

## Enclosure 2a

### Self-Report on Scientific Achievements

1. **Name:** Michał H. Jamróz, e-mail: micjam@wp.pl

#### 2. Scientific diplomas and achieved degrees

Scientific degrees:

M. Sc., Jagiellonian University, Cracow, 1977

Faculty of 'Mat-Fiz-Chem', Theoretical Physics

Ph. D. in technical sciences, Industrial Chemistry Research Institute, Warsaw, 1986

Doctoral dissertation title:

Algorithm of the substructure recognition in chemical compounds by the artificial intelligence method, on the basis of infrared spectra.

#### 3. Information on the employment in scientific institutions:

2014	C5 Department, Institute of Nuclear Chemistry and Technology, Warsaw
2013-1990	Spectroscopy and Molecular Modeling Group, Industrial Chemistry Research Institute, Warsaw
1989	Analytical Department, Industrial Chemistry Research Institute, Warsaw
1988-1979	Applied Spectroscopy Department, Industrial Chemistry Research Institute, Warsaw
1979-1977	Computational Methods Group, Industrial Chemistry Research Institute, Warsaw

#### 4. Scientific Achievement Summary (due to Journal Citation Report):

Number of publications: 60, after achieving Ph. D. degree: 56

Total Impact Factor: 122, after achieving Ph. D. degree: 117

Total number of citations: 579, without self-citations: 485

Hirsch Index: 13

Mono-thematic cycle of works consists of 15 works published in the international journals with the total IF of 37 on the basis Journal Citation Report.

Michał Jamróz

## 5. List of scientific achievements, R&D works and information on scientific co-operation and popularization of the science

### I. Scientific habilitation achievements to consider.

A) Title of the achievement: **PED Analysis of Theoretical Oscillation Spectra by the VEDA Program.**

B) Author(s), year of edition, title of publication, editor:

- H1 M. H. Jamróz (100%), 2013, **Vibrational energy distribution analysis (VEDA): Scopes and limitations**, *Spectrochim. Acta A*, 114 (2013) 220–230. This work is solely my contribution. It includes the description of the VEDA software for the interpretation of the vibrational theoretical spectra, as well as the explanation of its algorithm, enhanced by some model examples and the preparation of the manuscript. My share in this work is 100 %.
- H2 M.H. Jamróz (80%), J. Cz. Dobrowolski (20%), 2001, **Potential Energy Distribution Analysis (PED) of DFT Calculated IR Spectra of the most Stable Li, Na, Cu(I) Diformate Molecules**, *J. Mol. Struct.*, 565-566 (2001) 475-480. My contribution to this work consisted of the interpretation of the theoretical spectra, the development of the VEDA software, the discussion on the obtained results, and participation in the preparation of the manuscript. I estimate my share as 80 %.
- H3 M. H. Jamróz (80%), J. Cz. Dobrowolski (10%), J. E. Rode (5%), M. A. Borowiak (5%), 2002, **Theoretical and Experimental IR Spectra and Stability of Dibenzyl Carbamic Acid Dimer**, *J. Mol. Struct. (Theochem)*, 618(1-2) (2002) 101-108. My contribution to this work included interpretation of theoretical and experimental vibrational spectra of the studied molecules, the development of the VEDA software, the discussion on the obtained results, and participation in the preparation of the manuscript. I estimate my share as 80 %.
- H4 M. H. Jamróz (70%), J. Cz. Dobrowolski (30%), 2002, **Theoretical IR Spectra and Stability of Carbamic Acid Complexes**, *Vib. Spectr.*, 29 (2002) 217-221. My contribution to this work included the interpretation of the theoretical vibrational spectra of the studied compounds, the development of the VEDA software, discussion on results, and participation in the participation in preparation of the manuscript. I estimate my share as 70 %.
- H5 M. H. Jamróz (75%), R. Brzozowski (10%), J. Cz. Dobrowolski (15%), 2004, **Search for IR spectral features of less-abundant diisopropylnaphthalenes based on comparison of theoretical and experimental spectra**, *Spectrochim. Acta A. Mol. Biomol. Spectr.*, 60 (2004) 371-375. My contribution to this work included the interpretation of the theoretical and experimental vibrational spectra, the development of the VEDA software, discussion on results, and participation in the preparation of the manuscript. I estimate my share as 75 %.
- H6 J. Cz. Dobrowolski (25%), J. E. Rode (20%), Robert Kołos (20%), M. H. Jamróz (25%), K. Bajdor (5%), A. P. Mazurek (5%), 2005, **Ar-matrix IR Spectra of 5-Halouracils Interpreted by Means of DFT Calculations**, *J. Phys. Chem.*, 109 (2005) 2167-2182. My contribution to this work included the interpretation of the theoretical vibrational spectra of the studied molecules, discussion on results, and participation in the participation in preparation of the manuscript. I estimate my share as 25 %.
- H7 M. H. Jamróz (70%), J. Cz. Dobrowolski (10%), R. Brzozowski (20%), 2006, **Vibrational Modes of 2,6-, 2,7-, and 2,3-Diisopropylnaphthalene. A DFT Study**, *J. Mol. Struct.*, 787 (2006) 172-183. My contribution to this work included the interpretation of the theoretical and experimental spectra



of the studied compounds, the development of the VEDA software, discussion on results, and participation in preparation of the manuscript. I estimate my share as 70 %.

- H8 J. Sadlej (25%), J. Cz. Dobrowolski (25%), J. E. Rode (25%), M. H. Jamróz (25%), 2006, **DFT study of vibrational circular dichroism spectra of D-lactic acid-water complexes**, *Phys. Chem. Chem. Phys.*, 8 (2006) 101-113. My contribution to this work included co-interpretation of the theoretical vibrational spectra of the studied molecules, discussion on results, and participation in the preparation of the manuscript. I estimate my share as 25 %.
- H9 J. Cz. Dobrowolski (20%), M. H. Jamróz (20%), R. Kołos (20%), J. E. Rode (20%), J. Sadlej (20%), 2007, **Theoretical prediction and the first IR-matrix observation of several L-cysteine molecule conformers**, *Chem. Phys. Chem.*, 8 (2007) 1085-1094. My contribution to this work included co-interpretation of the theoretical vibrational spectra of the studied molecules, discussion on results, and participation in the preparation of the manuscript. I estimate my share as 20 %.
- H10 J. Sadlej (25%), J. Cz. Dobrowolski (25%), J. E. Rode (25%), M. H. Jamróz (25%), 2007, **Density Functional Theory Study on Vibrational Circular Dichroism as a Tool for Analysis of Intermolecular Systems: (1:1) Cysteine-Water Complex Conformations**, *J. Phys. Chem. A*, 111 (2007) 10703-10711. My contribution to this work included the interpretation of the theoretical vibrational spectra of the studied molecules, discussion on results. I estimate my share as 25 %.
- H11 J. Cz. Dobrowolski (15%), S. Ostrowski (15%), R. Kołos (30%), M. H. Jamróz (40%), 2008, **Ar-Matrix IR Spectra of 2-Propanol and its OD, D7 and D8 Isotopologues**, *Vib. Spec.*, 48 (2008) 82-91. My contribution to this work included the PED analysis of the theoretical vibrational spectra, co-interpretation of the experimental spectra and participation in the preparation of the manuscript. I estimate my share as 40 %.
- H12 J. Cz. Dobrowolski (15%), M. H. Jamróz (30%), R. Kołos (20%), J. E. Rode (15%), J. Sadlej (20%), 2008, **IR low-temperature matrix and ab initio study on  $\beta$ -alanine conformers**, *Chem. Phys. Chem.*, 9 (2008) 2042-2051. My contribution to this work included the PED analysis of the theoretical vibrational spectra, interpretation of the experimental spectra and participation in the preparation of the manuscript. I estimate my share as 30 %.
- H13 M. H. Jamróz (20%), M. E. Jamróz (20%), J. E. Rode (20%), E. Bednarek (20%), J. Cz. Dobrowolski (20%), 2009, **Interpretation of Vibrational and NMR Spectra of Allyl Acrylate. An Evidence for Several Conformers**, *Vib. Spec.* 50 (2009) 231-244. My contribution to this work included the PED analysis of the theoretical vibrational spectra, interpretation of the experimental spectra and participation in the preparation of the manuscript. I estimate my share as 20 %.
- H14 J. Cz. Dobrowolski (10%), M. H. Jamróz (25%), Robert Kołos (25%), J. E. Rode (5%), M. K. Cyrański (25%), J. Sadlej (10%), 2010, **IR low-temperature matrix, X-Ray and ab initio study on L-isoserine conformations**, *Phys. Chem. Chem. Phys.*, 12 (2010) 10818-10830. My contribution to this work included the PED analysis of the theoretical vibrational spectra, interpretation of the experimental spectra and participation in the preparation of the manuscript. I estimate my share as 25 %.
- H15 M. K. Cyrański (10%), M. H. Jamróz (20%), A. Ryguła (10%), J. Cz. Dobrowolski (10%), Ł. Dobrzycki (25%), M. Barańska (25%), 2012, **On Two Alizarin Polymorphs**, *Cryst. Eng. Comm.*, 14 (2012) 3667-3676. My contribution to this work included the PED analysis of the theoretical vibrational spectra, interpretation of the experimental spectra and participation in the preparation of the manuscript. I estimate my share as 20 %.



II. Other international and national scientific publications from the Journal Citation Reports (JRC) data base, not included in point I.

1. H. Ghalla, N. Issaoui, M. Govindarajan, H.T. Flakus, M.H. Jamróz, B. Oujia, 2014, Spectroscopic and molecular structure investigation of 2-furanacrylic acid monomer and dimer using HF and DFT methods, *J. Mol. Struct.*, 1059 (2014) 132–143 (not yet included in the Web of Science). My contribution to this work included the PED analysis of the theoretical spectra. I estimate my share as 10 %.
2. S. Ostrowski, M. H. Jamróz, J. Cz. Dobrowolski, 2013, On Stability, Chirality Measures, and Theoretical VCD Spectra of the Heterofullerenes  $C_{69}X$  ( $X = B, Si, Ge, N, P, As$ ), *Tetrahedron: Asymmetry*, 24 (2013) 1097–1109. My contribution to this work included the PED analysis of the theoretical vibrational spectra, and participation in the preparation of the manuscript. I estimate my share as 20 %.
3. J. E. Rode, M. H. Jamróz, J. Sadlej, J. Cz. Dobrowolski, 2012, On VCD Chirality Transfer in EDA Complexes. A Prediction for the Quinine••• $BF_3$  System, *J. Phys. Chem. A*, 116 (2012) 7916–7926. My contribution to this work included the PED analysis of the theoretical vibrational spectra, and participation in the preparation of the manuscript. I estimate my share as 20 %.
4. M. H. Jamróz, J. E. Rode, S. Ostrowski, P. F. Lipiński, J. Cz. Dobrowolski, 2012, Chirality Measures of alpha-Amino Acids, *J. Chem. Inform. Model.*, 52 (2012) 1462–1479. My contribution to this work included the testing of the chirality measures with written by me CHIMEA software, the development of the CHIMEA software and participation in the preparation of the manuscript. I estimate my share as 40 %.
5. M. K. Jamróz, M. H. Jamróz, J. Cz. Dobrowolski, J. A. Gliński, M. Gleńsk, 2012, One new and six known triterpene xylosides from *Cimicifuga racemosa*: FT-IR, Raman and NMR studies and DFT calculations, *Spectrochim. Acta A*, 93 (2012) 10–18. My contribution to this work included the PED analysis of the theoretical vibrational spectra, and participation in the preparation of the manuscript. I estimate my share as 15 %.
6. S. Ostrowski, M. H. Jamróz, J. E. Rode, J. Cz. Dobrowolski, 2012, On Stability, Chirality Measures, and Theoretical VCD Spectra of the Chiral  $C_{58}X_2$  Fullerenes ( $X=N, B$ ), *J. Phys. Chem. A*, 116 (2012) 631–643. My contribution here consists of the testing of the chirality measures with CHIMEA software and participation in the preparation of the manuscript. I estimate my share as 20 %.
7. M. K. Jamróz, M. H. Jamróz, J. Cz. Dobrowolski, J. A. Gliński, M. H. Davey, I. Wawer, 2011, Novel and unusual triterpene from Black Cohosh. Determination of structure of 9,10-seco-9,19-cyclolanostane xyloside (cimipodocarpaside) by NMR, IR and Raman spectroscopy and DFT calculations, *Spectrochim. Acta A*, 78 (2011) 107–112. My contribution to this work included the PED analysis of the theoretical spectra and participation in the preparation of the manuscript. I estimate my share as 15 %.
8. M. E. Jamróz, M. Jarosz, J. Witowska-Jarosz, E. Bednarek, Witold Tęcza, M. H. Jamróz, J. Cz. Dobrowolski, J. Kijeński, 2007, Mono-, di-, and tri-tertbutyl ethers of glycerol. A molecular spectroscopic study, *Spectrochim. Acta A*, 67 (2007) 980–988. My contribution to this work included the interpretation of the experimental IR spectra, the discussion on results, the PED analysis of the theoretical spectra and participation in the preparation of the manuscript. I estimate my share as 20 %.



