



ELSEVIER

Contents lists available at ScienceDirect

Data in Brief

journal homepage: www.elsevier.com/locate/dib

Data Article

DFT data to relate calculated LUMO energy with experimental reduction potentials of Cu(II)- β -diketonato complexes



Marrigje M. Conradie*, Ernst H.G. Langner, Jeanet Conradie

Department of Chemistry, Faculty of Natural and Agricultural Sciences, PO Box 339, University of the Free State, Bloemfontein, 9300, South Africa

ARTICLE INFO

Article history:

Received 9 June 2021

Revised 19 August 2021

Accepted 24 August 2021

Available online 27 August 2021

Keywords:

DFT

LUMO energy

Cu- β -diketonato complexes

ABSTRACT

We present data on the computed lowest unoccupied molecular orbital energy (E_{LUMO}) of two series of Cu(II)- β -diketonato complexes, calculated via density functional theory (DFT). These are correlated to experimental reduction potential data (E_{pc}), obtained by cyclic voltammetry under different experimental conditions (solvent, working and reference electrodes). All calculations were done with the B3LYP functional in the gas phase. Knowledge of the influence of different ligands on the redox potential of copper complexes, as measured by DFT calculated energy data, are very useful. These theoretical correlations are vital in the further design of similar compounds, to be customized for specific applications. The correlations can be used to predict and fine-tune redox potentials prior to synthesis, saving experimental chemists time and laboratory expenses. Redox potentials influence the catalytic property of bis(β -diketonato)copper(II) compounds. New catalysts can therefore be customized with a specific reduction potential and catalytic activity. Further, the Cu(II/I) redox couple is a potential alternative as electrolyte for dye-sensitized solar cells [1–3]. The redox potential of the electrolyte can drastically affect the photovoltage output and should therefore be optimized for efficiency and durability. By adjusting the reduction potential via different ligands on the complex, the properties of copper dyes can be

DOI of original article: [10.1016/j.poly.2021.115290](https://doi.org/10.1016/j.poly.2021.115290)

* Corresponding author.

E-mail address: ConradieMM@ufs.ac.za (M.M. Conradie).<https://doi.org/10.1016/j.dib.2021.107331>

2352-3409/© 2021 The Author(s). Published by Elsevier Inc. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>)

fine-tuned at molecular level. For more insight into the reported data, see the related research article "Synthesis, Characterization, DFT and Biological Activity of Oligothiophene β -diketone and Cu-complexes" published in Polyhedron [4].

© 2021 The Author(s). Published by Elsevier Inc.

This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>)

Specifications Table

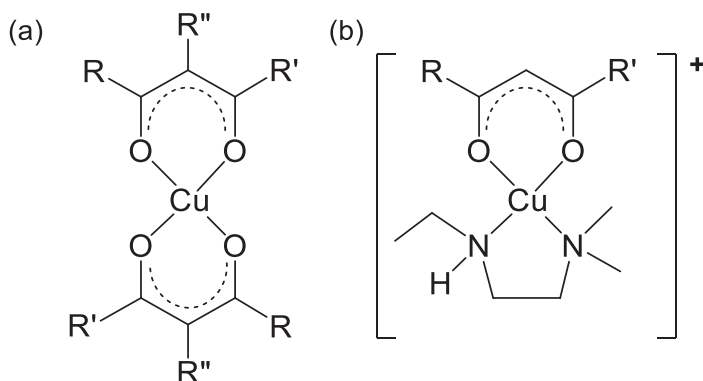
Subject	Physical and Theoretical Chemistry
Specific subject area	DFT calculations of chemical structures.
Type of data	Table Graph Figure
How data were acquired	Electronic structure calculations, using the Gaussian 16 program
Data format	Raw analysed
Parameters for data collection	Geometry optimizations were done using the Gaussian 16 software program, in gas phase, using the B3LYP functional and the 6–311G(d,p) basis set.
Description of data collection	Data was collected from DFT output files
Data source location	University of the Free State Bloemfontein South Africa
Data accessibility	With the article
Related research article	N.G.S. Mateyise, S. Ghosh, M. Gryzenhout, E. Chiyindiko, M.M. Conradie, E.H.G. Langner, J. Conradie, Synthesis, characterization, DFT and biological activity of oligothiophene beta-diketone and Cu-complexes, Polyhedron. 205 (2021) 115290. https://doi.org/10.1016/j.poly.2021.115290

