

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/230867420>

Computational note on anharmonic infrared spectrum of naphthalene

ARTICLE *in* JOURNAL OF MOLECULAR STRUCTURE THEOCHEM · DECEMBER 2007

Impact Factor: 1.37 · DOI: 10.1016/j.theochem.2007.08.022

CITATIONS

6

READS

26

3 AUTHORS, INCLUDING:



Vito Librando

University of Catania

144 PUBLICATIONS 1,263 CITATIONS

SEE PROFILE



Andrea Alparone

University of Catania

67 PUBLICATIONS 792 CITATIONS

SEE PROFILE

Computational note on anharmonic infrared spectrum of naphthalene

Vito Librando *, Andrea Alparone, Zelica Minniti

Research Centre for Analysis, Monitoring and Minimization Methods of Environmental Risk and Department of Chemistry, University of Catania, viale A. Doria 8, Catania 95125, Italy

Received 30 July 2007; accepted 24 August 2007

Available online 1 September 2007

Abstract

Harmonic and anharmonic vibrational wave numbers of fundamental and overtone transitions of naphthalene were computed using the B3LYP density functional and 6-311G** basis set. Anharmonic corrections were introduced through second-order perturbation theory. Comparisons between experimental and calculated data show that the anharmonic approach is significantly superior to both unscaled and scaled harmonic treatments.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Naphthalene; Polycyclic aromatic hydrocarbons; Anharmonic vibrational wavenumbers; Density functional theory

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous pollutants in the environment and are recognized to be hazardous species for human health due to their toxic, mutagenic and carcinogenic activities [1]. Vibrational spectra of naphthalene (NPH), the smallest PAH, were the subject of numerous experimental studies [2,3] and theoretical investigations under harmonic approximation [3–5]. However, it is well known that computed harmonic vibrational wavenumbers generally overestimate the corresponding observed data, owing to neglecting of anharmonic corrections, incompleteness of basis set as well as insufficient treatment of electron correlation effects. A commonly employed approach to correct harmonic wavenumbers is given by use of scaling techniques [6] that however, in some cases give rough estimations of anharmonic effects.

In this work harmonic (ω) and anharmonic (ν) fundamental vibrational wavenumbers as well as first overtone transitions of NPH were determined by using Density Functional Theory. Geometry of NPH was fully optimized under the D_{2h} point group symmetry by B3LYP method with 6-311G** basis set. Harmonic wavenumbers were cal-

culated analytically at B3LYP/6-311G** level and anharmonic corrections were introduced through second-order perturbation theory (PT2) described in detail in Ref. [7]. There are many indications showing that PT2 is reliable for determination of anharmonic effects of semirigid cyclic molecules [7,8]. Additionally, we corrected harmonic wavenumbers (ω') by a single scaling factor (0.9669) recently derived by Irikura et al. [9]. All calculations were performed with Gaussian 03 program [10].

Introduction of anharmonic contributions improves noticeably the agreement with experiment [2], with root-mean-squared deviation of 59, 21 and 13 cm^{-1} , respectively, for ω , ω' and ν values. The results show that the largest anharmonic effects occur for C–H stretches, with a decrease of harmonic wavenumbers by 120–150 cm^{-1} (4–5%). The present approach is potentially useful for studying PAHs of environmental interest for which experimental vibrational data are not yet available.

Acknowledgment

This work was carried out in the framework of the Project 1999/IT.16.1.PO.011/3.13/7.2.4/339 Prot. 238, “Formazione per la ricerca nel campo della bonifica dei siti contaminati”, supported by Regione Sicilia.

* Corresponding author.

E-mail address: vlibrando@unict.it (V. Librando).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.theochem.2007.08.022](https://doi.org/10.1016/j.theochem.2007.08.022).

References

- [1] R.G. Harvey, in: Polycyclic Aromatic Hydrocarbons: Chemistry and Carcinogenicity, Cambridge University Press, Cambridge, UK, 1991.
- [2] K.B. Hewett, M. Shen, C.L. Brummel, L.A. Philips, J. Chem. Phys. 100 (1994) 4077, and references therein.
- [3] E. Canè, P. Palmieri, R. Tarroni, A. Trombetti, N.C. Handy, Gazz. Chim. Ital., 126 (1996) 289, and references therein.
- [4] J.M.L. Martin, J. El-Yazal, J.-P. Francois, J. Phys. Chem. 100 (1996) 15358.
- [5] C.W. Bauschlicher, S.R. Langhoff, Spectrochim. Acta A 53 (1997) 1225.
- [6] G. Rauhut, P. Pulay, J. Phys. Chem., 99 (1995) 3093, and references therein.
- [7] V. Barone, J. Chem. Phys. 122 (2005) 014108.
- [8] R. Burcl, N.C. Handy, S. Carter, Spectrochim. Acta A 59 (2003) 1881.
- [9] K.K. Irikura, R.D. Johnson III, R.N. Kacker, J. Phys. Chem. A 109 (2005) 8430.
- [10] M.J. Frisch, et al., Gaussian, Inc., Gaussian 03, Revision B.03, Pittsburg, PA, 2003.