9. Ostrowski, S; Dobrowolski, JC; Jamróz, MH; Brzozowski, R, 2004, Equilibrium mixture of the diisopropylbenzenes: a DFT study, *Catal. Commun.*, 5 (2004) 733-737. My contribution to this work included discussion on results, and participation in the preparation of the manuscript. I estimate my share as 10 %.
10. R. Brzozowski, W. Skupinski, M. H. Jamróz, et al., Isolation and identification of diisopropylnaphthalene isomers in the alkylation products of naphthalene, 2002, *J. Chromatogr. A*, 946 (2002) 221-227. My contribution to this work included the analysis of the experimental IR spectra and discussion on results. I estimate my share as 10 %.
11. R. Brzozowski, J. Cz. Dobrowolski, M. H. Jamróz, 2002, Theoretical estimation of isomeric composition of cymenes in equilibrium mixture; *Catal. Commun.*, 3-4 (2002) 141-144. My contribution to this work included discussion on results, and participation in the preparation of the manuscript. I estimate my share as 20 %.
12. M. A. Borowiak, M. H. Jamróz, J. Cz. Dobrowolski, K. Bajdor, J. K. Kazimirski, J. Mascetti, E. Quaranta, I. Tomassi, M. Aresta, 2001, Application of the impulse-oscillation model for modelling the formation of peroxocarbonates via carbon dioxide reaction with dioxygen transition metal complexes. A comparison with the experimental results obtained for Rh( $\eta^2$ -O<sub>2</sub>)CIP3 [P=phosphane ligand], *J. Mol. Catal. A: Chemical.*, 165 (2001) 45-54. My contribution to this work included the performance of the calculations with the IOM model using the software designed by me, the analysis and discussion on results, and participation in the preparation of the manuscript. I estimate my share as 20 %.
13. R. Brzozowski, J. Cz. Dobrowolski, M. H. Jamróz, W. Skupinski, 2001, Studies on Diisopropylnaphthalene Substitutional Isomerism, *J. Mol. Catal. A Chemical*, 170 (2001) 95-99. My contribution to this work included discussion on results, and participation in the preparation of the manuscript. I estimate my share as 10 %.
14. J. Rode, J. Cz. Dobrowolski, M. H. Jamróz, M. A. Borowiak, 2001, Theoretical Vibrational and NMR Spectra of 1,2- and 1,3-dimethylenecyclobutane Molecules, *Vib. Spectrosc.*, 25 (2001) 133-149. My contribution to this work included the PED analysis of the theoretical spectra. I estimate my share as 10 %.
15. J. Rode, J. Cz. Dobrowolski, M. H. Jamróz, M. A. Borowiak, 2001, Theoretical Vibrational Spectra of the Diketene, its Isomers, and their Mono- and Disulphur Analogues, *J. Mol. Struct.*, 565-566 (2001) 433-438. My contribution to this work included the PED analysis of the theoretical spectra. I estimate my share as 10 %.
16. J. Zawadzki, W. Skupinski, P. Kirszensztejn, L. Wachowski, M. H. Jamróz, J. Cz. Dobrowolski, 2000, FT-IR Spectroscopic Studies of Tin-Modified Rhenium Alumina-Silica Methatesis Catalyst, *Pol. J. Chem.*, 74 (2000) 1755-1767. My contribution to this work included the analysis of the experimental IR spectra and discussion on results. I estimate my share as 5 %.
17. J. Cz. Dobrowolski, M.H. Jamróz, M. A. Borowiak, E. Quaranta, M. Aresta, 2000, Theoretical IR and Raman Spectra of Diketene and its 3-Methylene Isomer, *Vib. Spectr.*, 22 (2000) 19-28. My contribution to this work included the PED analysis of the theoretical spectra, discussion on results, and participation in the preparation of the manuscript. I estimate my share as 40 %.
18. M. H. Jamróz, J. Cz. Dobrowolski, M. A. Borowiak, 2000, Theoretical IR Spectra of the (2: 1) Ammonia-Carbondioxide System, *Vib. Spectr.*, 22 (2000) 157-161. My contribution to this work included the PED analysis of the theoretical spectra and participation in the preparation of the manuscript. I estimate my share as 50 %.



19. M. A. Borowiak, M. H. Jamróz, R. Larsson, 2000, Catalytic decomposition of formic acid on oxide catalysts - III. IOM model approach to bimolecular mechanism, *J. Mol. Catal. A*, 152 (2000) 121-132. My contribution to this work included the performance of the calculations with the IOM model using the software designed by me, the analysis and discussion on results, and participation in the preparation of the manuscript. I estimate my share as 30 %.
20. M. Malesa, W. Skupiński, M. Jamróz, 1999, Separation of Ammonium Dinitramide from Reaction Mixture. *Prop., Explos., Pyrotech.*, 24 (1999) 83- 89. My contribution to this work included the analysis of the experimental IR spectra and discussion on results. I estimate my share as 20 %.
21. M. H. Jamróz, J. Cz. Dobrowolski, M. Borowiak, 1999, The CO<sub>2</sub> with dimethylamine reaction: ab initio predicted spectra, *J. Mol. Struct.*, 482-483 (1999) 633-637. My contribution to this work included the PED analysis of the theoretical spectra, discussion on results, and the preparation of the manuscript. I estimate my share as 50 %.
22. J. Cz. Dobrowolski, M. H. Jamróz, J. K. Kazimirski, K. Bajdor, M. Borowiak, R. Larsson, 1999, Theoretical Spectra of Diformates: Diformate Anion, *J. Mol. Struct.* 482-483 (1999) 183-187. My contribution to this work included the PED analysis of the theoretical spectra. I estimate my share as 20 %.
23. M. A. Borowiak, M. H. Jamróz, R. Larsson, 1999, Catalytic decomposition of formic acid on oxide catalysts - an impulse-oscillation model approach to the unimolecular mechanism, *J. Mol. Catal. A*, 139 (1999) 97-104. My contribution to this work included the performance of the calculations with the IOM model using the software designed by me, the analysis and discussion on results, and participation in the preparation of the manuscript. I estimate my share as 30 %.
24. M. E. Jamróz, M. Palczewska-Tulińska, D. Wyrzykowska-Stankiewicz, A. Szafrński, J. Polaczek, J. Cz. Dobrowolski, M. H. Jamróz, A. P. Mazurek, 1998, The urea-phenol(s) systems, *Fluid Phase Equil.*, 152 (1998) 307-326. My contribution to this work included the analysis of experimental IR spectra. I estimate my share as 5 %.
25. M. A. Borowiak, M. H. Jamróz, 1998, Impulse oscillation model as a tool for catalyst design, *Intern. J. Chem.*, 1 (1998) CP1-U46. My contribution to this work included the development of the software for the IOM model and the participation on the model description. I estimate my share as 40 %.
26. R. Larsson, M. H. Jamróz, M. A. Borowiak, 1998, On the catalytic decomposition of formic acid. I. The activation energies for oxide catalysis, *J. Mol. Catal. A*, 129 (1998) 41-51. My contribution to this work included the performance of the calculations with the SET model using the software designed by me and the analysis and discussion on results. I estimate my share as 30 %.
27. Dobrowolski, JC; Jamróz, MH; Kazimirski, JK; Bajdor, K; Borowiak, MA; Manna, L; Miglietta, ML; Aresta, M, 1998, The M(O<sub>2</sub>) X(YH<sub>3</sub>)<sub>3</sub> dioxygen complexes (M = Rh, Co; X = F, Cl, Br, I; Y = N, P): An ab initio, DFT and semiempirical PM3(tm) study, *Pol. J. Chem.*, 72 (1998) 2205-2217. My contribution to this work included discussion on results, and participation in the preparation of the manuscript. I estimate my share as 20 %.
28. M. H. Jamróz, J. Cz. Dobrowolski, M. A. Borowiak, 1997, Ab initio study on the 1: 2 reaction of, CO<sub>2</sub> with dimethylamine, *J. Mol. Struct.*, 404 (1997) 105-111. My contribution to this work included the analysis of the theoretical IR spectra, discussion on results, and participation in the preparation of the manuscript u. I estimate my share as 40 %.
29. J. Cz. Dobrowolski, M. H. Jamróz, 1995, Background Elimination in Three-Dimensional Intension Method, *J. Math. Chem.*, 17 (1995) 111-121. My contribution to this work included participation in



the development of the Intensian Method to the analysis of the experimental spectra. I estimate my share as 30 %.

30. M. H. Jamróz, J. Cz. Dobrowolski, K. Bajdor, M. A. Borowiak, 1995, Ab Initio Study of the  $\nu$  ( $\text{CO}_2$ ) Mode in EDA Complexes, *J. Mol. Struct.*, 349 (1995) 9-12. My contribution to this work included calculation of the theoretical vibrational spectra, discussion on results, and preparation of the manuscript. I estimate my share as 30 %.
31. J. Cz. Dobrowolski, M. H. Jamróz, A. P. Mazurek, 1994, Infrared Study on the Double Hydrogen Bond between the Urea Molecule and Halogenated Aliphatic Hydrocarbon Solvents, *Vib. Spectr.*, 8 (1994) 53-60. My contribution to this work included discussion on results, and participation in the preparation of the manuscript. I estimate my share as 30 %.
32. Bajdor, K; Jamróz, MH, 1994, 2<sup>nd</sup> National Conference on Molecular Spectroscopy in Wroclaw, *Przemysł Chemiczny*, 2 (1994) 73-73. My contribution to this work included writing the report. I estimate my share as 30 %.
33. M. H. Jamróz, J. Cz. Dobrowolski, 1993, IR Study on  $\text{CH}_2\text{X}_2$  Double Hydrogen Bonding, *J. Mol. Struct.*, 293 (1993) 143-146. My contribution to this work included discussion on results, and participation in the preparation of the manuscript. I estimate my share as 40 %.
34. J. Cz. Dobrowolski, M. H. Jamróz, 1993, The IR Evidence of  $\text{H}_2\text{O}$  - Aromatic Hydrocarbons Single Hydrogen Bonding, *J. Mol. Struct.*, 293 (1993) 147-150. My contribution to this work included the interpretation of the experimental IR spectra, discussion on results, and participation in the preparation of the manuscript. I estimate my share as 40 %.
35. M. H. Jamróz, J. Cz. Dobrowolski, 1993, Autostandard Method: Quantitative IR Multicomponent Analysis for Films with Indeterminate Pathlength, *Appl. Spectr.*, 47 (1993) 1209-1213. My contribution to this work included participation in the development of the Autostandard method for the analysis of the experimental spectra, and participation in the preparation of the manuscript. I estimate my share as 50 %.
36. M. H. Jamróz, J. Cz. Dobrowolski, M. Glice, 1992, Asymmetric Stretching Vibration of  $\text{CO}_2$  Occluded in Halogen Salts of Alkaline Metals, *J. Mol. Struct.*, 267 (1992) 365-370. My contribution to this work included IR measurements, interpretation and discussion on results, as well as participation in the preparation of the manuscript. I estimate my share as 45 %.
37. J. Cz. Dobrowolski, G. J. Strzemecki, M. H. Jamróz, 1992, Theory of the Intensian Method. A Simple Way to Eliminate Baseline Interference with Spectral Band Intensity, *Chemom. Lab. Intel. Syst.*, 15 (1992) 39-50. My contribution to this work included participation in the development of the Intensian Method and discussion on results. I estimate my share as 10 %.
38. J. Cz. Dobrowolski, M. H. Jamróz, A. P. Mazurek, 1992, IR Study on Double Hydrogen Bonding in Dichloromethane, *J. Mol. Struct.*, 275 (1992) 203-210. My contribution to this work included the analysis of the experimental spectra, discussion on results, and participation in the preparation of the manuscript. I estimate my share as 30 %.
39. J. Cz. Dobrowolski, M. H. Jamróz, 1992, Infrared Evidence for  $\text{CO}_2$  Electron Donor-Acceptor complexes, *J. Mol. Struct.*, 267 (1992) 211- 219. My contribution to this work included the analysis of the experimental spectra, discussion on results, and participation in preparation of the manuscript. I estimate my share as 30 %.
40. J. Kozakiewicz, A. Orzechowski, A. Raszczuk, M. H. Jamróz, J. Cz. Dobrowolski, 1992, Studies on Curicing Urethane prepolymers with Aniline-Formaldehyde Resins, *J. Appl. Polym. Sci.*, 44 (1992) 1349- 1353. My contribution to this work included the IR spectra analysis, discussion on results, and participation in the preparation of the manuscript. I estimate my share as 30 %.

41. J. Dobrowolski, M. H. Jamróz, M. E. Jamróz, D. Wyrzykowska-Stankiewicz, A. M. Szafrński, J. Polaczek, 1988, Infrared, Cryometric and Calorimetric Studies on the Urea-Phenol System, *J. Mol. Struct.*, 175 (1988) 227-232. My contribution to this work included the experimental IR spectra analysis, discussion on results, and participation in the preparation of the manuscript. I estimate my share as 20 %.

Before PhD thesis defense:

1. M. Jamróz, Z. Latek, Z. Hippe, 1986, The Dynamic Interpretation of Infrared-Spectra, *Anal. Chim. Acta*, 181 (1986) 65-77.
2. M. Jamróz, Z. Latek, Z. Hippe, 1985, Recognition of Substructures in Organic-Compounds Based on Artificial-Intelligence - Interpretation of Infrared-Spectra, *Chem. Anal. (Warsaw)* 30 (1985) 599-608.
3. M. Jamróz, Z. Latek, 1984, The Algorithm Of Substructure Recognition in Organic-Compounds by The Artificial-Intelligence Method on The Basis of IR-Spectra, *J. Mol. Struct.*, 115 (1984) 277-280.
4. T. Biernacka J. Witwicka M. Jamróz et al., 1982, Determination of Free Fatty-Acids Of Ricinus Oil By IR Spectrometry, *Chem. Anal. (Warsaw)* 27 (1982) 11-23.

**In summary: 60 publications in the journals from the Journal Citation Reports (JRC) database.**

**Moreover, designed and written by me VEDA software, made available to the international community, is cited over 200 times by other authors in publications from the JCR database.**



**Patents:**

T. Opalińska, R. Brzozowski, M. H. Jamróz, S. Pawłowski, K. Bajdor, B. Ulejczyk

Polish title: 'Sposób modyfikacji katalizatorów heterofazowych, zwłaszcza zeolitów, z zastosowaniem plazmy'

English title: 'Method for modifying heterophase catalysts, particularly zeolites, with the help of plasma'

Patent no. PL 208435 (6.12.2010)

J. Polaczek, T. Kreczmer, Z. Lisicki, M.E. Jamróz, A. Krześlak, M.H.Jamróz, J. Dobrowolski, A.

Szafrąński, D. Wyrzykowska-Stankiewicz, T. Porębski

Polish title: 'Sposób wydzielania fenoli z ich roztworów'

English title: 'The method of phenols extraction from their solutions'

Patent no. 147 968 (1990r)

**Monographs: none****Expert opinions:**

M. H. Jamróz (100%), 1996-1999, Identification of the micro-contaminations of the TV screens by the IR microscopy method, for Polkolor, Warsaw, over 20 expert's reports (confidential)

M. H. Jamróz (100%), 1995-2004, Identification of the given materials by the IR spectroscopy, for the Polish Security Printing Works, Warsaw, over 10 expert's reports (confidential)

**Total Impact Factor** according to Journal Citation Reports (JCR): 122

My total number of citations according to Web of Science (WoS): 579, without self-citation: 485

**Hirsch Index** according to Web of Science (WoS): 13

**Participation in international projects:**

M. H. Jamróz was a project performer in grant RUCADI BRRT-CT95-CT98-5089, RUCADI WP5-CO2 Chemical Utilization, realized in 1995-1998 years, international coordinator: Prof. Michele Aresta, coordinator in Poland: Dr. hab. Marek Borowiak.

