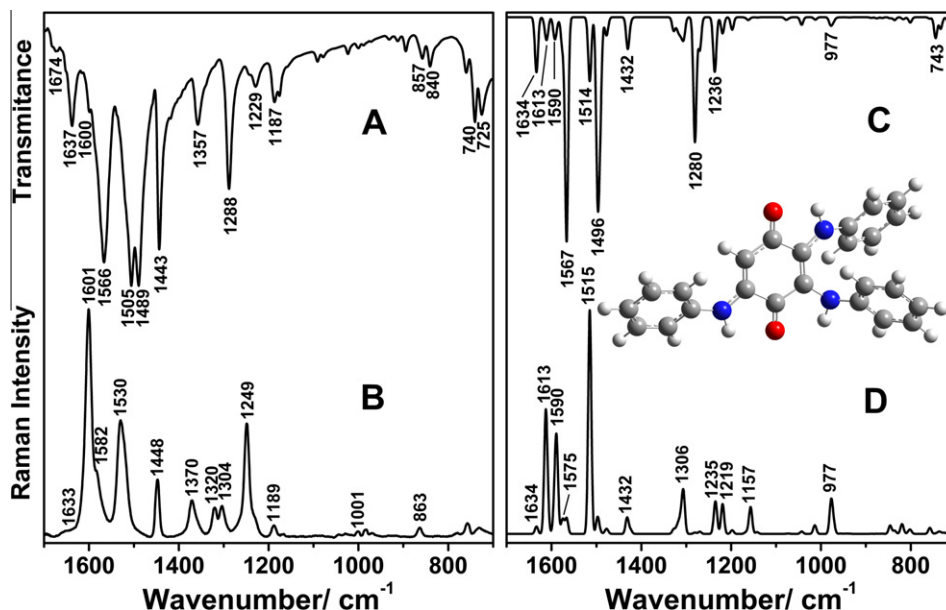


Figure 2. Experimental FTIR (A) and Raman (B) spectra of AnBzq ( $\lambda_0 = 458$  nm). DFT Calculated IR (C) and Raman (D) spectra for An3Bzq1 model.

Table 1

Assignment of FTIR and Raman bands of AnBzq based on DFT results for An3Bzq1 model (wavenumbers in  $\text{cm}^{-1}$ ).

Experimental FTIR	Experimental Raman	DFT An3Bzq1	Assignment <sup>b</sup>
1674	1676 <sup>a</sup>	1634	$\nu_{\text{as}}\text{C}=\text{O}$ (bzq) + $\nu\text{C}=\text{C}$ (bzq)
1637	1633 <sup>a</sup>	1613	$\nu_{\text{s}}\text{C}=\text{O}$ (bzq) + $\nu\text{C}=\text{C}$ (bzq)
1600	1601	1590	$\phi_{8a}$ + $\nu\text{C}=\text{C}$ (bzq)
–	1582 <sup>a</sup>	1575	$\nu\text{C}=\text{C}$ (bzq) + $\phi_{8b}$
1566	–	1567	$\nu\text{C}=\text{C}$ (bzq)
–	1529	1515	$\beta\text{N}-\text{H}$
1505–1489	–	1514–1496	$\beta\text{N}-\text{H}$
1443	1448	1432	$\phi_{15}$
1288	–	1280	$\nu\text{C}-\text{C}$ (bzq) + $\nu\text{C}-\text{N}$ (ph)
–	1249	1235	$\nu\text{C}-\text{N}$ (ph)
–	1001	977	$\phi_{12}$
740	–	743	$\phi_{11}$

<sup>a</sup> Bands observed with higher relative intensities in spectrum at 568 nm (see Figure 4).

<sup>b</sup> (bzq) and (ph) relates to benzoquinone and amino-phenyl moieties, respectively;  $\phi$  represents Varsanyi's notation for benzene modes.

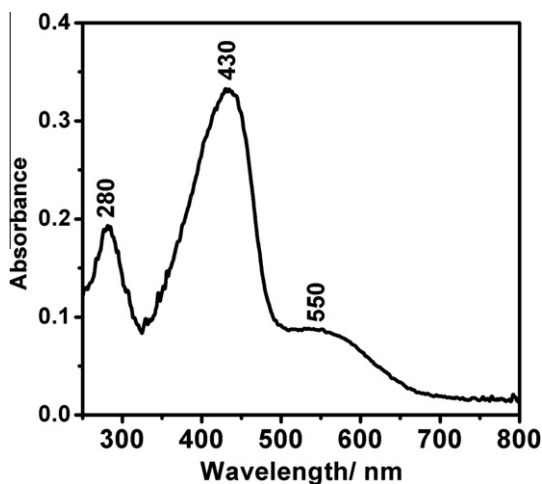


Figure 3. Solid state UV-VIS spectrum of AnBzq dispersed in  $\text{BaSO}_4$ .