Value of the Data

- The relationship between E_{LUMO} and the experimental reduction potential E_{pc} of copper(II)- β -diketonato complexes is important in the field of catalysis, as it allows to predict their catalytic activity.
- E_{pc} vs E_{LUMO} relationships can be used by experimental chemists in the design of customized complexes with a desired reduction potential.
- Calculated LUMO energy data provides insight into the influence of different ligands on the redox potential of copper complexes.
- Redox potentials are important for researchers interested in copper electrolytes under low light conditions, for commercialization of dye sensitized solar cell (DSSC) technology.

1. Data Description

The complexes shown in Scheme 1 have been studied via DFT and their optimized Cartesian coordinates are given in the supporting information. E_{LUMO} data and complex numbering are listed in Table 1. Linear relationships between experimental E_{pc} and computed E_{LUMO} of the copper (II/I) reduction, are shown in Figs. 1–4. These values were obtained for series of related molecules obtained under the same experimental conditions (solvent, working and reference electrodes). In Figs. 1 and 2, the E_{pc} vs E_{LUMO} relationships for two different series of $[Cu^{II}(\beta\text{-diketonato})_2]$ compounds are shown. For both these series, E_{pc} ($Cu^{II/I}$) was obtained in the same solvent CH_3CN , but with different working and reference electrodes [4–7]. In Fig. 3 the E_{pc} vs E_{LUMO} relationship is shown only for $[Cu^{II}(\beta\text{-diketonato})_2]$ compounds, with E_{pc} ($Cu^{III/I}$) obtained in DMSO as solvent [8]. Fig. 4 provides the E_{pc} vs E_{LUMO} relationship



Scheme 1. Copper(II)- β -diketonato compounds of this study: (a) $[\text{Cu}^{\text{II}}(\beta\text{-diketonato})_2]$ and (b) $[\text{Cu}^{\text{II}}(\beta\text{-diketonato})(\text{dmeen})]^+$ complexes, where dmeen = N,N-dimethyl-N'-ethyl-1,2-diaminoethane. Groups R, R' and R'' and complex numbering are indicated in Table 1.

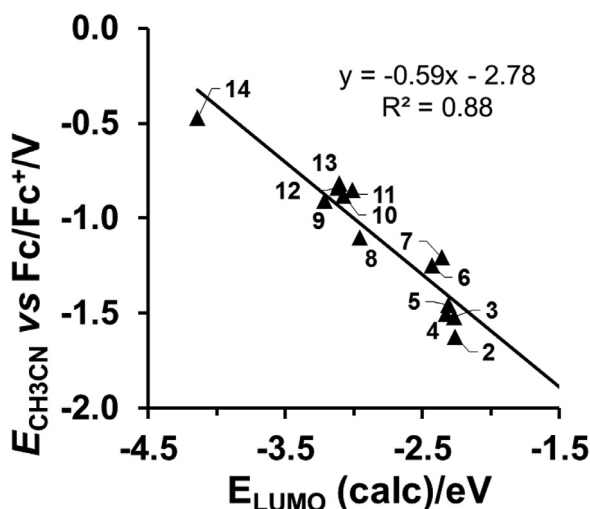


Fig. 1. CH_3CN as solvent and glassy carbon working electrode: Relationship between experimental reduction potentials E_{pc} (V versus Fc/Fc^+) of $[\text{Cu}^{\text{II}}(\beta\text{-diketonato})_2]$ complexes (2) - (14), and their DFT calculated energy E_{LUMO} . Data and complex numbering given in Table 1.

for $[\text{Cu}^{\text{II}}(\beta\text{-diketonato})(\text{dmeen})]^+$ compounds, with E_{pc} ($\text{Cu}^{\text{II/I}}$) also obtained in DMSO as solvent [8]. Experimental E_{pc} data is reported either versus the redox couple of ferrocene (Fc/Fc^+ [9]), or against the saturated calomel electrode (SCE) or the saturated salt calomel electrode (SSCE). The reference values used are either $E(\text{SCE}) = 0.241$ V or $E(\text{SSCE}) = 0.2360$ V, versus the normal hydrogen electrode (NHE). The catalytic property and application of copper- β -diketonato compounds as redox mediators for dye-sensitized solar cells (DSSC), depends on their redox potential [1–3,10,11]. This is why the theoretical prediction of the redox potential of copper- β -diketonato compounds from these existing $E_{\text{pc}} - E_{\text{LUMO}}$ relationships, is indispensable.