M. H. Jamróz was a project performer in grant COST D9/0012/98 Development and applications of theoretical models on catalysis to support the design of improved catalysts, realized in 1998-2002 years, international coordinator: Prof. Ragnar Larsson, coordinator in Poland: Dr. hab. Marek Borowiak.

M. H. Jamróz was a project performer in grant COST D3/0107/94 Modelling of Selective Energy Transfer, Spatial and Time Coherence in Catalytic Reactions, tested on carbon Dioxide reactions, realized in 1994-1998 years, international coordinator: prof. Ragnar Larsson, coordinator in Poland: Dr. hab. Marek Borowiak.

### **Participation in national grants:**

M. H. Jamróz was a project performer in grant N N204 242034, 'Biology inspired spectroscopy: structure, energy, spectra and dynamics of the  $\beta$  amino acids' (Spektroskopia inspirowana biologią: struktura, energia, widma i dynamika betaaminokwasów), headed by Prof. Dr. hab. Joanna Sadlej, realized in 2008-2010 years in Department of Chemistry, UW..

M. H. Jamróz was a performer in grant N R05 0010 04 'Fuel cells with polymer electrolyte using new generation of platinum-less electro-catalysts (Ogniwa paliwowe z elektrolitem polimerowym wykorzystujące bezplatynowe elektrokatalizatory nowej generacji), headed by Dr Piotr Piela, realized in 2008-2010 years.

M. H. Jamróz was a project performer in grant 3T09A 088 28, 'The influence of intermolecular interactions on the parameters of the vibrational circular dichroism spectra VCD' (Wpływ oddziaływań międzymolekularnych na parametry widm oscylacyjnego dichroizmu kołowego VCD), headed by Prof. Dr. hab. Joanna Sadlej, realized in 2005-2007 years.

M. H. Jamróz was a project performer in grant PBZ/KBN/018/T09/99/1a 'Activators and activation of the carbon-hydrogen bond in methane' (Aktywatory i aktywacja wiązania węgiel-wodór w metanie), headed by Dr. hab. Marek A. Borowiak, realized in 2000-2003 years.

M. H. Jamróz was a project performer in grant 3 T09B05017 'Development and application of the theoretical models of the catalysis in the designing of enhanced catalysts' (Rozwój i zastosowanie modeli teoretycznych katalizy w projektowaniu ulepszonych katalizatorów), headed by Dr. hab. Marek Borowiak, realized in 1999-2002 years.

M. H. Jamróz was a project performer in grant 3 T09B03309 Modeling of the selective energy transfer, spatial conditions (relations) and synchronization in catalytic reactions on the basis of CO<sub>2</sub> reactions' (Modelowanie selektywnego przenoszenia energii, warunków przestrzennych i synchronizacji w reakcjach katalitycznych na przykładach reakcji dwutlenku węgla), headed by Dr. hab. Marek Borowiak, realized in 1995-1998 years.

### **Other projects:**

M. Borowiak, R. Brzozowski, J. Cz. Dobrowolski, M. H. Jamróz, A. Zimowski, B. Kąkol, J. Kozakiewicz, A. Lipkowski, S. Ostrowski, J. Przybylski, J. Rzepkowska-Rode, W. Skupiński (M. H. Jamróz – project performer) - Tools and techniques for computer-aided methods of chemical engineering CAPE: molecular modeling. ICRI investigation report, 2002, Warsaw

### **National awards for R&D activity**

2013, First award for J. Cz. Dobrowolski group (including M. H Jamróz) in the 'Świętosławski' competition, Industrial Chemistry Research Institute, Warsaw.

2011, Gold medal for lifetime achievements, the President of the RP



### III Teaching and popularization output and information on international cooperation

Papers delivered on international conferences (from 1991) by me:

Jamróz M.H., Dobrowolski J.Cz., Glice M.

Asymmetric Stretching Vibration of CO<sub>2</sub> Occluded in Halogen Salts

First National Conference on Molecular Spectroscopy: Vibrational Spectroscopy (with international participation), Wrocław, Poland, 28-30 October 1991

Jamróz M.H., Dobrowolski J.Cz.

CO<sub>2</sub> Inclusion in Halogen Salts of Alkaline Metals

XX European Congress on Molecular Spectroscopy, Zagreb, Yugoslavia, 25-30 August 1991,  
Presentation on post-conference meeting

Jamróz M.H., Dobrowolski J.Cz.

IR study on CH<sub>2</sub>X<sub>2</sub> Double Hydrogen Bonding

XXI European Congress on Molecular Spectroscopy EUCMOS, Wien, Austria, 23-28 August 1992

Jamróz M.H., Dobrowolski J.Cz., Jamróz M.E., Polaczek J.

Infrared Determined Thermodynamic Parameters and SEL-Diagrams of Carbazole-Tertiary Amide Systems

II<sup>nd</sup> Conference on Molecular Spectroscopy with international participation, Wrocław, Poland, September, 1993

Jamróz M.H., Dobrowolski J.Cz., Jamróz M.E., Polaczek J.

Hydrogen Bond in Carbazole-Tertiary Amide System

European Conference on Analytical Chemistry EUROANALYSIS VIII, Edinburgh, Great Britain, September 1993

Jamróz M.H., Dobrowolski J.Cz., Bajdor K., Borowiak M.

Ab Initio Study of the  $\nu_2$ (CO<sub>2</sub>) Mode in EDA Complexes

XXII European Congress on Molecular Spectroscopy EUCMOS, Essen, Germany, 11-16 September 1994

Jamróz M.H., Dobrowolski J.Cz., Borowiak M.

Ab initio Study on the CO<sub>2</sub> with Dimethylamine 1:2 Reaction

III<sup>rd</sup> Conference on Molecular Spectroscopy with international participation, Wrocław, Poland, 7-9 December 1995

Jamróz M.H., Dobrowolski J.Cz., Borowiak M.

The, CO<sub>2</sub> with Dimethylamine Reaction: ab initio Predicted Vibrational Spectra

XXIV European Congress on Molecular Spectroscopy EUCMOS, Prague, Czech Republic, 23-28 August 1998

Jamróz M.H., Dobrowolski J.Cz., Borowiak M.

Theoretical IR Spectra of Ammonia-Carbon Dioxide 2:1 System

7th Austrian Hungarian International Conference on Vibrational Spectroscopy, Balatonfured, Hungary, 8-11 April 1999

Jamróz M.H., Dobrowolski J.Cz.

Potential Energy Distribution Analysis of DFT and ab initio Calculated IR Spectra of the Most Stable Li, Na and Cu(I) Diformalate Molecules

International Conference on Progress in Computing of Physicochemical Properties, Warsaw, 18-20 November 1999

Jamróz M.H., Dobrowolski J.Cz.

Potential Energy Distribution Analysis (PED) of DFT and ab initio Calculated IR Spectra of the Most Stable Li, Na and Cu Diformalate Molecules

XXV European Congress on Molecular Spectroscopy EUCMOS, Coimbra, Portugal, 27 August - 1 September 2000

Jamróz M.H., Dobrowolski J.Cz.

Theoretical IR Spectra and Stability of Carbamic Acid Complexes

The First International Conference on Advanced Vibrational Spectroscopy ICAVS-1, Turku, Finland, 19-24 August 2001

Jamróz M. H.

Theoretical and Experimental IR Spectra and Stability of Dibenzyl Carbamic Acid Complex

Seminar of the COST Group, Budapest, Hungary, march 2002

Jamróz M.H., Brzozowski R., Dobrowolski J.Cz.

Elucidation of Experimental IR Spectra of Diisopropyl-naphthalenes Based on Analysis of Theoretical Spectra

XXVI European Congress on Molecular Spectroscopy EUCMOS'2002, Villeneuve d'Ascq, France, 1-6 September 2002

Jamróz M.H., Ostrowski S., Dobrowolski J.Cz.

Modelling of a Methane Reaction on Rh Catalyst

18th Dubrovnik International Course & Conference on the Interfaces among Mathematics, Chemistry and Computer Sciences, Dubrovnik, Croatia, 23-28 June 2003

Jamróz M.H., Dobrowolski J.Cz.

Experimental and Theoretical Vibrational Spectra of the  $((CH_3)_3P)_2ClRhCO$  Catalyst

18th Dubrovnik International Course & Conference on the Interfaces among Mathematics, Chemistry and Computer Sciences, Dubrovnik, Croatia, 23-28 June 2003

Jamróz M.H., Brzozowski R., Dobrowolski J.Cz.

Elucidation of Theoretical IR Spectra of Diisopropyl-naphthalenes. PED Analysis

XXVII European Congress on Molecular Spectroscopy EUCMOS'2004, Cracow, Poland, 5-10 September 2004



Papers delivered on international conferences (from 1991) by co-authors:

Dobrowolski J.Cz., Jamróz M.H.

Infrared Evidence of CO<sub>2</sub> Electron Donor-Acceptor Complexes

First National Conference on Molecular Spectroscopy: Vibrational Spectroscopy (with international participation), Wrocław, Poland, 28-30 October 1991

Skarżyński M., Wawer J. Bednarek E., Jamróz M. H, Polaczek J.

Investigation of Conformational Transitions in N-methyl -E-caprolactam with <sup>1</sup>H and <sup>13</sup>C NMR  
XXVII Colloquium Spectroscopicum Internationale, Bergen, Norway, 9-14 June 1991

Dobrowolski J.Cz., Jamróz M.H., Mazurek A. P.

The IR Study of Hydrogen Bonded Methyl of CH<sub>3</sub>I

European Conference on Analytical Chemistry EUROANALYSIS VIII, Edinburgh, Great Britain, September 1993

Dobrowolski J.Cz., Manna L, Migietta M, Jamróz M.H., Bajdor K, Borowiak M

Semiempirical PM3(tm) Study on the (YH<sub>3</sub>)MeO<sub>2</sub> Complexes

XXIII European Congress on Molecular Spectroscopy EUCMOS, Balatonfüred, Hungary, 25-30 September 1996

Dobrowolski J.Cz., Jamróz M.H., Palczewska-Tulińska M, Szafranski A., Wyrzykowska-Stankiewicz D., Polaczek J., Mazurek A. P.

Solid-Liquid Equilibria and Hydrogen Bond Interaction Studies in Urea-Phenols Binary Systems

International Conference on Applied Physical Chemistry, Warsaw, Poland, 13-16 November 1996

Jamróz M. E., Lisicki Z., Palczewska-Tulińska, Polaczek J., Jamróz M.H., Kazimirski J., Dobrowolski J.Cz.

The Carbazole-Tertiary Amide Systems

International Conference on Applied Physical Chemistry, Warsaw, Poland, 13-16 November 1996

Borowiak M, Jamróz M. H.

Impulse Oscillation Model as a Tool for Catalyst Design

4th Electronic Computational Chemistry Conference ECCC-4, November 1997

Larsson R., Borowiak M, Jamróz M. H. Kazimirski J., Bajdor K., Dobrowolski J.Cz.

The HCOOH Catalytic Decomposition on Metal Oxides Considered as Vibrationally Activated Reaction

3<sup>rd</sup> European Congress on Catalysis Europa CAT 3, Cracow, Poland, 23 August -6 September 1997

Dobrowolski J.Cz., Kazimirski J., Bajdor K., Jamróz M.H., Borowiak M, Larsson R.

Theoretical Vibrational Spectra of Anion Diformates

XXIV European Congress on Molecular Spectroscopy EUCMOS, Prague, Czech Republic, 23-28 August 1998

Dobrowolski J.Cz., Jamróz M.H., Borowiak M, Quaranta E., Aresta M

Theoretical IR and Raman spectra of Diketene and Its 3-Methylene Isomer  
7th Austrian Hungarian International Conference on Vibrational Spectroscopy, Balatonfüred, Hungary, 8-11 April 1999

Ostrowski S., Jamróz M.H., Borowiak M.  
Modelling of HCOOH Decomposition Reactions on Metal Catalysts  
International Conference on Progress in Computing of Physicochemical Properties, Warsaw, Poland, 18-20 November 1999

Zawadzki J., Skupiński W., Jamróz M.H., Dobrowolski J.Cz., Kirszensztejn P., Wachowski L.  
FTIR Studies of Re<sub>2</sub>O<sub>7</sub>/Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>/TMT Systems  
13<sup>th</sup> International Symposium on Olefin Methathesis, Reldur, the Netherlands, 11-15 July 1999

Rzepkowska J., Dobrowolski J.Cz., Jamróz M.H., Borowiak M.,  
Theoretical Vibrational Spectra of the Diketene, and Their Mono- and Disulphur Analogues  
XXV European Congress on Molecular Spectroscopy EUCMOS, Coimbra, Portugal, 27 August - 1 September 2000

Rzepkowska J., Dobrowolski J.Cz., Jamróz M.H., Borowiak M.,  
Theoretical Vibrational and NMR Spectra of 1,2 and 1,3-Dimethylcyclobutane Molecules  
XXV European Congress on Molecular Spectroscopy EUCMOS, Coimbra, Portugal, 27 August - 1 September 2000

Ostrowski S., Jamróz M.H., Larsson R., Borowiak M.  
Decomposition of HCOOH on Metal Catalysts: Cu and Mo Catalysts  
5th European Congress on Catalysis EuropaCat-V, Limerick, Ireland, 1-7 September 2001

Dobrowolski J.Cz., Jamróz M.H., PAH Molecules of the Belt and Moebius Types  
17th Dubrovnik International Course & Conference on the Interfaces among Mathematics, Chemistry and Computer Sciences, Dubrovnik, Croatia, 24-29 June 2002

Ostrowski S., Jamróz M.H., Borowiak M.  
Modelling of Catalytic Reaction in [CO<sub>2</sub>+H<sub>2</sub>+NH<sub>3</sub>] System: Impulse Oscillation Model Study  
17<sup>th</sup> Dubrovnik International Course & Conference on the Interfaces among Mathematics, Chemistry and Computer Sciences, Dubrovnik, Croatia, 24-29 June 2002

Dobrowolski J.Cz., Rzepkowska-Rode J., Dobrosz-Teperek K., Kołos R., Jamróz M.H., Lewandowski W., Bajdor K., Mazurek A.P.  
Vibrational Spectra of 5-Halogenouracils. Part III. Deformation Modes  
10th European Conference on the Spectroscopy of Biological Molecules, Szeged, Hungary, 30 August - 4 September 2003

Borowiak M., Dobrowolski J.Cz., Jamróz M.H., Ostrowski S., Rzepkowska-Rode J.  
Development and Applications of Theoretical Models on Catalysis to Support the Design of Improved Catalysis



Seminar of the COST Group, Bordeaux, France, 28 June - 1 July 2001

Dobrowolski J.Cz., Rzepkowska-Rode J., Kołos R., Jamróz M.H., Bajdor K., Mazurek A.P.