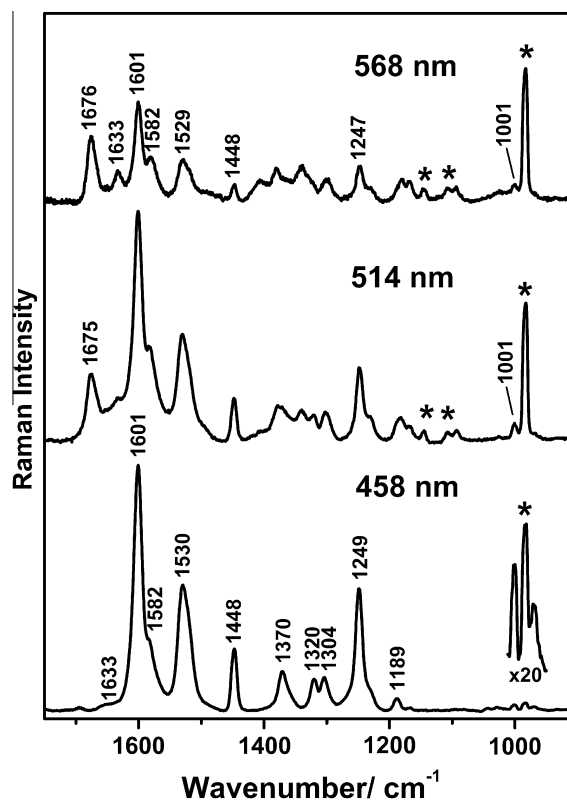


Figure 4. Raman spectra of AnBzq obtained at different excitation radiations. \*bands of internal standard  $\text{K}_2\text{SO}_4$ . The highlight in the spectrum at 458 nm shows in more detail the relative intensity of the band at  $1001 \text{ cm}^{-1}$ .

They are composed by an intense band at ca. 370 nm and a weak absorption band at ca. 510 nm. The solid state UV-VIS spectrum of AnBzq (Figure 3) shows that both absorption bands are red-shifted (430 and 550 nm), probably due to stronger  $\pi-\pi$  interactions in solid state.

In order to characterize the electronic transitions observed in the UV-VIS spectrum (Figure 3), the Raman spectra were obtained

at different excitation radiations (Figure 4). In the spectrum excited at 458 nm it can be observed bands of relative high intensities, assigned to vibrations of the phenyl moieties ( $1601$ ,  $1448$ ,  $1249$  and  $1001\text{ cm}^{-1}$ ) and amine groups ( $1530\text{ cm}^{-1}$ ). Such results indicate that the electronic transition corresponding to the band at 430 nm mainly involves the amino-phenyl moieties in AnBzq system. On the other hand, when the Raman spectrum is excited at 514 nm, all the bands become weaker relatively to standard  $\text{K}_2\text{SO}_4$  bands, except for the band at  $1676\text{ cm}^{-1}$ , assigned to the benzoquinone moieties. When the Raman spectrum is obtained in strictly resonant conditions ( $\lambda_0 = 568\text{ nm}$ ) with the low-energy electronic transition (band at 550 nm), the bands related to the benzoquinone moieties at  $1676$ ,  $1633$  and  $1582\text{ cm}^{-1}$  are selectively enhanced, while the bands at  $1601$ ,  $1529$ ,  $1447$ ,  $1247$  and  $1001\text{ cm}^{-1}$  become weaker. Such results clearly show that the electronic transition corresponding to the band at 550 nm involves the delocalized  $\pi$ -system of the benzoquinone moieties. Therefore, the distinct resonance Raman spectral profiles observed at 458 and 568 nm excitations reveal that AnBzq is a bichromophoric system, which transitions at 430 and 550 nm are related to amino-phenyl and benzoquinone moieties, respectively.

#### 4. Conclusions

In this letter it was showed that AnBzq is a model system for the characterization of products from aniline oligomerization in low acidic media. The detailed assignment of the IR and Raman bands of AnBzq was presented based on DFT calculations for a simple model structure. The Raman spectra excited at different laser lines showed the bichromophoric nature of AnBzq, whose absorption bands at 550 nm and 440 nm can be attributed to  $\pi$ - $\pi^*$  transitions of the delocalized benzoquinone and amino-phenyl moieties, respectively.

#### Acknowledgements

The authors acknowledge the Brazilian agencies CNPq and FAPESP for fellowships and financial support. The authors are also

grateful to Prof. Luiz Henrique Catalani and Dr. Vânia A. B. Bueno (IQ-USP) for HPLC measurements.