Table 1

B3LYP/6–311G(d,p) calculated LUMO energies and experimental reduction potentials measured in different solvents and with different reference electrodes. Values are listed both for $[\text{Cu}^{\text{II}}(\beta\text{-diketonato})_2]$ compounds (**1**) – (**22**) and $[\text{Cu}^{\text{II}}(\beta\text{-diketonato})(\text{dmeen})]^+$ compounds (**23**) – (**30**), with $\beta\text{-diketonato} = (\text{R}'\text{COCR}''\text{COR})^-$.

No	R'	R''	R	E_{LUMO} (eV)	E_{pc} (V) vs SSCE ^a	E_{pc} (V) vs SCE ^b	E_{pc} (V) vs Fc/Fc ⁺ ^c
$[\text{Cu}^{\text{II}}(\beta\text{-diketonato})_2]$							
1	C(CH ₃) ₃	H	C(CH ₃) ₃	–2.33	–1.06	–0.91	
2	Fc ^d	H	CH ₃	–2.26			–1.624
3	Fc	H	Fc	–2.26			–1.520
4	Fc	H	Ph	–2.33			–1.503
5	CH ₃	H	CH ₃	–2.31	–0.83	–0.82	–1.458
6	Ph ^d	H	Ph	–2.43	–0.75		–1.247
7	Ph	H	CH ₃	–2.36	–0.89	–0.75	–1.207
8	CF ₃	H	Fc	–2.96			–1.102
9	CF ₃	H	CH ₃	–3.21	–0.32	–0.32	–0.907
10	CF ₃	H	C ₄ H ₃ O	–3.07			–0.881
11	CF ₃	H	C ₄ H ₃ SC ₄ H ₂ S	–3.01			–0.852
12	CF ₃	H	Ph	–3.12	–0.27	–0.34	–0.838
13	CF ₃	H	C ₄ H ₃ S	–3.11	–0.27		–0.815
14	CF ₃	H	CF ₃	–4.14	–0.05	0.27	–0.473
15	Ph	H	H	–2.52		–0.63	
16	H	H	C(CH ₃) ₃	–2.50		–0.56	
17	CH ₃	NO ₂	CH ₃	–3.41		–0.08	
18	CH ₃	CN	CH ₃	–3.35		–0.19	
19	Ph	NO ₂	CH ₃	–3.33		0.21	
20	CH ₃	H	C(CH ₃) ₃	–2.33		–0.88	
21	H	H	C ₁₀ H ₇	–2.50		–0.53	
22	CH ₃	H	C ₁₀ H ₇	–2.35		–0.72	
$[\text{Cu}^{\text{II}}(\beta\text{-diketonato})(\text{dmeen})]^+$							
23	C(CH ₃) ₃	H	C(CH ₃) ₃	–6.07	–0.73		
24	CH ₃	H	CH ₃	–6.20	–0.64		
25	Ph	H	CH ₃	–6.08	–0.59		
26	Ph	H	Ph	–5.99	–0.58		
27	CF ₃	H	CH ₃	–6.63	–0.45		
28	CF ₃	H	Ph	–6.45	–0.38		
29	CF ₃	H	C ₄ H ₃ S	–6.42	–0.41		
30	CF ₃	H	CF ₃	–7.07	–0.16		

^a E_{pc} obtained from cyclic voltammetry data, in DMSO as solvent, with a carbon fibre working electrode, from reference [8].

^b E_{pc} obtained from cyclic voltammetry data, in acetonitrile as solvent, with a carbon fibre working electrode, from reference [7].

^c E_{pc} obtained from cyclic voltammetry data, in acetonitrile as solvent, with a glassy carbon working electrode, from references [4–6].