Ar-Matrix IR Spectra of 5-Halouracils

XXVII European Congress on Molecular Spectroscopy EUCMOS, Cracow, Poland, 5-10 September 2004

Dobrowolski J.Cz., Sadlej J., Rzepkowska-Rode J., Jamróz M.H., Kołos R.

DFT Study on Vibrational Spectroscopy Markers of Conformations of the Cysteine Molecule in the Gas Phase

XXVIII European Congress on Molecular Spectroscopy EUCMOS'2006, Istanbul, Turkey, 3-8 September 2006

Jamróz M.E., Jarosz M., Witowska-Jarosz J., Bednarek E., Tęcza W., Jamróz M.H., Dobrowolski J.Cz., Kijeński J.

Mono-, di-, and tri-tert-Butyl Ethers of Glycerol. A Spectroscopic Study XXVIII European Congress on Molecular Spectroscopy EUCMOS'2006, Istanbul, Turkey, 3-8 September 2006

Ostrowski S., Kołos R., Jamróz M.H., Kijeński J., Dobrowolski J.Cz.

Ar-Matrix IR Spectra of 2-Propanol and Its OD, D7, and D8 Isotopomers

XXVIII European Congress on Molecular Spectroscopy EUCMOS, Istanbul, Turkey, 3-8 September 2006

Sadlej J., Dobrowolski J.Cz., Rzepkowska-Rode J., Jamróz M.H.

DFT Study of Vibrational Circular Dichroism Spectra of D-Lactic Acid-Water

XXVIII European Congress on Molecular Spectroscopy EUCMOS, Istanbul, Turkey, 3-8 September 2006

Dobrowolski J.Cz., Jamróz M.H., Kołos R., Rzepkowska-Rode J., Sadlej J.

Theoretical Prediction and the First IR-Matrix Observation of Several L-Cysteine Molecule

Conformers 4th International Conference on Advanced Vibrational Spectroscopy, Corfu, Greece, 10-15 June 2007

Dobrowolski J.Cz., Ostrowski S., Kołos R., Jamróz M.H., Kijeński J.

Ar-Matrix IR Spectra of 2-Propanol and Its OD, D7 and D8 Isotopomers 4th International Conference on Advanced Vibrational Spectroscopy, Corfu, Greece, 10-15 June 2007

Dobrowolski J.Cz., Jamróz M.H., Kołos R., Rzepkowska-Rode J., Sadlej J.

IR Low-Temperature Matrix and ab initio Study on beta-Alanine Conformers

XXIX European Congress on Molecular Spectroscopy EUCMOS'2008, Opatija, Croatia, 31 August -5 September 2008

Jamróz M.E., Jamróz M.H., Rzepkowska-Rode J., Dobrowolski J.Cz.

Interpretation of Vibrational Spectra of Allyl Acrylate

XXIX European Congress on Molecular Spectroscopy EUCMOS'2008, Opatija, Croatia, 31 August -5 September 2008

Baran A., Jamróz M.H., Dobrowolski J.C., Barańska M.  
The Interpretation of Vibrational Spectra of Alizarin. Experimental and Computational Study.  
Xth International Conference on Molecular Spectroscopy "From Molecules to Molecular Materials and Biological Systems", Cracow-Białka Tatrzańska, Poland, 6-10 September 2009

Dobrowolski J.C., Jamróz M.H., Kołos R., Rzepkowska-Rode J., Sadlej J.  
L-isoserine Conformation in Low-Temperature IR Matrix Spectra Interpreted by Means of the DFT Calculations  
XIII European Conference on the Spectroscopy of Biological Molecules, Palermo, Italy, 28 August -2 September 2009

Dobrowolski J.C., Jamróz M.H., Kołos R., Rzepkowska-Rode J., Sadlej J.  
L-isoserine Conformation in Low-Temperature IR Matrix Spectra Interpreted by Means of the DFT Calculations  
Xth International Conference on Molecular Spectroscopy "From Molecules to Molecular Materials and Biological Systems", Cracow-Białka Tatrzańska, Poland, 6-10 September 2009

Jamróz M.H., Rode J.E., Ostrowski S., Dobrowolski J.Cz.  
On chirality of amino acids  
13<sup>th</sup> International Conference on Chiroptical Spectroscopy, Oxford, Great Britain, 24-28 July 2011

Rode J.E., Dobrowolski J. Cz., Jamróz M.H., Sadlej J.  
VCD chirality transfer: a new insight into the intermolecular interactions  
XIIth International Conference on Molecular Spectroscopy, Białka Tatrzańska, Poland, 8-12 September 2013



Review of articles in the international journals

1. Spectrochimica Acta A, 9 reviews
2. Journal of Molecular Structure, 5 reviews
3. Vibrational Spectroscopy, 3 reviews
4. Zeitschrift für Physikalische Chemie, 1 review

Other achievements not listed above:

Development of analytical methods for spectroscopy:

Participation in the development of methods for quantitative analysis of the bands located at a non-linear background, or bands in two-dimensional spectroscopy (Intensian method).

Participation in the development of the new method for application in the quantitative analysis of vibrational spectra, which use internal standard (Autostandard method).

Development of computer programs:

- a) construction of the computer program IRDIN for the experimental IR spectra interpretation on the basis of the dynamic applying of correlation tables (1984-1986, doctor thesis).
- b) construction of the software for testing of the two models for predicting the properties of catalysts and their suitability in the studied chemical reactions. The tested models were:

1) IOM Model (Impulse Oscillation Model) proposed by Borowiak [12, 19, 23, 25]

2) SET Model (Selective Energy Transfer) proposed by Larsson [26].

- c) SPESCA program for the comparison between the theoretical and experimental vibrational spectra by weighted linear regression. The software is accessible on Web page [www.smmg.pl](http://www.smmg.pl).
- d) Design, write and test the CHIMEA software [4, 6] defining the class of the chirality measures of the molecules based on the similarity of enantiomers.

6. Discussion on the scientific purpose of the presented work and achieved results including their application.

Dr Michał H. Jamróz. Institute of Nuclear Chemistry and Technology, Warsaw

## **PED analysis of theoretical vibrational spectra by the VEDA software**

### **Preface**

Since the eighties of the twentieth century I was engaged in the interpretation of experimental vibrational spectra. My scientific interests resulted in doctoral thesis in 1986, in which I designed and described a software for the interpretation of experimental spectra on the basis of dynamic assignment of spectral bands with the usage of correlation tables. For years the software had been applied for educational purposes at the University of Wrocław and the Rzeszow University of Technology, as well as for analytical investigations at the Industrial Chemistry Research Institute in Warsaw. However, it should be emphasized that in many cases experimental spectrum cannot be interpreted unambiguously, especially in the so-called *finger print* region. This is due to the overlapping of the spectral bands, complexity of skeletal vibrations, as well as the dependence of position, intensity and width of characteristic IR bands on the chemical environment.

In the middle of the 90. of the twentieth century, apart from experimental spectroscopy, I begun to use quantum chemical calculations, with the special emphasis on the theoretical vibrational spectra, used for the proper interpretation of the experimental ones. This new approach bring new difficulties to be overcome, among them technical aspects as the choice of calculation method, basis set, anharmonicity corrections and so on. However, the most crucial was the understanding of the calculated normal modes. A normal mode is a motion of all atoms in a molecule conserving the position of the mass center. Generally, there is an infinite number of internal coordination sets of a molecule, but normal coordination set is distinguished by the orthogonality of all motions. Most of the vibrations consist of a complex motion of the whole molecule and only few of the vibrations can be assign to a particular, small molecular fragment. The assignment of the analyzed vibration is the more difficult, the larger the analyzed molecule is. For a proper interpretation of the normal modes, a procedure in which the normal coordinations are expressed as a sum of local coordinations, resulting from particular functional groups and skeletal elements was introduced. The local coordinates are expressed as changes in the bond lengths, angles and torsion angles values. In this work, such a coordination set is designated as SBT („Stretching, Bending, and Torsion”). The described procedure, here designated as Potential Energy Distribution (PED) Analysis, allows for expressing the energy of a normal mode as a sum of the energies of fragments vibrations. The most crucial issue in the PED procedure is such a construction of the local coordinations set to be as close as possible to the normal modes coordinates. At the beginning of my work with the PED procedure, it was used for the interpretation of vibrational spectra of small molecules, with the number of atoms not exceeding 20. For larger molecules the construction of the appropriate local coordination set was too difficult.

Vibrational spectroscopy (IR and Raman) is one of the most commonly used methods for the characterization of organic and inorganic compounds, as well as in the polymer and new materials chemistry, physical chemistry (incl. intra- and intermolecular interactions), physics, medicinal chemistry (pharmacy) and medicine. In all of these, the understanding of the observed vibrational bands is of



importance. Currently, to comprehend experimental spectra, calculations of theoretical spectra of the studied systems and their proper interpretation is necessary. For this purpose the most accurate method is the PED analysis.

The aim of my studies was the improvement of the interpretation of theoretical vibrational spectra by the PED analysis. To that purpose many features of the PED analysis had to be developed and automatized. In order to meet these needs, I wrote a software for the interpretation of theoretical vibrational spectra, and designated it as VEDA (Vibrational Energy Distribution Analysis). The main development introduced in my software was the automatic construction of linearly independent local coordination sets. Next, I expanded the automatic procedure on finding the complex coordinates, representing the normal modes. I also added the possibility to analyze medium-sized molecules, which are more important for the applied chemistry than small ones. To achieve all of these, and so ensure the proper interpretation, an optimal solution to a following issue had to be found: coordinates had to represent as well as possible the normal modes, they had to be understandable to the interpreter, and, at the same time, as simple as possible. Unfortunately, these mentioned three goals are in opposition to each other. The PED analysis is ambiguous, but one can say that the PED interpretation can be done properly, under the condition that it will be able to explain the studied problem. That inspired me to enable the interpreter to have such an approach to a problem, so that the studied spectroscopic effect is best described. Finally, the last end of a proper interpretation of the vibrational theoretical spectra is always the best possible accuracy. The VEDA software fulfills that condition well. It is documented by the fact, that only after few years accessibility to the international scientific community, it was applied in more than 200 scientific investigations, published in renowned journals.

The VEDA software was developed step by step, by applying it in consecutive problems involving the interpretation of the theoretical vibrational spectra. The first step was the automatic construction of the local coordination set [H2, 9]. Then, the VEDA software was used for more complex systems [H3, H4]. The next innovation, used in the spectral analysis of large molecules, was the separation of the analysis of vibrations originating only from the skeletal fragments, *e.g.* CC, and from those originating from aromatic and aliphatic CH groups [H5, H7]. The separation of the heavy atoms vibrations from the CH ones made the analysis considerably more clear. Such a separation can be expanded also to NH and OH groups. The success of this approach revealed the usefulness of the introduction of a new category of vibrations, which was designated by me as 'User'. Its application permitted the choice of vibrations of the fragments of molecules, which are the most crucial in solving a particular issue, and the treatment of the selected vibrations in an alternative way. This approach can be applied in many different ways, *e.g.* when comparing vibrational spectra of series of derivatives, conformers, isomers, isotopologues, etc. [H6, H9 – H14]. During the PED analysis, the most crucial step is optimization, *i.e.* achievement of the best and the simplest approximation of the normal modes coordinates by the local ones [H1 – H15]. In the optimization procedure also the movements of particular atoms are included (the AMD procedure), as well as the coordinates reduction and normalization. The software, together with its algorithm and examples, was described in a publication [H1].

Entirely new features of my approach is automatic construction of local coordinates, complex coordinates, optimization of the PED analysis, analysis of large molecules consisting of 240 (and in a special edition of 480) atoms, and the possibility of interactive user interference at all stages of the analysis. Due to above



mentioned features, the VEDA software can be applied an inexperienced researchers, but is also a powerful tool for the experienced spectroscopist.

## 1. Introduction [H1]

1.1. Usually, the studies of the changes in the vibrational spectra require support by the calculated theoretical spectra, since it is not possible to assign many bands in the '*finger print*' region ( $1400\text{--}400\text{ cm}^{-1}$ ) only on the basis of experimental knowledge. The usage of the state-of-the-art quantum chemical methods bring reliable results in the calculation of the theoretical spectra. As for the interpretation of the theoretical spectra, there are two accepted ways: visualization of the atomic vibrations in the normal modes and '*Potential Energy Distribution*' (PED) analysis [1–6]. The first one is easy to use and due to that commonly applied, but it is also misleading, since light atoms motions are not associated with the considerable change in the potential energy. The second way, however, despite being more difficult, is preferable. It grants much more reliable results due to being based on the analysis of the force constants matrix and therefore allows the qualitative and quantitative observations of the changes in the spectra. On the other hand, the PED analysis is in a way arbitrary and require spectroscopic knowledge. The fact of being arbitrary results from the necessity of the replacement of the normal modes ( $3N-6$  orthogonal, harmonic motions of all atoms in an  $N$ -atomic molecule in relation to the center of the mass) with the vibrations that reflect in a clear manner the movements of the functional groups of a molecule. The mentioned clear manner depends on the interpreter willing. I begun the studies at the interpretation of the theoretical vibrational spectra by the PED analysis method in the nineties of the twentieth century, and in 2013 I described in the article in *Spectrochimica Acta A* [H1] the entirety of my experience and the usage of the VEDA software (*Vibrational Energy Distribution Analysis*), which I wrote for the analysis of the theoretical vibrational spectra.