#### References

- [1] A.G. MacDiarmid, J.C. Chiang, A.F. Richter, *Conducting Polymers*, Riedel Publications, Dordrecht, 1987.
- [2] E.M. Geniès, A. Boyle, M. Lapkowski, C. Tsintavis, *Synth. Met.* 36 (1990) 139.
- [3] Y. Yang, J. Ouyang, L. Ma, R.J.-H. Tseng, C.-W. Chu, *Adv. Funct. Mater.* 16 (2006) 1001.
- [4] R.J. Tseng, J. Huang, J. Ouyang, R.B. Kaner, Y. Yang, *Nano Lett.* 5 (2005) 1077.
- [5] Q. Wu, Y. Xu, Z. Yao, A. Liu, G. Shi, *ACS Nano* 4 (2010) 1963.
- [6] X.Y. Zhang, W.J. Goux, S.K. Manohar, *J. Am. Chem. Soc.* 126 (2004) 4502.
- [7] K. Zhang, L.L. Zhang, X.S. Zhao, J.S. Wu, *Chem. Mater.* 22 (2010) 1392.
- [8] V. Gupta, N. Miura, *Mater. Lett.* 60 (2006) 1466.
- [9] J. Huang, S. Virji, B.H. Weiller, R.B. Kaner, *Chem. Eur. J.* 10 (2004) 1315.
- [10] S. Virji, J.X. Huang, R.B. Kaner, B.H. Weiller, *Nano Lett.* 4 (2004) 491.
- [11] S. Virji, J.D. Fowler, C.O. Baker, J.X. Huang, R.B. Kaner, B.H. Weiller, *Small* 1 (2005) 624.
- [12] D. Li, J.X. Huang, R.B. Kaner, *Acc. Chem. Res.* 42 (2009) 135.
- [13] C.M. Hangarter, M. Bangar, A. Mulchandani, N.V. Myung, *J. Mater. Chem.* 20 (2010) 3131.
- [14] J. Stejskal, M. Trchová, *Polym. Int.* 61 (2012) 240.
- [15] G. Ciric-Marjanovic, M. Trchova, J. Stejskal, *J. Raman Spectrosc.* 39 (2008) 1375.
- [16] L.J. Zhang, Z.D. Zujovic, H. Peng, G.A. Bowmaker, P.A. Kilmartin, J. Travas-Sejdic, *Macromolecules* 41 (2008) 8877.
- [17] Z.D. Zujovic, L. Zhang, G.A. Bowmaker, P.A. Kilmartin, J. Travas-Sejdic, *Macromolecules* 41 (2008) 3125.
- [18] Z.D. Zujovic, C. Laslau, G.A. Bowmaker, P.A. Kilmartin, A.L. Webber, S.P. Brown, J. Travas-Sejdic, *Macromolecules* 43 (2010) 662.
- [19] Z.F. Ding, T. Sanchez, A. Labouiriau, S. Iyer, T. Larson, R. Currier, Y.S. Zhao, D.L. Yang, *J. Phys. Chem. B* 114 (2010) 10337.
- [20] S.P. Surwade, V. Dua, N. Manohar, S.K. Manohar, E. Beck, J.P. Ferraris, *Synth. Met.* 159 (2009) 445.
- [21] D.C. Ferreira, J.R. Pires, M.L.A. Temperini, *J. Phys. Chem. B* 115 (2011) 1368.
- [22] C.H.B. Silva, D.C. Ferreira, V.R.L. Constantino, M.L.A. Temperini, *J. Raman Spectrosc.* 42 (2011) 1653.
- [23] M.J. Frisch et al., *Gaussian 03, Revision D.01*, Gaussian, Inc., Wallingford, CT, 2004.
- [24] A.D. Becke, *J. Chem. Phys.* 98 (1993) 5648.
- [25] C.T. Lee, W.T. Yang, R.G. Parr, *Phys. Rev. B* 37 (1988) 785.
- [26] P.J. Stephens, F.J. Devlin, C.F. Chabalowski, M.J. Frisch, *J. Phys. Chem.* 98 (1994) 11623.
- [27] J.P. Merrick, D. Moran, L. Radom, *J. Phys. Chem. A* 111 (2007) 11683.
- [28] E.E. Zvereva, A.R. Shagidullin, S.A. Katsyuba, *J. Phys. Chem. A* 115 (2011) 63.
- [29] M. Trchova, I. Sedenkova, E.N. Konyushenko, J. Stejskal, P. Holler, G. Ciric-Marjanovic, *J. Phys. Chem. B* 110 (2006) 9461.
- [30] M. Trchova, J. Stejskal, *Pure Appl. Chem.* 83 (2011) 1803.