^d Fc = ferrocene = $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2$; Ph = phenyl = C_6H_5 .

2. Experimental Design, Materials and Methods

The optimized geometry of the specified molecules were obtained by DFT calculations, similar to the computations described in our previous publication [12]. The Gaussian 16 package [13] was used, together with the hybrid functional B3LYP [14,15], while applying the GTO (Gaussian type orbital) triple- ζ basis set 6–311G(d,p) for all the atoms. The optimization of the molecules was done in the gas phase. The Beryny optimization algorithm [16] was used, requesting a convergence on energy of 1.0D–8 atomic unit. The input coordinates for the compounds were constructed using Chemcraft software [17]. The coordinates and multiplicity (2) were specified in the input files of the DFT calculations. Frequency calculations were done on all

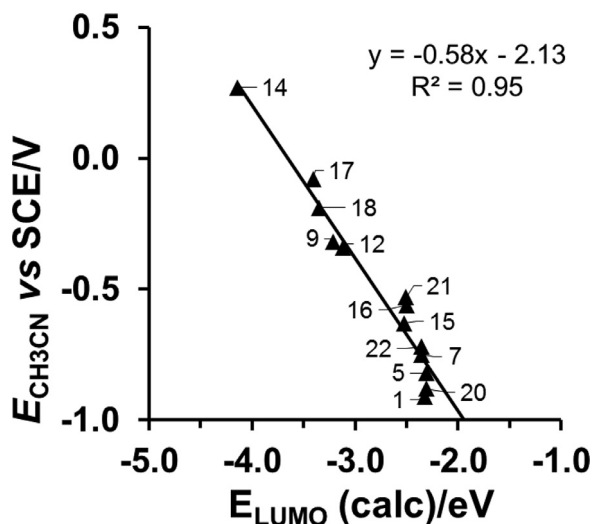


Fig. 2. CH_3CN as solvent and carbon fibres working electrode: Relationship between experimental reduction potentials E_{pc} (V versus SCE) of $[\text{Cu}^{\text{II}}(\beta\text{-diketonato})_2]$ complexes (1), (5), (7), (9), (12), (14), (15) – (18), (20) – (22), and their DFT calculated energy E_{LUMO} . Data and complex numbering given in Table 1. Complex (19) did not fit the trend.

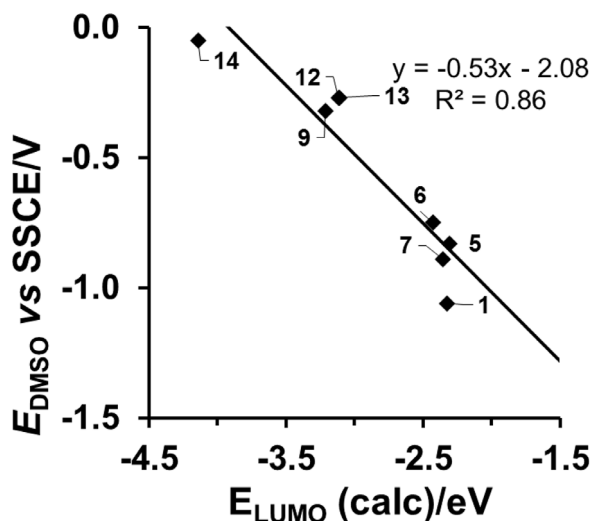


Fig. 3. DMSO as solvent and carbon fibres working electrode: Relationship between experimental reduction potentials E_{pc} (V versus SSCE) of $[\text{Cu}^{\text{II}}(\beta\text{-diketonato})_2]$ complexes (1), (5) – (7), (9), (12) – (14), and their DFT calculated energy E_{LUMO} . Data and complex numbering given in Table 1.

molecules to ensure true minimum energy (no imaginary frequency). The LUMO energies were obtained from the output files, searching for “Orbital energies and kinetic energies” from the bottom of the file and identifying the LUMO from the orbital energies and the provided occupations.