1.2. *PED analysis.* To describe the vibration of a  $N$ -atomic molecule (or a system of interacting molecules), the PED analysis require the construction of the set of  $3N-6$  local, linearly independent, internal coordinates, which represents stretching, bending and deformation motions of the functional groups or the chosen fragments of the molecule. The introduction of such a coordination set instead of the normal modes causes that the potential energy distribution matrix, the PED matrix, ceases to be diagonal, but the energy distribution originating from the motions of particular functional groups is understandable for the interpreter. In 1970 a software for the PED analysis was written by Balga, and later modified by Lapinski [7, 8]. The software, however, requires that the user will define a coordination set manually. Meanwhile, even for 16-atomic molecule, the task is difficult, since it involves the introduction of 42 independent definitions of coordinates. For the 50-atomic molecules it is nearly impossible.

1.3. *The origin and development of the VEDA software.* In the late nineties I begun to construct the software, which automatically generate the set of local coordinates, *i.e.* the VEDA software [H2]. It was cited for the first time after its application in the analysis of a 9-atomic molecule [9]. Three years later it was used for more complicated systems [H3, H4], including a 66-atomic one [H3]. Since then, the software has been developed by me and repeatedly applied. Recently it has been made accessible to the international scientific community. In the current basic edition of the software it is possible to analyze 120-atomic system, and in the expanded versions even 240- (VEDAx1) and 480-atomic (VEDAx1) ones. The software is accessible *via* Internet: <http://www.smmg.pl>



## 2. Fundamental problems solved during the construction of the VEDA software.

### 2.1. *SBT (stretch, bend, tors) coordination set vs. the normal modes [H1, H2].*

For the description of the studied system vibrations, the VEDA software uses local coordinates defined in a following manner: 'stretching' S, 'bending' B and 'torsion or/and out-of-plane' T. The definition of the S coordinate requires the indication of two atoms A-B, the B definition – three atoms A-B-C and the T definition – four atoms A-B-C-D. The S coordinate describes two-atomic stretching motion, B – motion in the ABC plane and T – the change in the value of torsion angle between ABD and BCD planes (torsion) or the AD vector deflection from the ABC plane (out-of-plane). These definitions are in accordance with those in the Balga software [7, 8].

The introduction of the automatic generation of the SBT coordination set was one of the essential innovations in my software [9, H2]. VEDA uses atoms connected with bonds in order to create the SBT coordinates. That is why the connectivity matrix is generated beforehand (.mpo file). For the N-atomic system the software creates in an unaffected way  $3N-6$  coordinates:  $N-1$  S coordinates,  $N-2$  B coordinates and  $N-3$  T coordinates. First, for the consecutive terminal atoms, one S, one B and one T coordinate is created by VEDA. The atom that was used in the previous definitions is not included in the construction of the next coordinates. When there are only ring-bonded atoms left, the system is torn between the two least cross-linked and, at the same time, the farthest away atoms. When there are only three atoms left, the T coordinate cannot be constructed. Similarly, for the last two remaining atoms, only the S coordinate is created. The importance of the automatic construction of the SBT coordination set grows with the size of the analyzed system. The experienced spectroscopist can manage with the construction of the SBT coordination set for small molecules, but more than 20-atomic molecules are difficult to analyze for anybody. However, it is worth to stress, that despite the automatic generation of the coordination set, the user intervention in the SBT set construction is still possible in the software.

### 2.2. *Linear independence of coordinates.*

The linear independence of the coordinates is a necessary condition during solving the system of equations that leads to the PED matrix determination [H1]. The assurance of the coordinates linear independence in the PED analysis can be difficult for symmetrical molecules, even as small as 8-atomic urea molecule [17].

Each start of the VEDA software is associated with the coordinates linear independence check. For non-planar, non-symmetrical structures, which do not have perpendicular planes, the construction method described in 2.1 is practically unfailing. In the case of linear dependence of the coordinates (caused by e.g. co-incidence of bending and torsion coordinates) the user is informed by the software and he can either choose the VEDA software to solve the problem or edit the conflicted definition by himself. The manual edition of the coordinates require extensive expertise, and that is why I devoted a lot of work to the automatic procedures in VEDA, that can solved the mentioned problem. The automatic procedure uses alternative coordinates, that are described in the 2.4. subsection. The alternative coordinates testing by the software can be preceded by the coordinates group exchange between basic and alternative coordinates

sets. Additionally, there are several ways of constructing the basic coordinates in the software, *e.g.* the deformation vibrations can be expressed solely by the torsion coordinates (then the out-of-plane coordinates are placed in the alternative coordinates set) or for ring-containing structures, the coordinates can be defined differently, by using the existence of an additional bond. These alternative ways can be used with the try-and-error method, without considering the essence of the issue. This is of importance especially for large systems. Usually, the VEDA software eliminates the problem of linear dependence of the coordinates easily, which was confirmed by the analysis of the theoretical IR spectra of symmetrical conformers of small molecule of isopropanol and its isotopologues [H11], as well as of dibenzylcarbamic acid dimer with a planar, symmetrical fragment containing intermolecular bonds [H3].

### 2.3. *Complex coordinates.*

The necessity of the introduction of the complex coordinates exists even for 3-atomic molecules, such as H<sub>2</sub>O and CO<sub>2</sub>, in which the stretching bonds vibrations are coupled, and one can observe symmetrical and asymmetrical stretching. The SBT set automatic generation procedure evokes, that in the vibrations description of the studied structure (PED matrix), even for simple molecules, many modes are explained by several simple coordinates. In addition, some of the vibrations remain unexplained (*i.e.* there are no coordinates, which contribute not more than 10% to PED). That is why, from its beginnings, the VEDA software automatically groups similar vibrations and links them into the complex coordinates [9, H2]. The earlier computer programs imposed on the user the necessity to create such complex coordinates by himself. In the VEDA software, the construction of complex coordinates is aimed at the more precise imitation of the normal modes by the local ones and the enhancement of the diagonality degree of the PED matrix. As a result, a new SBT coordination set is created, in which coordinates are more revealing and easily understandable for the user. Also, the optimization of the complex coordinates, which is based on an iterative change of the coordinates and testing the diagonality degree of the PED matrix (see subsection 3.2) was implemented in the software. The optimization procedure was positively verified in the analysis of 66-atomic dibenzylcarbamid acid dimer, which has 192 basic normal modes [H3].

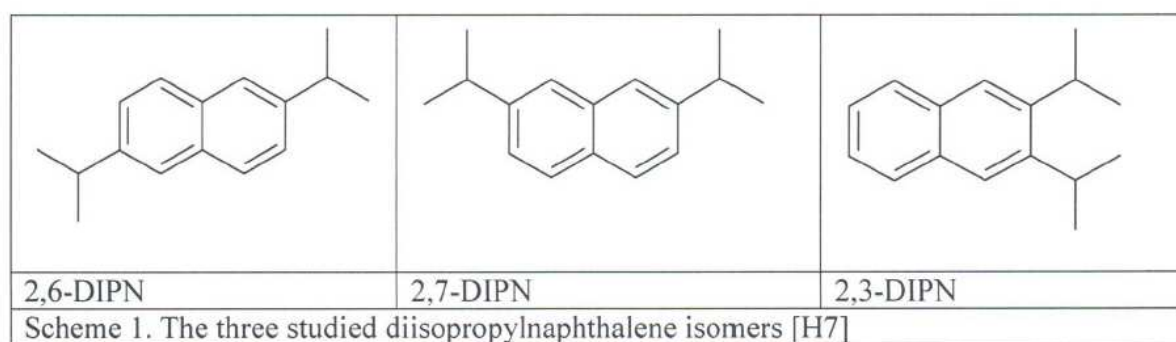
### 2.4. *Alternative coordinates.*

For the terminal atoms only one S coordinate can be determined, but there are at least two possible B coordinates and several possibilities of determining a T coordinate. Additionally, for the ring-containing systems, there can be some choice of the S coordinates. Due to that the VEDA software generates, beside the basic SBT coordination set, the alternative coordination set. The alternative coordinates can, but do not have to, be used. They are of use when eliminating linear dependence of the coordinates [17, H11], as well as in the optimization procedure (subsection 3.2), especially in the intermolecular systems [H3, H4].



## 2.5. *CH and not CH categories* [H5, H7].

During the analysis of isomers of a large molecule, diisopropylnaphthalene (Scheme 1), consisting only of CH aromatic and aliphatic groups, which are characterized by 102 vibrations [H5, H7], I became convinced, that it is worth to treat separately coordinates with the H atom, from those containing only heavy atoms. Otherwise, the complex coordinates (subsection 2.3) are too complicated, even for the systems with only 20 atoms. The PED analysis, in which such a separation was made, fully explained the impact of structural differences of the diisopropylnaphthalene isomers on the vibrational spectra characteristics. Since then, the distinction between *CH* and *not CH* categories has been implemented in the VEDA software. Optionally, to the *CH* category, also NH and OH groups can be included. Still, the user can always choose not to treat *CH* and *not CH* vibrations separately, which is of use for the small systems.



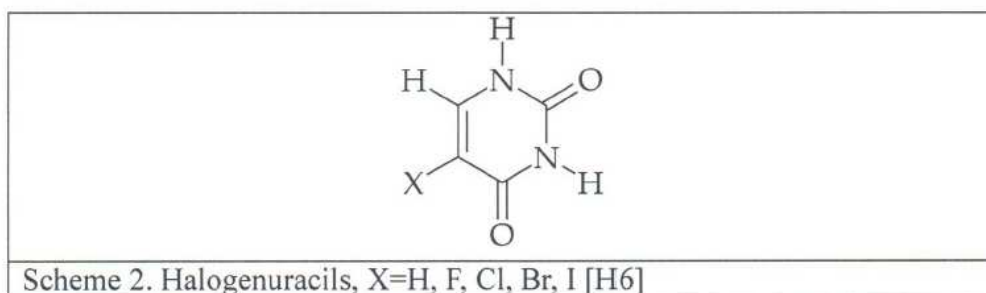
## 2.6. 'User' category [H6, H8 – H14].

Before, after and during the optimization procedure, the user can edit the file with vibrations definitions (.dd2 file) and introduce his own definitions for the chosen vibrations. Then, these vibrations can be treated independently. The user can exclude the chosen definitions from the optimization procedure, or oppositely, he can choose to optimize only the chosen definitions. This category was designed with the aim of finding the common features of series of analyzed systems, as well as understanding the differences between these systems. In such series particular structural features have their own representations in the coordinates and their contributions to the PED matrix. It has to be stressed, that the change of one of the coordinates influences the PED contributions of the other coordinates, so that it is necessary to re-optimize the system.

Below the detailed applicability of this innovation is described.

### 2.6.1. Halogenuracils [H6].

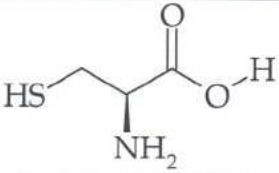
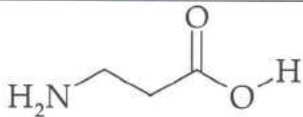
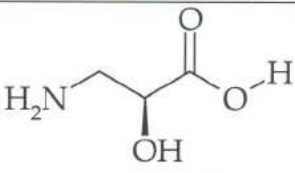
5-substituted uracils, including 5-halogenuracils (Scheme 2), were investigated in our group in the late nineties [17-21]. The gathered experience and new computational possibilities, such as calculations of anharmonic vibrations frequencies and determination of the Fermi resonances, inspired us in 2004 to perform anew the full analysis of the IR matrix spectra of 5-halogenuracils. We encountered many difficulties during the experimental spectra analysis of the series of seemingly simple, 12-atomic molecules ( $C_4N_2O_2H_3X$ ,  $X=F, Cl, Br, I$ ). This was due to the fact, that with the change of halogen atom, many intramolecular couplings were changed, because of the changes in the halogen atom mass, as well as in the electronic structure and electronegativity. The systematic PED analysis of 5-halogenuracils was possible only after separation in the SBT set following vibrations: stretching C-X, bending C-C-X and C=C-X, and torsion CCCX. Then, it was possible to assign the differences in the low-temperature matrix spectra to appropriate fragments, characteristic for the halogen atom [H6].



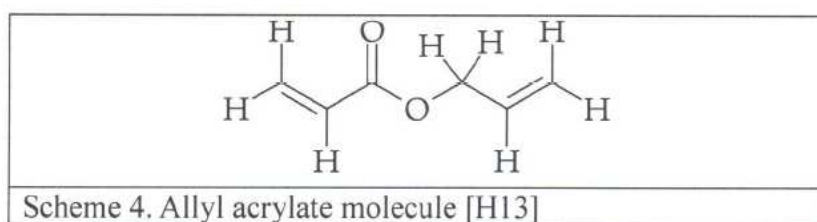
### 2.6.2. Conformers [H9, H12-H14]

The possibilities of the present-day computational chemistry allow for studying flexible molecules, in which rotations around single bonds can lead to co-existence of many conformers. Since 2006, in a cooperation with prof. Joanna Sadlej from the Faculty of Chemistry at the Warsaw University and prof. Robert Kołos from Physical Chemistry Institute PAS, I have been studying, together with a group of prof. Jan Cz. Dobrowolski from the Industrial Chemistry Research Institute, the IR spectra of amino acids (L-cysteine [H9],  $\beta$ -alanine [H-12] and L-isoserine [H-14], Scheme 3) in the low-temperature matrices. Small molecules of cysteine,  $\beta$ -alanine and isoserine have tens of neutral conformers – 50, 18 and 54, respectively. In all cases all of the conformers have such a low Gibbs free enthalpy, that all of them have to be included during the interpretation of the IR spectra registered in the low-temperature matrices. It has to be stated, that the amino acids, before being deposited in the matrix, are evaporated, and thus the conformational composition of the matrix represents the composition of the gas phase.



		
L-cysteine [H9]	$\beta$ -alanine [H12]	L-isoserine [H14]
Scheme 3. The three studied amino acids		

Amino acids conformers structures differ mainly in the net of intramolecular hydrogen bonds, which decide on the shape of the matrix spectrum. Among these bonds are COOH...NH<sub>2</sub>, HNH...O=C, HNH...OH, OH...SH, SH...NH<sub>2</sub>, and in isoserine also OH<sub>aliph</sub>...NH<sub>2</sub>, OH<sub>aliph</sub>...O=C and OH<sub>aliph</sub>...OH<sub>carboxyl</sub>. Additionally, the skeletal conformation influence the IR spectrum. Therefore, due to all the mentioned factors, all the common features of the IR spectra, as well as all the discrepancies, have to be revealed in order to properly interpret the spectra. Without the PED analysis it is impossible. The analysis is much easier, when the VEDA user define those SBT coordinates in the 'User' category, which for the whole set of conformers are identical. Then, the chosen identical coordinates remain unchanged during other operations run by the software. My PED analysis with the VEDA software demonstrated, that for each of the studied amino acids it is best to use different spectral region to assign the spectral bands and identify conformers. In the case of the matrix IR spectrum of cysteine the most characteristic is the SH and C=O stretching vibrations regions at *ca.* 2600 cm<sup>-1</sup> and 1750 cm<sup>-1</sup>, respectively [H9], whereas for  $\beta$ -alanine it is the *finger-print* region (660 - 460 cm<sup>-1</sup> [H12]) and for isoserine – C-O stretching vibrations region at *ca.* 1200 - 1000 cm<sup>-1</sup> [H14].

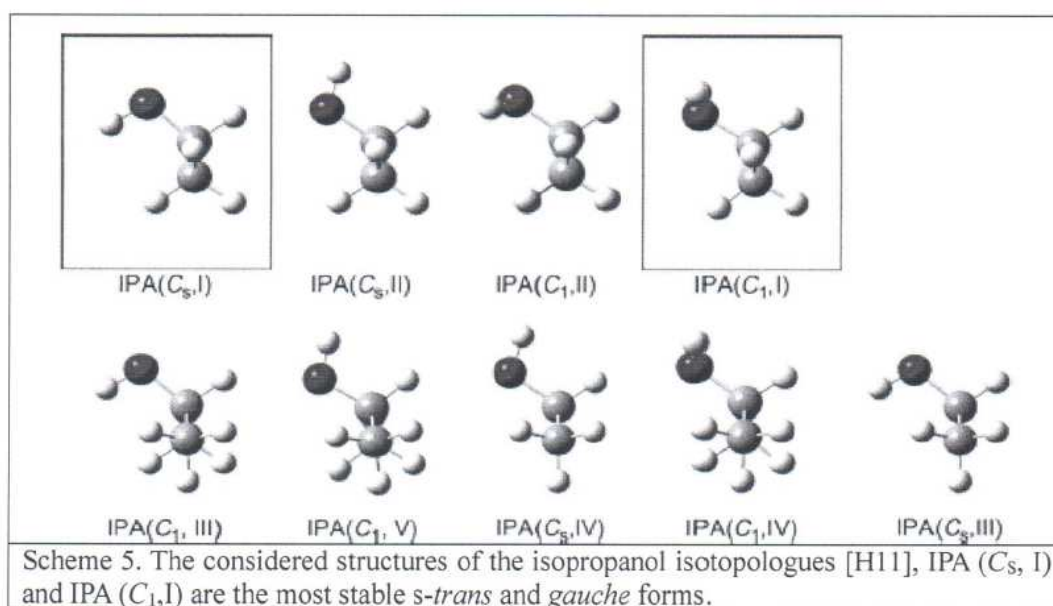


Another example of application of the VEDA software to the determination of the conformational composition on the basis of the IR spectra is the analysis of the theoretical and experimental spectra of liquid allyl acrylate ([H13, Scheme 4). The stability analysis of allyl acrylate indicated, that there are two main *s-cis* conformers in the equilibrium mixture. It was confirmed by the vibrational spectra of liquid allyl acrylate. On the basis of the PED analysis of the calculated, harmonic and anharmonic, spectra of ten

*s-cis* and *s-trans* conformers of allyl acrylate, I demonstrated, that the bands associated with the C-O stretching vibrations coupled with the C=C vibrations, located at 1270 and 1260  $\text{cm}^{-1}$ , confirm the presence of the *s-trans* conformers. The *s-cis* conformers are represented by the 1190  $\text{cm}^{-1}$  C-O/C=C band. Similarly, other C-O vibrations absorb at 1050  $\text{cm}^{-1}$  in the *s-trans* conformers, whereas in the *s-cis* conformers – at 970  $\text{cm}^{-1}$ .

### 2.6.3 Isotopologues spectra [H11]

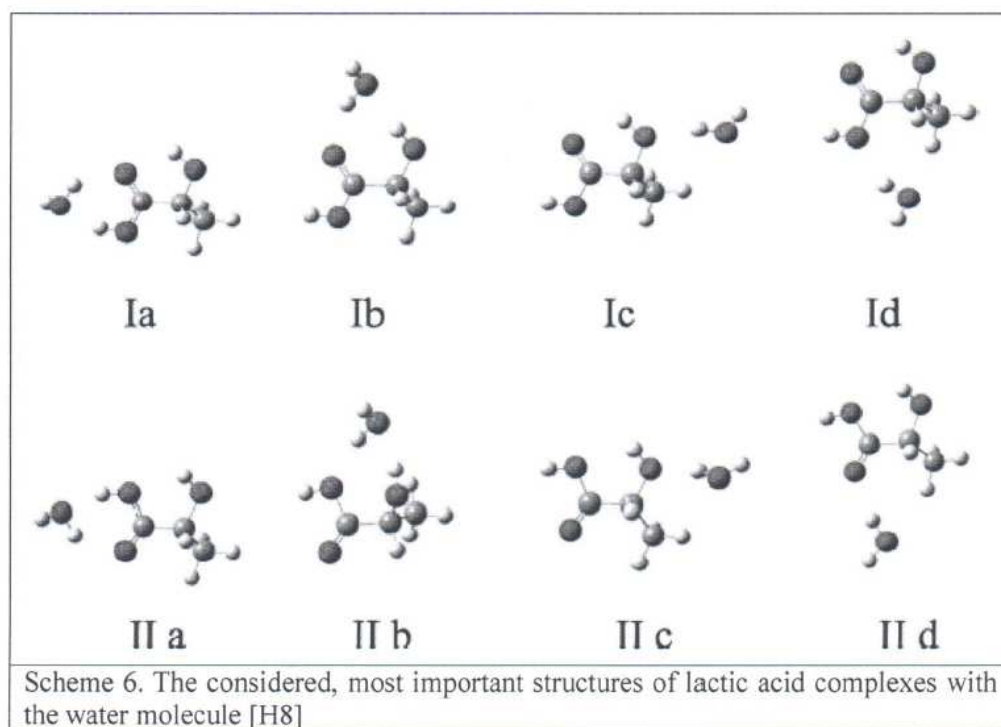
In the times when theoretical calculations were untrustworthy, the isotopic substitution was used in the vibrational spectroscopy to enhance the reliability of the bands assignment. Today the quality of the calculations depends mainly on the computing power of the available CPU machine. However, there are still some fragments of the IR spectra, which are difficult to interpret without the isotopic substitution. Such fragment, in the case of the small molecule of isopropanol, is the C-H stretching vibration region, in which many Fermi resonances, visible in the calculated anharmonic spectra, occur. In the paper [H11] the IR spectra in the low-temperature matrices were studied, which allowed the direct comparison of the experimental spectra with the calculated ones. We compared two 2-isopropanol rotamers: *trans* and *gauche* and their isotopologues: OD, D7 and D8 (Scheme 5). The presence of the symmetry plane influence considerably the vibrations, the SBT coordinates and the assignments done with the PED analysis. In order to compare the studied structures, I performed the PED analysis for each of them independently, and then I searched for similarities and discrepancies. Next, I defined the chosen common coordinates as belonging to the 'User' category and re-optimized the coordinates excluding the chosen ones. Such a detailed analysis demonstrated, that in the low-temperature matrices only *gauche* form is present, possibly because the matrix material impose the asymmetry of the molecule.



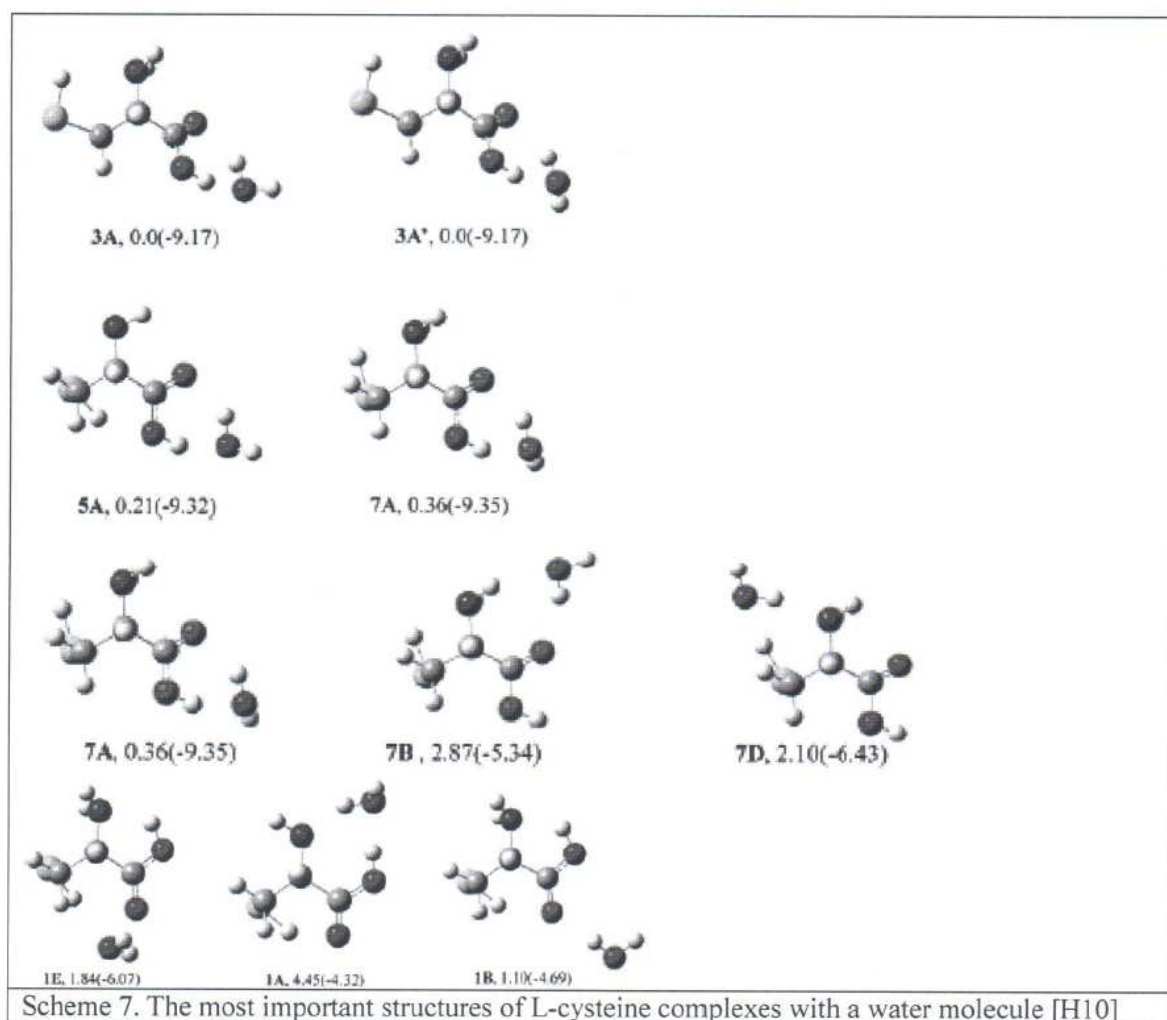


#### 2.6.4 Spectra of intermolecular complexes with the water molecule [H8, H10]

It is anticipated that the vibrational spectra of conformers will be very similar. Usually, in the liquid state the broad bands in the IR or Raman spectra do not permit the assignment of the conformers distribution. However, one can use the low-temperature matrices, which results in such bands narrowing, that the analysis of the contribution to the spectrum of the particular conformer is possible. In 2004 Borba *et al.* published the IR spectrum of lactic acid in the low-temperature matrices, showing not only the presence of the two dominant conformers, but also two other conformers of very low abundance [23]. One year after that our group described the calculated lactic acid VCD spectrum, in which the influence of the formation of the complexes with one water molecule and the conformational changes on the VCD spectrum were visible. To that purpose the very detailed PED analysis of the lactic acid conformers and its complexes with a water molecule was necessary. The conformers spectra are different from each other, due to the formation of two kinds of intramolecular hydrogen bonds between the OH group in the 'a' position in regard to the carboxyl group. The hydrogen bonds can be formed with the oxygen atom either from the C=O group, or from the OH in the carboxylic fragment. Also, there are conformers, in which the intramolecular hydrogen bond is broken. These seemingly small structural changes cause serious changes in the IR and VCD spectra, since the influence of the hydrogen bonds on the vibrational spectra is considerable. The case is still more complicated, when there are additional interactions with the water molecule, which can be either an H atom donor or its acceptor (Scheme 6). In these systems, the elucidation of the common structural features, giving consistent contributions to the vibrational spectrum, is of fundamental importance for the proper spectroscopic analysis. Such analysis is possible with the 'User' category and was described in the paper [H8], and documented in the supplementary materials.