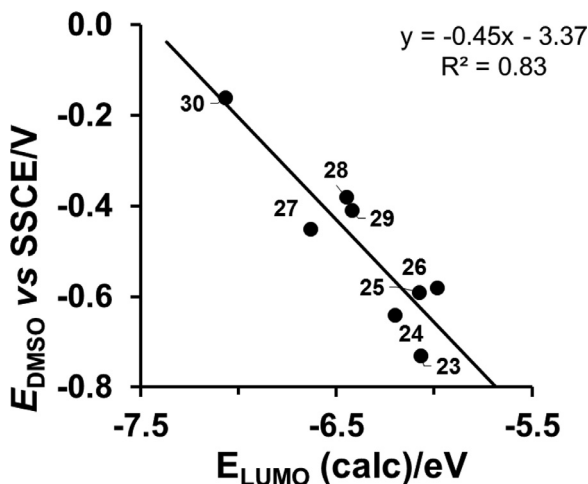


Fig. 4. DMSO as solvent and carbon fibres working electrode: Relationship between experimental reduction potentials E_{pc} (V versus SSCE) of $[\text{Cu}^{\text{II}}(\beta\text{-diketonato})(\text{dmeen})]^+$ complexes (23) - (30), and their DFT calculated energy E_{LUMO} . Data and complex numbering given in Table 1.

Ethics Statement

This work does not require any ethical statement.

CRedit Author Statement

Marrigje M Conradie: Conceptualization, Methodology, Writing - review & editing; **Ernst H.G. Langner:** Writing - review & editing; **Jeanet Conradie:** Conceptualization, Methodology, Writing - review & editing.

Supplementary data files

Optimized coordinates (xyz) of the molecules.

Declaration of Competing Interest

The authors declare no known competing financial interests or personal relationships which have or could be perceived to have influenced the work reported in this article.

Acknowledgments

This work has received support from the South African National Research Foundation (Grant numbers 129270, 132504 (JC) and 108960 (MMC)), from the Sasol University Collaboration Programme (EHGL) and the Central Research Fund of the University of the Free State, Bloemfontein, South Africa. The Norwegian Supercomputing Program (UNINETT Sigma2, Grant No. NN9684K), CHPC of South Africa and the High Performance Computing facility of the UFS are acknowledged for computer time.

Supplementary Materials

Supplementary material associated with this article can be found in the online version at doi:[10.1016/j.dib.2021.107331](https://doi.org/10.1016/j.dib.2021.107331).