In another paper the theoretical VCD spectra of L-cysteine complexes with one water molecule were studied [H10]. Such complexes can be observed in the low-temperature matrices, but the matrix VCD spectra are still very unique. From among *ca.* forty 1:1 complexes, three groups were selected. For each of the group  $\nu(\text{OH})$ ,  $\nu(\text{NH})$ ,  $\beta(\text{NH}_2)$  and  $\beta(\text{H}_2\text{O})$  bands were analyzed. The analysis demonstrated that the VCD spectrum is very sensitive to the conformational changes and to the changes in the location and type of complex with a the water molecule. Water can be either an H donor, or its acceptor, and cysteine molecule can be an H acceptor through C=O, OH, NH<sub>2</sub> and SH groups, or its donor through OH, NH<sub>2</sub> and SH groups. Also, the cyclic complexes are possible. Then, both molecules are simultaneously H donors and acceptors. In such a complicated case the selection of the common vibrations through the 'User' category enabled us to understand the complexity of the VCD spectrum and to propose consistent interpretation.





### 3. Block diagram of the VEDA software [H1]

The block diagram (Fig. 1) specifies the input data, presents introductory operations, optimization procedure and final operations. The necessary input data for the VEDA software are: atomic Cartesian coordinates and Cartesian force constants. Desirable data are also the calculated vibrational frequencies and atomic deflections matrix (ADM). These data are automatically extracted from the Gaussian output files. If the data are formally correct, VEDA generates its own file format (.fmv file), which is sufficient for the next opening of the software. The next step is the generation of the atomic connectivity matrix (.mpo file) and the SBT coordination set (.dd2 file). At this stage, VEDA permits the user interference. Here, he can introduce his own coordinates definitions (.dd2 file) and/or connectivity matrix. The change in the connectivity matrix will impose the changes in the generated .dd2 file.

#### 3.1. Preliminary generation of the complex coordinates

Based on the system geometry and the connectivity matrix, VEDA generates the complex coordinates set, where similar coordinates are grouped. This procedure is aimed at sustaining the symmetry of the system. It is worth remembering, that the next operations, conducted during the optimization procedure, are not convertible, and therefore the starting point is insignificant. The generation of the complex coordinates set is optional and can be omitted for simple systems, or when problems with linear independence of the coordinates occur.

#### 3.2. Optimization: the AMD procedure, reduction and normalization [H1 – H15]

All stages of the optimization procedure can be turned off and on interactively. The activity of the particular procedures are checked by the software at the beginning of each of the steps. In the optimization procedure the main step is based on the replacement of the chosen coordinates with their sum and difference. This operation is guided by the PED matrix. The evaluation criterion of the optimization progress is the EPM parameter value, which is defined as the average [%] from the maximal values of all the PED matrix columns (which represents coordinates). Firstly, the S coordinates are processed (separately for the *CH* and *not CH* categories, if it is the will of the user), next, similarly, the B coordinates, and finally – the T coordinates. When the number of changes and the change of the EPM value is significant, the whole procedure is repeated. Also, the alternative coordinates can be included. The constructed complex coordinates are then reduced (*i.e.* components not leading to the EPM value increase are eliminated). The components of the complex coordinates can have different weights (factors). The higher the factor value is, the more relevant is the contribution of this component to the complex coordinate. At the first stages of the optimization the ( $\pm 1$ ) weights are preferred. The preliminary optimization is performed with the exclusion of the well-defined coordinates. Then, more precise optimization can be applied, including the coordinates, for which the PED factors exceed 75%.

During the optimization, the AMD procedure is of importance. The AMD uses deflections (changes in the atomic placement) matrix for each of the vibrations, obtained from the Gaussian output file. On the basis of the matrix, VEDA creates additional coordinates (a new matrix), which can replace consecutively the existing ones. However, if one want to create this new matrix basing solely on the atomic deflections matrix, one will obtained a very complex and hard to reduce coordination set. Meanwhile, not all changes

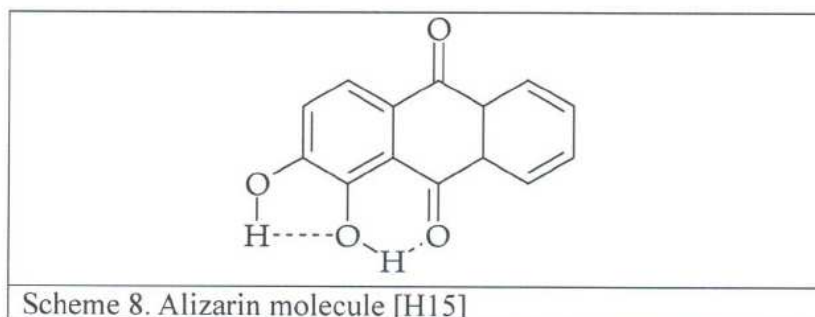
in the atomic placement cause significant changes in the potential energy. That is why the AMD procedure should not be used at the very beginning, but rather applied during the next starts of the software. The AMD procedure give a 10% increase to the EPM value.

The optimization is finalized with the coordinates normalization and reduction. During the normalization the coordinates weights are tried to be set to ( $\pm 1$ ) and then the software evaluates the change in the weights influence on the EPM value. The reduction is the consecutive elimination from the complex coordinates irrelevant components, with only small allowance of the EMP valued decrease. After the optimization, the EPM value is *ca.* 50 – 80 %. Around half of the vibrations are described by only one coordinate. Around 40% of the vibrations are described by the sum of two or three coordinates, which is a result of the separation of the S, B and T coordinates, as well as *CH* and *not CH* ones. No more than 10% of the vibrations are scattered on the whole molecule and described by many coordinates. However, the definitions of these scattered coordinates have to be formally correct – their role is not to impair the definitions of the other coordinates.

The optimization procedure application was described in [H1]. It was used in the PED analyses in [H2 – H15], and the AMD procedure was applied in [H1, H5-H15].

### 3.2.1 Exemplary application of the optimization. The PED analysis of alizarin [H15].

In the paper describing crystallographic structure and spectroscopic studies of an organic dye, alizarin (Scheme 8) we calculated vibrational harmonic and anharmonic theoretical spectra of its monomer with the DFT method and compared them with the experimental IR and Raman spectra, being aware of the fact, that the experimental spectra refer to the alizarin polycrystalline forms. The theoretical spectra were in a very good agreement with the experimental ones, excluding the expected differences on the OH bands and the bands of one of the C=O group, which was involved in the intramolecular hydrogen bond formation. The observed agreement permitted the reliable PED analysis in order to explain the experimental spectra. Alizarin spectrum consists of 72 vibrations. For the initial coordination set the EPM value was below 30%, and only for several vibrations the PED factor was higher than 50%. After the preliminary optimization, the EPM value increased to above 50% and after the AMD procedure – to above 60%, with PED factor of less than 40% for only several vibrations. The performed PED analysis permitted the assignment of all the bands in the region below 1650  $\text{cm}^{-1}$ . It would have been impossible basing solely on the experimental knowledge, especially for the bending and torsion vibrations.



Scheme 8. Alizarin molecule [H15]



### 3.3. Coordinates edition, 'step-by-step' procedure, repeated optimization

The next step depends solely on the software user. He should critically review the obtained coordination set in regard to its clarity and understandability. Sometimes, the user will want to emphasize the symmetry of the molecule, find the common features for a series of compared systems, separate and treat differently the coordinates of a particular functional group (*e.g.* C=O), bring to forth the coordinates describing intermolecular vibrations, *etc.* Usually, the introduced changes lead to the decrease of the EPM value. Therefore, the EPM value should be examined during the coordinates edition. After the edition, it is necessary to re-optimize the coordination set. To preserve the introduced changes, one should define 'User' category in the .dd2 file and specify, which coordinates belong to this category. At the next stages the user declare which of the coordinates are to be excluded from the optimization ('User', 'CH', *etc.*), or otherwise he can indicate the subset for the further optimization.

The coordinates definition types can be ambiguous, especially for the '*finger-print*' region (1400-400  $\text{cm}^{-1}$ ). Some of the vibrations can be described with heavy atoms or CH motions, or (more often) a vibration can be described with the B or T coordinate. The user can choose his own way of defining specific coordinate in the '*step-by-step*' procedure. It is associated with the EPM value decrease, at least at the early stage. However, it has to be stressed, that this part of the software is designed for the users with extensive knowledge on the vibrational spectra interpretation. The less experienced users are encouraged to use only automatic analysis, performed by VEDA.

In most cases, one should not confine on a singular optimization. As was mentioned earlier, it is advisable to perform the AMD procedure just in the second or third cycle. Also, exemplary, the coordinates reduction can result in the new possibilities of generating the complex coordinates.

The described way of the PED analysis with the use of the VEDA software was constructed on the basis of scientific problems solved in [H1-H15].

## 4. Frontiers in the VEDA software applications

With an increase in the number of atoms in a studied system, the PED analysis become more and more difficult. Then, the complex coordinates multiplicity (the number of components) is increased, the EPM value is decreased, there are more vibrations scattered on a whole molecule, the system is more difficult to understand, and, additionally, the computational time increase exponentially. The largest systems that were published with my contribution, were the 90-atomic molecules [15, 16]. I had fixed the frontiers of the applicability of the software to 120 atoms, but, due to international scientific community interest, it was later expanded to 240 (VEDAx1) and 480 (VEDAx1) atoms. The largest systems calculated by me are 200-atomic molecules (not yet published).

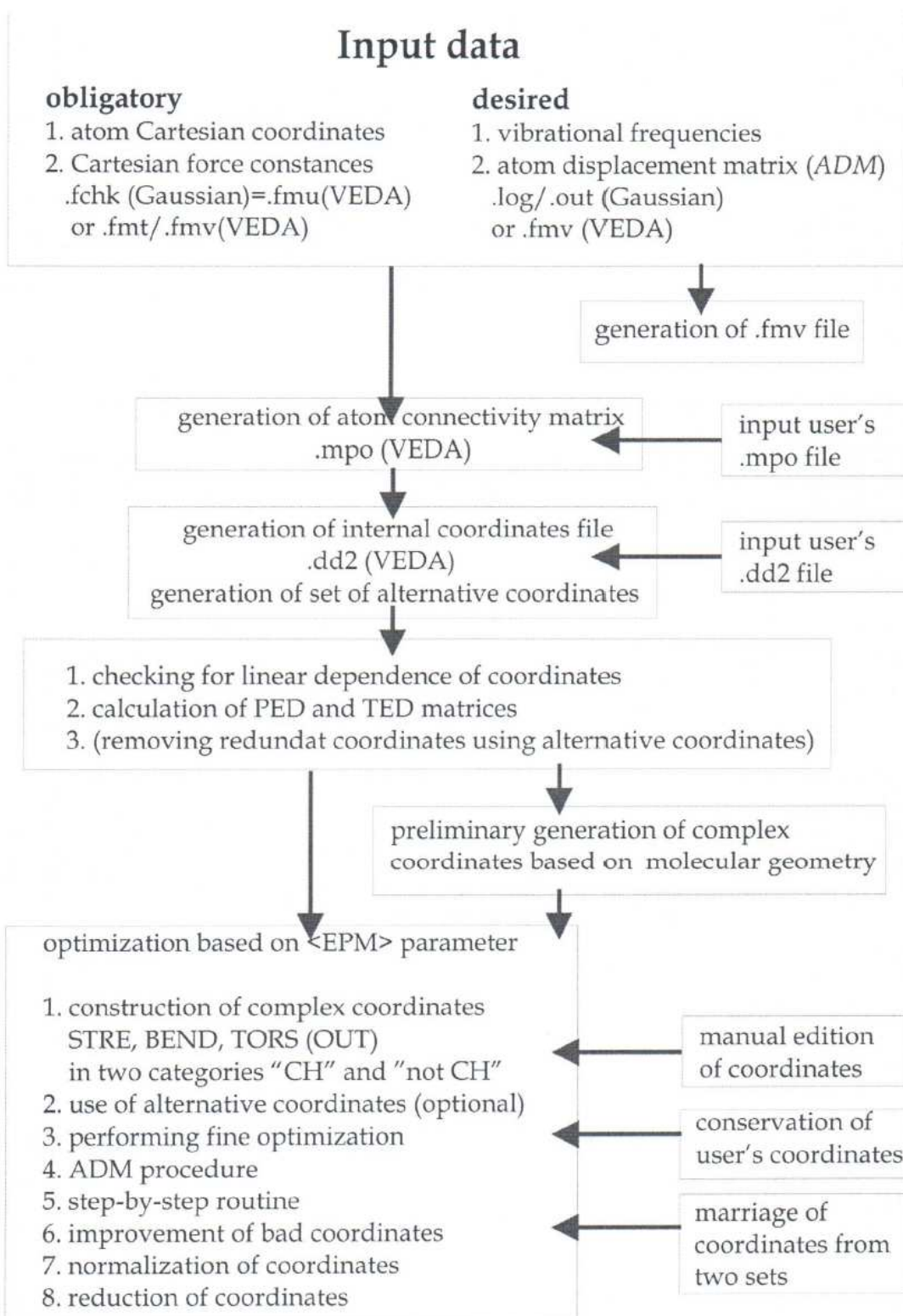


Fig. 1. The block diagram of VEDA



## 5. Conclusions

The main goal of my scientific work was such a representation of the theoretical vibrational spectra, so that it would be possible to interpret the experimental spectra of 50- and higher-atomic molecules. For that purpose the interpretation based on the analysis (visualization) of atoms deflections in particular vibration is used commonly, throughout the world. This method, however, is incorrect from the point of view of the energy vibrations fragments, since then the force constants matrix is ignored. The PED analysis takes into consideration the atomic deflections, as well as the force constants, and through them, the energy of the particular vibration. The difficulty in the PED analysis is the representation of the normal modes as the local coordination set, which describes vibrations of the particular fragments of the molecule. Manual construction of such a local coordination set is nearly impossible even for molecules as small as 20 atoms and, for larger molecules, the issue is combinatorial too complex. Additionally, the vibrations of molecular fragments are coupled with each other, which impose the superposition of many local coordinates.

In my scientific work I improved and developed the interpretation of the theoretical vibrational spectra by the PED analysis method, included in my software VEDA. The main innovation was the automatic construction of the linearly independent local coordination sets. In addition, VEDA automatically create complex coordinates, which accurately represent the normal modes. Due to that it is possible to interpret the vibrations of medium-sized molecules, which are of much greater importance for the applied chemistry, than small molecules. In general, the PED analysis can be ambiguous. The PED interpretation is regarded as a good one, if it enables the understanding of the observed experimental effect. Therefore, in my software, the interpreter can use such an approach, so that he can describe the observed spectroscopic effect in the best possible way. The final goal of the proper representation of the theoretical vibrational spectra is always the most accurate interpretation of the experimental ones. The VEDA software fulfills this condition well.