References

- [1] Y. Liu, S.-C. Yiu, C.-L. Ho, W.-Y. Wong, Recent advances in copper complexes for electrical/light energy conversion, *Coord. Chem. Rev.* 375 (2018) 514–557, doi:[10.1016/j.ccr.2018.05.010](https://doi.org/10.1016/j.ccr.2018.05.010).
- [2] K.S. Srivishnu, S. Prasanthkumar, L. Giribabu, Cu(II/I) redox couples: potential alternatives to traditional electrolytes for dye-sensitized solar cells, *Mater. Adv.* 2 (2021) 1229–1247, doi:[10.1039/D0MA01023E](https://doi.org/10.1039/D0MA01023E).
- [3] M. Magni, P. Biagini, A. Colombo, C. Dragonetti, D. Roberto, A. Valore, Versatile copper complexes as a convenient springboard for both dyes and redox mediators in dye sensitized solar cells, *Coord. Chem. Rev.* 322 (2016) 69–93, doi:[10.1016/j.ccr.2016.05.008](https://doi.org/10.1016/j.ccr.2016.05.008).
- [4] N.G.S. Mateyise, S. Ghosh, M. Gryzenhout, E. Chiyindiko, M.M. Conradie, E.H.G. Langner, J. Conradie, Synthesis, characterization, DFT and biological activity of oligothiophene beta-diketone and Cu-complexes, *Polyhedron* 205 (2021) 115290, doi:[10.1016/j.poly.2021.115290](https://doi.org/10.1016/j.poly.2021.115290).
- [5] E. Chiyindiko, J. Conradie, Redox behaviour of bis(β -diketonato)copper(II) complexes, *J. Electroanal. Chem.* 837 (2019) 76–85, doi:[10.1016/j.jelechem.2019.02.011](https://doi.org/10.1016/j.jelechem.2019.02.011).
- [6] C.C. Joubert, L. van As, A. Jakob, J.M. Speck, H. Lang, J.C. Swarts, Intramolecular electronic communication in ferrocene-based β -diketonato copper(II) complexes as observed by an electrochemical study, *Polyhedron* 55 (2013) 80–86, doi:[10.1016/j.poly.2013.02.059](https://doi.org/10.1016/j.poly.2013.02.059).
- [7] C. Tsiamis, S. Cambanis, A.D. Jannakoudakis, N. Theodoridou, Electrochemical behaviour of bis(1,3-dionato)copper(II) chelates on mercury and carbon fibre electrodes, *J. Electroanal. Chem. Interfacial Electrochem.* 252 (1988) 109–123, doi:[10.1016/0022-0728\(88\)85076-9](https://doi.org/10.1016/0022-0728(88)85076-9).
- [8] C. Tsiamis, P.D. Jannakoudakis, N. Sachsinger, H. Hennig, Substituent effects in the electrochemical behaviour of some mixed-ligand copper(II) chelates containing β -ketoenols and 1,2-diamines, *Electrochim. Acta.* 38 (1993) 2623–2630, doi:[10.1016/0013-4686\(93\)80161-R](https://doi.org/10.1016/0013-4686(93)80161-R).
- [9] G. Gritzner, J. Kuta, Recommendations on reporting electrode potentials in nonaqueous solvents (Recommendations 1983), *Pure Appl. Chem.* 56 (1984) 461–466, doi:[10.1351/pac19845604061](https://doi.org/10.1351/pac19845604061).
- [10] M. Munakata, S. Nishibayashi, H. Sakamoto, Copper(I) complex-catalysed reduction of dioxygen to water and oxidation of alcohols: a model of copper(I)-containing oxidase, *J. Chem. Soc. Chem. Commun.* (1980) 219, doi:[10.1039/c39800000219](https://doi.org/10.1039/c39800000219).
- [11] L. Kavan, Y. Saygili, M. Freitag, S.M. Zakeeruddin, A. Hagfeldt, M. Grätzel, Electrochemical Properties of Cu(II/I)-Based Redox Mediators for Dye-Sensitized Solar Cells, *Electrochim. Acta.* 227 (2017) 194–202, doi:[10.1016/j.electacta.2016.12.185](https://doi.org/10.1016/j.electacta.2016.12.185).
- [12] N.G.S. Mateyise, J. Conradie, M.M. Conradie, Density functional theory calculated data of the iodomethane oxidative addition to oligothiophene-containing rhodium complexes – importance of dispersion correction, *Data Br* 35 (2021) 106929, doi:[10.1016/j.dib.2021.106929](https://doi.org/10.1016/j.dib.2021.106929).
- [13] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, G.A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A.V. Marenich, J. Bloino, B.G. Janesko, R. Gomperts, B. Mennucci, H.P. Hratchian, J.V. Ortiz, A.F. Izmaylov, J.L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V.G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. Montgomery, J. A. Jr., J.E. Peralta, F. Ogliaro, M.J. Bearpark, J.J. Heyd, E.N. Brothers, K.N. Kudin, V.N. Staroverov, T.A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A.P. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, J.M. Millam, M. Klene, C. Adamo, R. Cammi, J.W. Ochterski, R.L. Martin, K. Morokuma, O. Farkas, J.B. Foresman, D.J. Fox, *Gaussian 16, Revision B.01*, 2016.
- [14] A.D. Becke, Density-functional exchange-energy approximation with correct asymptotic behavior, *Phys. Rev. A.* 38 (1988) 3098–3100, doi:[10.1103/PhysRevA.38.3098](https://doi.org/10.1103/PhysRevA.38.3098).
- [15] C. Lee, W. Yang, R.G. Parr, Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density, *Phys. Rev. B.* 37 (1988) 785–789, doi:[10.1103/PhysRevB.37.785](https://doi.org/10.1103/PhysRevB.37.785).
- [16] X. Li, M.J. Frisch, Energy-represented direct inversion in the iterative subspace within a hybrid geometry optimization method, *J. Chem. Theory Comput.* 2 (2006) 835–839, doi:[10.1021/ct050275a](https://doi.org/10.1021/ct050275a).
- [17] <http://www.chemcraftprog.com/>, (n.d.) <http://www.chemcraftprog.com/>.