The automatic generation of the local coordination set in VEDA [H2] permitted the performance of the PED analysis of 60- and higher-atomic systems [H3, H4]. The introduced optimization of the PED analysis enabled the achievement of the best, and, at the same time, the simplest solution to problems arising from the interpretation of vibrational spectra of molecules [H1 – H15]. This is of great importance especially for larger molecules. In the optimization procedure the atomic motions are taken into account (the AMD procedure), as well as the coordinates reduction and normalization. Such optimization has never been performed before. The separation of vibrations originating from the skeletal motions, *e.g.* CC and those originating from CH aromatic and aliphatic motions resulted in much clearer and precise interpretation of large molecules spectra (*e.g.* alkyl aromatics) [H5, H7]. The introduction of the 'User' vibrations category enabled the interpreter the selection of fragments of special importance in solving a particular spectroscopic problem [H6, H8 – H14]. For example, the comparison of a series of theoretical spectra of 5-halogenuracils allowed for the consistent assignment of the bending C-C-X and C=C-X, and the torsion CCCX vibrations in the matrix spectra [H6]. Another application of the 'User' category was logical interpretation of the theoretical IR spectra of many conformers of amino acids (L-cysteine [H9],  $\beta$ -alanine [H12] and L-isoserine [H14]), which allowed the interpretation of the experimental spectra of these molecules in the low-temperature matrices. The analysis of theoretical and experimental spectra of 10 main conformers of liquid allyl acrylate is the next example [H13]. On the basis of the PED analysis of these 10 conformers it was possible to assign the bands corresponding to the presence of *s-trans* and *s-cis* conformers of allyl acrylate. Another analyses, in which the 'User' category application was crucial, were

the analysis of vibrational spectra of intramolecular complexes of lactic acid with a water molecule [H8] and complexes of L-cysteine with a water molecule [H10]. These studies contributed to a better understanding of chirality transfer, monitored by the VCD (*Vibrational Circular Dichroism*) spectra. At last, the 'User' category was also critical in the analysis of IR matrix spectra of isopropanol isotopologues [H11]. As a result of this analysis it was proven that in the low-temperature matrices only asymmetric form of isopropanol molecule is present. The whole software, together with its algorithm and examples of application was described in [H1].

The VEDA software came into being as a direct result of the needs of the Molecular Modelling Group. The software is extremely helpful, sometimes even indispensable, in the interpretation of the vibrational theoretical spectra, though it will not replace in 100% the experienced interpreter. The software was applied in ca. 30 published papers of our Group [10-22]. The gained experience while using VEDA, resulted in many its modifications and improvements. In the recent years VEDA has been made accessible to the international scientific community. It is used in laboratories in Europe (Poland, Russia, Ukraine, Spain, and France), Asia (Turkey, India, China, and Iran), Africa (Tunis, Egypt, Algeria, and RSA) and America (USA, Canada). The software has been cited independently more than 200 times.

Micheł Jamroz



## Literature concerning habilitation achievements

- H1 M. H. Jamróz (100%), **Vibrational energy distribution analysis (VEDA): Scopes and limitations**, *Spectrochim. Acta A*, 114 (2013) 220–230.
- H2 M.H. Jamróz (80%), J. Cz. Dobrowolski (20%), **Potential Energy Distribution Analysis (PED) of DFT Calculated IR Spectra of the most Stable Li, Na, Cu(I) Diformate Molecules**, *J. Mol. Struct.*, 565-566(2001)475-480.
- H3 M. H. Jamróz (80%), J. Cz. Dobrowolski (10%), J. E. Rode (5%), M. A. Borowiak (5%), **Theoretical and Experimental IR Spectra and Stability of Dibenzyl Carbamic Acid Dimer**, *J. Mol. Struct. (Theochem)*, 618(1-2) (2002)101-108.
- H4 M. H. Jamróz (70%), J. Cz. Dobrowolski (30%), **Theoretical IR Spectra and Stability of Carbamic Acid Complexes**, *Vib. Spectry*, 29(2002)217-221.
- H5 M. H. Jamróz (75%), R. Brzozowski (10%), J. Cz. Dobrowolski (15%), **Search for IR spectral features of less-abundant diisopropylnaphthalenes based on comparison of theoretical and experimental spectra**, *Spectrochim. Acta A. Mol. Biomol. Spectr*, 60(2004)371-375.
- H6 J. Cz. Dobrowolski (25%), J. E. Rode (20%), Robert Kołos (20%), M. H. Jamróz (25%), K. Bajdor (5%), A. P. Mazurek (5%), **Ar-matrix IR Spectra of 5-Halouracils Interpreted by Means of DFT Calculations**, *J. Phys. Chem.*, 109(2005)2167-2182.
- H7 M. H. Jamróz (70%), J. Cz. Dobrowolski (10%), R. Brzozowski (20%), **Vibrational Modes of 2, 6-, 2, 7-, and 2, 3-Diisopropylnaphthalene. A DFT Study**, *J. Mol. Struct.*, 787(2006)172-183.
- H8 J. Sadlej (25%), J. Cz. Dobrowolski (25%), J. E. Rode (25%), M. H. Jamróz (25%), **DFT study of vibrational circular dichroism spectra of D-lactic acid-water complexes**, *Phys. Chem. Chem. Phys.*, 8(2006)101-113.
- H9 J. Cz. Dobrowolski (20%), M. H. Jamróz (20%), R. Kołos (20%), J. E. Rode (20%), J. Sadlej (20%), **Theoretical prediction and the first IR-matrix observation of several L-cysteine molecule conformers**, *ChemPhysChem.*, 8(2007)1085-1094.
- H10 J. Sadlej (25%), J. Cz. Dobrowolski (25%), J. E. Rode (25%), M. H. Jamróz (25%), **Density Functional Theory Study on Vibrational Circular Dichroism as a Tool for Analysis of Intermolecular Systems: (1:1) Cysteine-Water Complex Conformations**, *J. Phys. Chem. A*, 111(2007)10703-10711.
- H11 J. Cz. Dobrowolski (15%), S. Ostrowski (15%), R. Kołos (30%), M. H. Jamróz (40%), **Ar-Matrix IR Spectra of 2-Propanol and its OD, D7 and D8 Isotopologues**, *Vib. Spec.*, 48(2008)82-91.
- H12 J. Cz. Dobrowolski (15%), M. H. Jamróz (30%), R. Kołos (20%), J. E. Rode (15%), J. Sadlej (20%), **IR low-temperature matrix and *ab initio* study on  $\beta$ -alanine conformers**, *ChemPhysChem.*, 9(2008) 2042-2051.
- H13 M. H. Jamróz (20%), M. E. Jamróz (20%), J. E. Rode (20%), E. Bednarek (20%), J. Cz. Dobrowolski (20%), **Interpretation of Vibrational and NMR Spectra of Allyl Acrylate. An Evidence for Several Conformers**, *Vib. Spec.* 50 (2009) 231–244.
- H14 J. Cz. Dobrowolski (10%), M. H. Jamróz (25%), Robert Kołos (25%), J. E. Rode (5%), M. K. Cyrański (25%), J. Sadlej (10%), **IR low-temperature matrix, X-ray and *ab initio* study on L-isoserine conformations**, *Phys. Chem. Chem. Phys.*, 12(2010) 10818–10830.
- H15 M. K. Cyrański (10%), M. H. Jamróz (20%), A. Rygula (10%), J. Cz. Dobrowolski (10%), Ł. Dobrzycki (25%), M. Barańska (25%), **On Two Alizarin Polymorphs**, *CrystEngComm*, 14(2012)3667-3676.

## Other references

- [1] Y. Morino, K. Kuchitsu, **A note on the classification of normal vibrations of molecules**, *J. Chem. Phys.* 20 (1952) 1809–1810.
- [2] W.J. Taylor, **Distribution of kinetic and potential energy in vibrating molecules**, *J. Chem. Phys.* 22 (1954) 1780–1781.
- [3] T. Miyazawa, T. Shimanouchi, S. Mizushima, **Normal vibrations of *N*-methylacetamide**, *J. Chem. Phys.* 29 (1958) 611–616.
- [4] G. Zerbi, J. Overend, B. Crawford, Urey—Bradley force constants of methanol, *J. Chem. Phys.* 38 (1963) 122–127.
- [5] G. Keresztury, G. Jalsovszky, **Alternative calculation of vibrational potential energy distribution**, *J. Mol. Struct.* 10 (1971) 304.
- [6] P. Pulay, G. Fogarasi, F. Pang, J.E. Boggs, **Systematic ab initio gradient calculation of molecular geometries, force constants, and dipole moment derivatives**, *J. Am. Chem. Soc.* 101 (1979) 2550–2560.
- [7] L. Lapinski, P. Pongor, **PED-program**, Warsaw, 1994
- [8] L. Lapinski, M.J. Nowak, **BALGA – Computer Program for PED Calculation**, Institute of Physics Polish Academy of Sciences, Warsaw.
- [9] J. Cz. Dobrowolski (40%), M. H. Jamróz (20%), J. K. Kazimirski (10%), K. Bajdor (10%), M. Borowiak (10%), R. Larsson (10%), **Theoretical Spectra of Diformates: Diformate Anion**, *J. Mol. Struct.* 482-483(1999)183-187.
- [10] M. H. Jamróz (50%), J. Cz. Dobrowolski (30%), M. Borowiak (20%), **The CO<sub>2</sub> with dimethylamine reaction: ab initio predicted spectra**, *J. Mol. Struct.*, 482-483(1999)633-637.
- [11] J. Cz. Dobrowolski (40%), M.H. Jamróz (40%), M. A. Borowiak (10%), E. Quaranta (5%), M. Aresta (5%), **Theoretical IR and Raman Spectra of Diketene and its 3-Methylene Isomer**, *Vib. Spectry*, 22(2000)19-28.
- [12] J. Rode (50%), J. Cz. Dobrowolski (30%), M. H. Jamróz (10%), M. A. Borowiak (10%), **Theoretical Vibrational Spectra of the Diketene, its Isomers, and their Mono- and Disulphur Analogues**, *J. Mol. Struct.*, 565-566(2001)433-438.
- [13] J. Rode (50%), J. Cz. Dobrowolski (30%), M. H. Jamróz (10%), M. A. Borowiak (10%), **Theoretical Vibrational and NMR Spectra of 1,2- and 1,3-dimethylenecyclobutane Molecules**, *Vib. Spectrosc.*, 25(2001)133-149.
- [14] J. E. Rode, J. Cz. Dobrowolski, **Chiral Allenes: Theoretical VCD and IR Spectra**, *J. Mol. Struct. (Theochem)*, 635(2003)151-159.
- [15] Marta K. Jamróz (70%), Michał H. Jamróz (15%), Jan Cz. Dobrowolski (5%), Jan A. Gliński, Michał Głęńsk, **One new and six known triterpene xylosides from *Cimicifuga racemosa*: FT-IR, Raman and NMR studies and DFT calculations**, *Spectrochim. Acta A*, 93(2012)10-18.
- [16] M. K. Jamróz (70%), M. H. Jamróz (15%), J. Cz. Dobrowolski (10%), J. A. Gliński, M. H. Davey, I. Wawer, **Novel and unusual triterpene from Black Cohosh. Determination of structure of 9,10-seco-9,19-cyclolanostane xyloside (cimipodocarpaside) by NMR, IR and Raman spectroscopy and DFT calculations**, *Spectrochim. Acta A*, 78 (2011) 107–112.
- [17] J. Cz. Dobrowolski, R. Kołos, J. Sadlej, A. P. Mazurek, **Theoretical and IR-matrix isolation studies on the urea and urea-D<sub>4</sub>, -<sup>13</sup>C, and -1,3-<sup>15</sup>N<sub>2</sub> substituted molecules**, *Vib. Spectry*, 29(2002)261-282.



- [18] Z. Zwierzchowska, K. Dobrosz-Teperek, W. Lewandowski, R. Kołos, K. Bajdor, J. Cz. Dobrowolski, A. P. Mazurek, **Vibrational spectra of 5-halogenouracils: Part I.** *J. Mol. Struct.*, 410(1997)415-420.
- [19] K. Dobrosz-Teperek, Z. Zwierzchowska, W. Lewandowski, K. Bajdor, J. Cz. Dobrowolski, A. P. Mazurek, **Vibrational spectra of 5-halogenouracils: Part II - Solids.** *J. Mol. Struct.*, 470(1998)115-125.
- [20] E. Bednarek, J. Cz. Dobrowolski, K. Dobrosz-Teperek, J. Sitkowski, L. Kozerski, W. Lewandowski, A. P. Mazurek, **Theoretical and Experimental  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{15}\text{N}$ , and  $^{17}\text{O}$  NMR Spectra of 5-Nitro, 5-Amino, and 5-Carboxy Uracils,** *J. Mol. Struct.*, 482-483(1999)333-337.
- [21] E. Bednarek, J. Cz. Dobrowolski, K. Dobrosz-Teperek, J. Sitkowski, L. Kozerski, W. Lewandowski, A. P. Mazurek, **The  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{15}\text{N}$ , and  $^{17}\text{O}$  NMR Spectra of 5-Halogeno-uracils: Theoretical and Experimental Spectra,** *J. Mol. Struct.*, 554 (2000)233-243.
- [22] M. E. Jamróz, M. Jarosz, J. Witowska-Jarosz, E. Bednarek, W. Tęcza, M. H. Jamróz, J. Cz. Dobrowolski, J. Kijeński, **Mono-, di-, and tri-tertbutyl ethers of glycerol. A molecular spectroscopic study.,** *Spectrochim. Acta, A.*, 67(2007)980-988.
- [23] A. Borba, A. Gómez-Zavaglia, L. Lapinski, R. Fausto, Rotational isomers of lactic acid: first experimental observation of higher energy forms, *Phys. Chem. Chem. Phys.*, 2004, 6, 2101-2108.